

REVIEW PAPER

## Defence Applications of Polymer Nanocomposites

R.V. Kurahatti\*, A.O. Surendranathan#, S. A. Kori\*, Nirbhay Singh†,  
A.V. Ramesh Kumar†, and Saurabh Srivastava†

\*Basaveshwar Engineering College, Bagalkot-587 102

#National Institute of Technology Karnataka, Surathkal-575 025

† Defence Materials and Stores Research & Development Establishment, Kanpur-208 013  
E-mail: \*rajukurahatti@gmail.com

### ABSTRACT

The potential opportunities promised by nanotechnology for enabling advances in defence technologies are staggering. Although these opportunities are likely to be realised over a few decades, many advantages are currently being explored, particularly for defence applications. This review provides an insight into the capabilities offered by nanocomposites which include smart materials, harder/lighter platforms, new fuel sources and storage as well as novel medical applications. It discusses polymer-based nanocomposite materials, nanoscale fillers and provides examples of the actual and potential uses of nanocomposite materials in defence with practical examples.

**Keywords:** Nanocomposites, nanotechnologies, defence applications, smart materials, polymer-based nanocomposites, medical applications, fuel sources

### 1. INTRODUCTION

Nanotechnologies promise revolutionary technological changes for a wide range of military applications and platforms. Technologies to be incorporated within the platforms which are directly relevant to the defence arena include: aerodynamics, mobility, stealth, sensing, power generation and management, smart structures and materials, resilience and robustness, etc. In addition, nanotechnologies will have impact on battlespace systems concerned with information and signal processing, autonomy and intelligence. With regard to information technology, in particular, substantial advantages are expected to be gained from these new enabling capabilities which include threat detection, novel electronic displays and interface systems, as well as a pivotal role for the development of miniaturised unmanned autonomous vehicles (UAVs) and robotics. Nanotechnology will enable the development of novel materials providing the basis for the design and development of new properties and structures which will result in increased performance (e.g., nano-energetics and new types of catalysts), reduced cost of maintenance (e.g., wear reduction, self-healing and self-repair), enhanced functionality (eg adaptive materials) and new types of electronic/opto-electronic/magnetic material properties.

### 2. POLYMER NANOCOMPOSITES

#### 2.1 Definition

The reinforcement of polymers using fillers, whether inorganic or organic, is common in the production of modern plastics. Polymeric nanocomposites (PNCs) represent a

radical alternative to the conventional filled polymers or polymer blends. In contrast to conventional systems, where the reinforcement is of the order of microns, PNCs are exemplified by discrete constituents of the order of a few nanometers (<100 nm) in at least one dimension (Fig. 1).

The small size of the fillers leads to an exceptionally large interfacial area in the composites. The interface controls the degree of interaction between the filler and the polymer and thus controls the properties. As in conventional composites, the interfacial region is the region beginning at the point in the fibre at which the properties differ from those of the bulk filler and ending at the point in the matrix at which the properties become equal to those of the bulk matrix<sup>1</sup>.

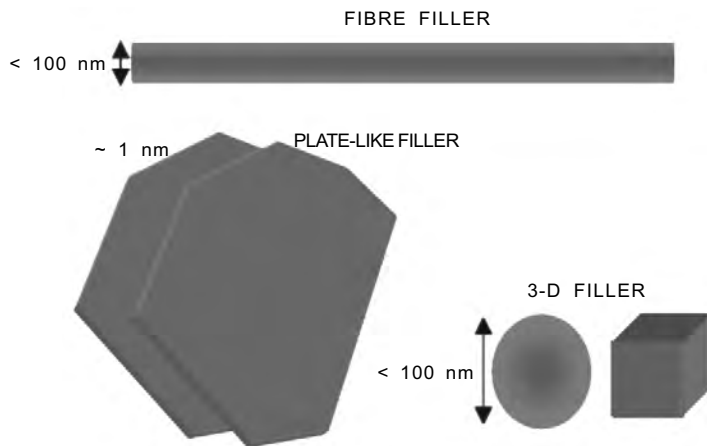


Figure 1. Schematic of nanoscale fillers.

It can be a region of altered chemistry, altered polymer chain mobility, altered degree of cure, and altered crystallinity. Interface size has been reported to be as small as 2 nm and as large as about 50 nm. Even if the interfacial region is only a few nanometer, very quickly the entire polymer matrix has a different behaviour than the bulk. If the interfacial region is more extended, then the polymer matrix behaviour can be altered at much smaller loadings. To implement the novel properties of nanocomposites, processing methods that lead to controlled particle size distribution, dispersion, and interfacial interactions are critical.

## 2.2 Classification

Polymeric nanocomposites can be broadly classified as

- Nanoclay-reinforced composites
- Carbon nanotube-reinforced composites
- Nanofibre-reinforced composites, and
- Inorganic particle-reinforced composites.

### 2.2.1 Nanoclay-reinforced Composites

Historically, the term clay has been understood to be made of small inorganic particles (part of soil fraction < 2 mm), without any definite composition or crystallinity. The clay mineral (also called a phyllosilicate) is usually of a layered type and a fraction of hydrous, magnesium, or aluminum silicates<sup>6</sup>. Every clay mineral contains two types of sheets, tetrahedral (*T*) and octahedral (*O*)<sup>6</sup>. For a better understanding the major clay mineral groups along with their ideal structural chemical compositions are listed in Table 1.

Hectorite, saponite, and montmorillonite are the most commonly used smectite type layered silicates for the preparation of nanocomposites. Montmorillonite (MMT) has the widest acceptability for use in polymers because of their high surface area, and surface reactivity<sup>7</sup>. It is a hydrous aluminosilicate clay mineral with a 2:1 expanding layered crystal structure, with aluminum octahedron sandwiched between two layers of silicon tetrahedron. Each layered sheet is approximately 1 nm thick (10 Å), the lateral dimensions of these layers may vary from 30 nm to several microns or larger, depending on the particular layered silicate. The aspect ratio is about 10–1000 and the surface area is in the range<sup>6</sup> of 750 m<sup>2</sup>/g. When one octahedral sheet is

bonded to one tetrahedral sheet, a 1:1 clay mineral results. The 2:1 clays are formed when two tetrahedral sheets bond with one octahedral sheet<sup>6,7</sup>. The aspect ratio of 1000 is possible when a clay platelet is well-dispersed into the polymeric matrix without breaking. Practically, breaking up of clay platelets during mixing process at high shear and large shear stress condition results in an aspect ratio of 30–300.

Graphite has a similar geometry (layered structure) with nanoclay, therefore a clay-polymer reinforcement concept is applicable<sup>8</sup>. Graphite flakes have been known as host materials for intercalated compounds. By applying rapid heating, some of the graphite-intercalated compounds (GICs) expand and a significant increase in volume takes place. Many literature citations identify the expanded graphite flakes with polymer systems for lightweight and conductive polymer composites<sup>9-13</sup>.

In polymer-layered silicate (PLS) nanocomposites, stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery. Isomeric substitution (for example tetrahedral  $Si^{4+}$  by  $Al^{3+}$  or octahedral  $Al^{3+}$  by  $Mg^{2+}$  or  $Fe^{2+}$ ) within the layers generates negative charges that are counterbalanced by alkali and alkaline earth cations (typically  $Na^+$  or  $Ca^{2+}$ ) situated inside the galleries<sup>7</sup>. This type of layered silicate is characterised by a moderate surface charge known as the cation exchange capacity (CEC). Details regarding the structures and chemical formulae of the layered silicates are provided in Fig. 2. In general, the organically modified silicate nanolayers are referred to as nanoclays or organosilicates<sup>4</sup>. It is important to know that the physical mixture of a polymer and layered silicate may not form nanocomposites<sup>7</sup>. Pristine-layered silicates usually contain hydrated  $Na^+$  or  $K^+$  ions<sup>7</sup>. To render layered silicates miscible with other polymer matrices, it is required to convert the normally hydrophilic silicate surface to an organophilic one, which can be carried out by ion-exchange reactions with cationic surfactants<sup>7</sup>.

Sodium montmorillonite ( $Na_x(Al_{2-x}Mg_x)(Si_4O_{10})(OH)_2 \cdot H_2O$ ) type layered silicate clays are available as micron size tactoids, which consist of several hundreds of individual plate-like structures with dimensions of 1  $\mu m \times 1 \mu m \times 1$  nm. These are held together by electrostatic forces (gap in between two adjacent particles  $\sim 0.3$  nm). The MMT particles, which are not separated, are often referred to

Table 1. Classification and example of clay minerals<sup>5</sup>.

Structure	Group	Mineral examples	Ideal composition	Basal spacing (Å)
2 : 1(TOT)	Smectite	Montmorillonite	$[(Al_{3.5-2.8}Mg_{0.5-0.2})(Si_8)O_{20}(OH)_4] Ex_{0.5-0.2}$	12.4-17.0
		Hectorite	$[(Mg_{5.5-4.8}Li_{0.5-1.2})(Si_8)O_{20}(OH)_4] Ex_{0.5-0.2}$	
		Saponite	$[(Mg_6)(Si_{7.5-6.8}Al_{0.5-1.2}O_{20}(OH)_4] Ex_{0.5-0.2}$	
2 : 1(TOT)	Illite	Illite	$[(Al_4)(Si_{7.5-6.8}Al_{0.5-1.2}O_{20}(OH)_4] K_{0.5-1.5}$	10.0
2 : 1(TOT)	Vermiculite	Vermiculite	$[(Al_4)(Si_{8.8-8.2}Al_{1.2-1.8}O_{20}(OH)_4] Ex_{1.2-1.8}$	9.3-14.0
1 : 1(TOT)	Kaolin serpentine	Kaolinite	$Al_4Si_4O_{10}(OH)_8$	7.14
		dickite, nacrite		

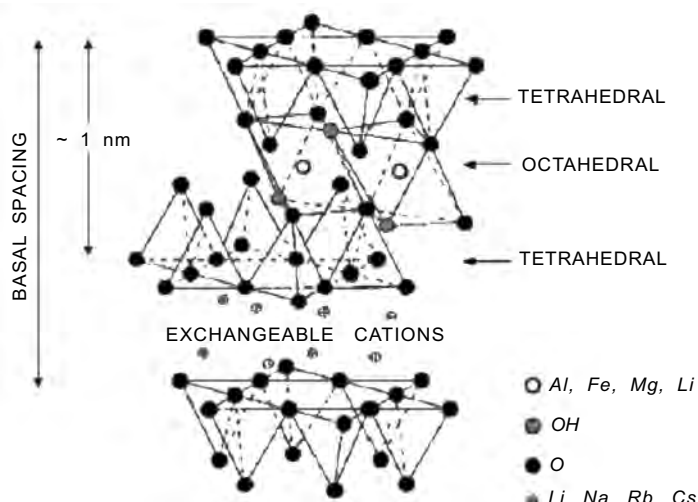


Figure 2. Basic structures of 2:1 clay minerals<sup>7,14</sup>.

as tactoids. The most difficult task is to breakdown the tactoids to the scale of individual particles in the dispersion process to form true nanocomposites, which has been a critical issue in current research in different literatures<sup>3, 15-24</sup>.

### 2.2.1.1 Properties and Applications

Theoretical predictions have shown that the modulus for well aligned platelets can be three times that for well-aligned fibres, especially as the aspect ratio of clay layers increases<sup>14</sup>. Other studies however, suggest that the modulus increase is not entirely due to the load-carrying ability of the platelets, but is caused by the volume of polymer constrained by the platelets<sup>14</sup>. This suggests that to optimise the increase in modulus, the degree of dispersion must be optimised to maximise the degree of matrix/filler interaction. Work on PP nanocomposites in which adding maleic anhydride (MA) to the matrix changed the degree of filler dispersion supports this suggestion that despite the plasticising effect of MA, the modulus improved due to enhanced dispersion of the clay<sup>107</sup>. Lan and Pinnavaia<sup>108</sup> found that, 'as the degree of exfoliation increased by changing the length of alkylammonium intercalating chain, the modulus and strength improved'.

As the polymer intercalates and swells, the layers and the area of interaction between the polymer and the filler increases and the modulus increases significantly. Figure 3 represents three main types of composites for layered silicate materials. The polymer/clay interaction plays a significant role in controlling mechanical behaviour is also evident from the fact that improvement in properties tends to be higher above the glass transition temperature than below it<sup>15</sup>. However, proper dispersion is critical for achieving this. Hasegawa<sup>37</sup>, *et al.* studied the dispersion of clays in polypropylene. They found that the strain-to-failure ratio in nanocomposites remains

high (>200 per cent) even at reinforcement loadings of 3 per cent. But even a small amount of aggregation decreased the strain-to-failure ratio to 5 per cent-8 per cent. A similar effect was also observed in polyimide matrices, in which the strain-to-failure ratio decreases by 72 per cent due to aggregation. A significant improvement in flexural modulus (1.5 GPa to 2.1 GPa) and tensile strength (29 MPa to 40 MPa) and impact strength (18 J/m to 24 J/m) of PP/clay nanocomposites is reported on addition of about 15 per cent PP-g-MAH to PP-organoclay system<sup>16</sup>. Xu<sup>68</sup>, *et al.* have reported similar improvements in tensile strength and impact strength of the composites with a nanoclay addition of 10 per cent to 15 per cent.

Unprecedented combinations of properties have been observed in some thermoplastics too. The inclusion of equi-axed nanoparticles in semicrystalline thermoplastics has resulted in increase in yield stress, the tensile strength, and Young's modulus of the polymers. A volume fraction of only 0.04 mica-type silicates (MTS) in epoxy increases the modulus below the glass transition temperature by 58 per cent and the modulus in the rubbery region by 450 per cent. In addition, the permeability of water in poly( $\alpha$ -caprolactone) decreases by an order of magnitude with the addition of 4.8 per cent silicate by volume. Yuno<sup>17</sup>, *et al.* showed a 50 per cent decrease in the permeability of polyimides at a 2 per cent loading of MTS. Many of these nanocomposites are optically transparent and/or optically active.

### 2.2.2 Carbon Nanotube-reinforced Composites

Micrometer-size carbon tubes, which are similar in structure (but not in dimensions) to the recently discovered multi-walled carbon nanotubes, were first found in 1960 by Roger Bacon<sup>26</sup>. These nanosized, near-perfect whiskers (termed nanotubes) were first noticed and fully characterised in 1991 by Sumio Iijima<sup>25</sup> of NEC Corporation in Japan.

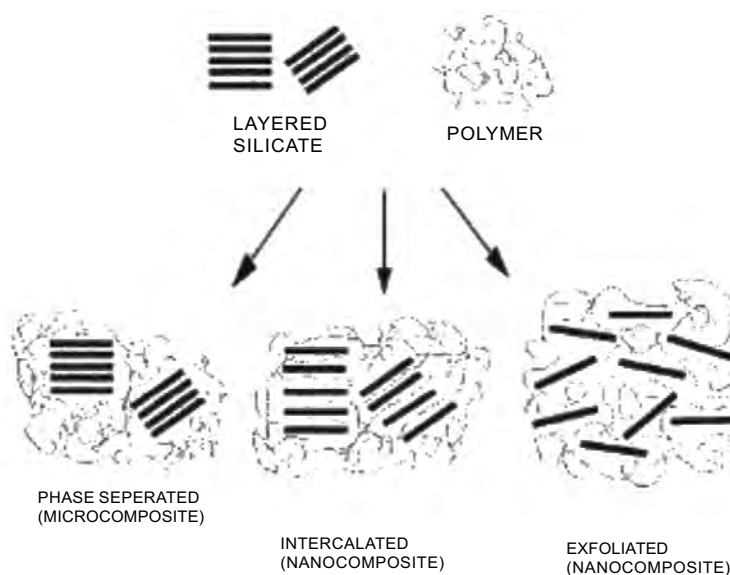


Figure 3. Scheme of three main types of layered silicates in polymer matrix<sup>5</sup>.

He was investigating the surface of carbon electrodes used in an electric arc discharge apparatus that had been used to make fullerenes. Several exciting developments have taken place in this field since then<sup>27</sup>.

The first nanotubes observed were multi-walled nanotubes (MWNT). MWNTs consist of two or more concentric cylindrical shells of graphene sheets coaxially arranged around a central hollow core with interlayer separation, as in graphite (0.34 nm)<sup>28</sup>. In contrast, single-shell or single-walled nanotubes<sup>29,30</sup> (SWNT) are made of single graphene (one layer of graphite) cylinders and have a very narrow size distribution (1–2 nm). Often many (tens) single-shell nanotubes pack into larger ropes. Figure 4 shows electron micrographs of SWNT and MWNT. Both types of nanotubes have the physical characteristics of solids and are microcrystals, although their diameters are close to molecular dimensions. In nanotubes, the hexagonal symmetry of the carbon atoms

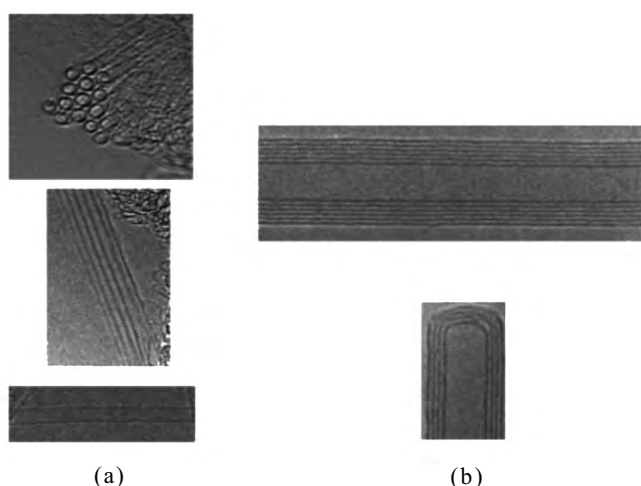


Figure 4. (a) HRTEM image showing the SWNT in bundles, (b) HRTEM images of a MWNT along its length and at the end.

in planar graphene sheets is distorted, because the lattice is curved and must match along the edges (with dangling bonds) to make perfect cylinders. This leads to a helical arrangement of carbon atoms in the nanotube shells. Depending on the helicity and dimensions of the tubes, the electronic structure changes considerably<sup>31,32</sup>. Hence, although graphite is a semi-metal, carbon nanotubes (CNTs) can be either metallic or semiconducting. Nanotubes are closed by fullerene-like end caps that contain topological defects (pentagons in a hexagonal lattice). The electronic character of the ends of these tubes differs from the cylindrical parts of the tubes and is more metallic due to the presence of defects in these regions<sup>33</sup>. The discovery of nanotubes has complemented the excitement and activities associated with fullerenes<sup>34</sup>. Although fullerenes have fascinating physical properties, their relevance in the nanocomposite field is limited.

The properties of CNTs are unique compared to other graphite fibres. Their structure remains distinctly different from that of traditional carbon fibres<sup>2</sup>, which have been used industrially for several decades (e.g., as reinforcements in tennis rackets, airplane body parts and batteries). Nanotubes represent the ideal, most perfect, ordered carbon fiber, the structure of which is entirely known at the atomic level. Table 2 shows measured and theoretical properties of both SWNT and MWNT.

#### 2.2.2.1 Properties and Applications

Qian<sup>11</sup>, *et al.* and Yu<sup>44</sup>, *et al.* have shown, as first described by Wagner<sup>61</sup>, that MWNTs fail via a sword-and-sheath mechanism. This situation limits the efficiency of MWNT/polymer composites because only a small portion of the volume fraction of the MWNT carries load. Evidence for this was shown for MWNT/polystyrene composites<sup>18</sup>, in which the effective modulus of the MWNT in the composite was only 500 GPa but the measured modulus of the MWNT

Table 2. Theoretical and experimentally measured properties of carbon nanotubes

Property	Nanotubes	Graphite
Lattice structure	(Cylindrical) hexagonal lattice helicity Nanotubes: ropes, tubes arranged in triangular lattice with lattice parameters of $a = 1.7 \text{ nm}$ , tube-tube distance = 0.315	Planar hexagonal. plane-to-plane distance = 0.335
Specific gravity	0.8 - 1.8 $\text{g cc}^{-1}$ (theoretical)	2.26 $\text{g cc}^{-1}$
Elastic modulus	~ 1 TPa for SWNT ~ 0.3–1 TPa for MWNT	1 TPa (in plane)
Strength	~50-500 GPa for SWNT, 10-60 GPa for MWNT	50 (in plane)
Resistivity	5-50 micro-ohm-cm	50 (in plane)
Thermal conductivity	3000 $\text{W m}^{-1}\text{K}^{-1}$ (theoretical)	3000 $\text{W m}^{-1}\text{K}^{-1}$ (in plane) 6 $\text{W m}^{-1}\text{K}^{-1}$ (c axis)
Thermal expansion	Negligible (theoretical)	$-1 \times 10^{-6} \text{ K}^{-1}$ (in plane) $29 \times 10^{-6} \text{ K}^{-1}$ (c axis)
Oxidation in air	> 700 °C	450-650 °C

is close to 1 TPa. Therefore, to minimise the number of layers not carrying load, 2-3 layers are preferable. In addition, CNTs are over 105 times more resistant to the electron radiation than polyethylene and about 103 times more resistant than highly radiation-resistant rigid-rod polymers<sup>18</sup> such as poly(p-phenylene benzobisoxazole).

For SWNT composites, the SWNT are in a bundle and individual SWNTs may slip within the bundle. Work by Yu<sup>44</sup>, *et al.* showed that if only the nanotubes on the outer edge of a SWNT in a bundle are used to calculate the modulus, it is close to the predicted 1 TPa. However, if the whole area of the bundle is used, the calculated modulus is considerably lower. This suggests that, unless the SWNTs are isolated from the bundles, the modulus of the composites made from these materials will be limited.

Some promising results have been reported by Biercuk and others<sup>41</sup>. They observed a monotonic increase of indentation (Vickers hardness) by up to 3.5 times on loading up to 2 per cent SWNTs and a doubling of thermal conductivity with 1 per cent SWNTs. Also, 1 per cent MWNT loading in polystyrene increases the modulus and breaking stress by up to 42 and 25 per cent, respectively<sup>41</sup>. Similarly, the strength of 1 per cent PS/MWNTs is found to increase by 25 per cent (13-16 MPa) and strain at yield by 10 per cent<sup>42</sup>. One of the major benefits expected from incorporating CNTs in polymers is an increase in both the electrical and thermal properties of polymers. The electrical characteristic of interest in polymers is percolation threshold. For CNTs/epoxy system a very low percolation threshold of below 1 per cent is reported. Likewise, the electrical conductivity of CNTs/PMMA composites is reported to increase by about nine times with the addition of 5-8 per cent CNTs. While the polystyrene is insulating, the films doped with MWNTs are conducting (conductivity  $7.1 \times 10^{-2} \text{ Ohm}^{-1} \text{ cm}^{-1}$ ). Electrical conductivity<sup>31</sup> of 0.5 per cent MWNT/PFA is  $1.3 \times 10^{-2} \text{ Ohm}^{-1} \text{ cm}^{-1}$ .

### 2.2.3 Nanofiber-reinforced Composites

Carbon nanofibers (CNF) are a unique form of vapour-grown carbon fibres that fill the gap in physical properties between conventional carbon fibres (5–10  $\mu\text{m}$ ) and carbon nanotubes (1–10 nm). The reduced diameter of nanofiber provides a larger surface area with surface functionalities in the fiber<sup>55</sup>. Typically CNF are not concentric cylinders; the length of the fibre can be varied from about 100  $\mu\text{m}$  to several cm, and the diameter is of the order of 100–200 nm with an average aspect ratio greater than 100. The most common structure of CNF is the truncated cones, but there are wide ranges of morphologies (cone, stacked coins, etc). CNF have the morphology where these are hollow at the centre (much like a MWNT) and have a larger diameter than MWNT but the individual layers are not arranged in concentric tubes.

#### 2.2.3.1 Properties and Applications

Tandon and Ran<sup>56</sup> enhanced the thermomechanical properties of conventional aerospace carbon fibre-reinforced

(IM7) composites using carbon nanofiber. They manufactured IM7/CNF matrix unidirectional laminate aerospace structures using the filament-winding technique. Glasgow and Tibbetts<sup>57</sup> oxidised the surface of carbon nanofiber to improve the tensile behaviour in PP composites. Lafdi and coworkers<sup>58</sup> showed improved flexural strength and modulus in epoxy-based composites with oxidised nanofibres. Finegan and Tibbetts<sup>59</sup> incorporated CNF in a PP with improved strength and stiffness. Thermal transport across bonded radiator panels is important where thermally-conductive adhesives play an important role. Electrically-conductive bonded joints are needed in spacecraft to eliminate the build up of static charge on the structure due to the impingement of charged particles. Gibson<sup>60</sup>, *et al.* modified the epoxy-based adhesives formulated with silver-coated and uncoated vapour-grown carbon nanofibers for several aerospace applications such as electrical conductivity, thermal transport, and mechanical properties. But they concluded that it does not help to remove the waste heat<sup>60</sup>. Lao<sup>54</sup>, *et al.* used CNF, clay platelets, and silica nanoparticles to find the relationship between the flammability and mechanical properties of nylon-11. They achieved a combination of enhanced mechanical and flammability properties in clay platelets and CNF. In their analysis, clay-based nanocomposites showed better flammability, while the CNF-based nanocomposites showed better mechanical properties.

### 2.2.4 Inorganic Particle-reinforced Composites

Nanoparticles are often defined as particles of < 100 nm in diameter<sup>61</sup>. Nanometer-sized particles have been made from different organic–inorganic particles and these impart improved properties to composite materials<sup>51</sup>. Different particles have been used to prepare polymer/inorganic particle nanocomposites, including:

- Metals (*Al, Fe, Au, Ag*, etc.)
- Metal oxides (*ZnO, Al<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub>, TiO<sub>2</sub>*, etc.)
- Nonmetal oxide (*SiO<sub>2</sub>*)<sup>52</sup>
- Other (*SiC*)

The selection of nanoparticles depends on the desired thermal, mechanical, and electrical properties of the nanocomposites. For example, *Al* nanoparticles are often selected due to their high conductivity; calcium carbonate (*CaCO<sub>3</sub>*) particles are chosen because of their low cost and silicon carbide (*SiC*) nanoparticles are used because of their high hardness, corrosion resistance, and strength<sup>53</sup>.

#### 2.2.4.1 Properties and Applications

Polymer/inorganic particle-based nanocomposites have shown significant improvement in mechanical, thermal, and electrical properties. For example, in nylon-6 filled with 5 Wt % 50 nm silica nanoparticles, an increase in tensile strength by 15 per cent, strain-to-failure by 150 per cent, Young's modulus by 23 per cent and impact strength by 78 per cent were reported<sup>62</sup>. Jiang,<sup>63</sup> *et al.* investigated ABS (acrylonitrile butadiene styrene) reinforced with both microsized and nanosized calcium carbonate particles through melt compounding. It was found that

the ABS/micron-sized particle composites had higher Young's modulus but lower tensile and impact strengths than neat ABS. However, the ABS/nano-sized particle composites increased the Young's modulus as well as impact strength. Ma<sup>65</sup>, *et al.* showed an improvement in electrical properties of polyethylene nanocomposites by introducing functional groups at  $TiO_2$  nanoparticles. Zhang and Singh<sup>67</sup> improved the fracture toughness of nominally brittle polyester resin systems by incorporating  $Al_2O_3$  (15 nm). An  $Al_2O_3$  particle has been found to be effective in improving the dielectric constant of a polymer in other studies<sup>64</sup> also. Koo<sup>48-50</sup>, *et al.* used AEROSIL (silicon dioxide, 7–40 nm) silica nanoparticles to process different nanocomposites with different resin systems (phenolic, epoxy, cyanate ester) for high-temperature applications. Recently, creep tests were performed on  $TiO_2/PA6,6$  nanocomposites by Zhang and Yang<sup>47</sup>. Poor creep resistance and dimensional stability have been improved by adding  $TiO_2$  in polyamide 6,6 thermoplastic composites. Chisholm<sup>55</sup>, *et al.* investigated micro- and nano-sized  $SiC$  in an epoxy matrix system. In their study, an equal amount of loading, nanoparticle infusion brings superior thermal and mechanical properties than micro-sized particle-based composites.

### 3. NANOCOMPOSITES—DEFENCE APPLICATIONS

In materials technology, there are relatively few examples of nanocomposites developed specifically for defence applications.

#### 3.1 High Performance Fibre/Fabrics

The first attempt to produce nanotubes resulted in very small quantities of tangled nanotubes, which however has created interest in these materials as non-oriented mats. Further developments had led to the development of techniques for spinning nanotubes into fibres in a polymer matrix, which is of special interest for mechanical and electronic fabric applications<sup>69,70</sup>. By infiltrating nanotube mats or woven fibres with a polymer, continuous sheets or films of a nanocomposite can be produced<sup>71,72</sup>. The nanotubes will contribute to mechanical properties (strength and stiffness) of the film as well as to electrical conductivity.

The production of polymer fibres was until recently limited to extruding fibres of relatively large (micrometer diameter) sizes. Recently, an electrospinning technique<sup>73,74</sup> has been shown to be effective to produce pure polymer and polymer nanocomposite fibres with diameters in the range of 200 nm to 300 nm. More interesting is, in electrospun nanocomposite fibres, the nanoparticles were found to be highly aligned. This is likely to significantly effect the optical and mechanical properties, although no results were reported.

For non-woven fabrics to achieve electrical conductivity, a simple and flexible method has been reported, where the non-woven mat was exposed to a high intensity light source (e.g., from a flash tube), which resulted in immediate

joining of fibres at cross-over points of contact. Using a mask, fibres can be joined in any desired pattern<sup>73</sup>. Such materials may find wide applications in defence as electrically conductive fabrics, sensors, electromagnetic shielding, microwave absorption, electrical energy storage (capacitors), actuators, and materials for micro UAVs.

#### 3.2 Ballistic Protection

The reports of ballistic testing of PNCs are very few and this may be due to secrecy associated with such materials and lack of suitable nanocomposite materials. For light protection (body armour and vehicle liners) woven materials such as Kevlar are commonly used. It is likely that electrospun nanofibres, spun CNTs could be useful in such applications.

There are few reports of the promising application of nanocomposites in body armour. Shear thickening fluids<sup>74-77</sup> consist of a fluid containing a dispersion of particles and this fluid stiffens and resists deformation if sheared rapidly by an external force. Reports from the US Army Research Laboratory indicate promising results when combining inorganic nanoparticles (of silica) in polyethylene glycol. When this shear thickening fluid is impregnated into conventional Kevlar, the ability of the material to absorb energy is greatly improved. In one example, the ballistic performance (in terms of absorbed energy) was more than doubled so that four layers of Kevlar impregnated with the shear thickening fluid absorbed as much energy as would have been absorbed by 10 layers without the shear thickening fluid. This will lead to a more flexible armour with reduced weight. Such materials find applications for body/personal armour where flexibility of movement is required besides protection against blunt weapons (stones, sticks and bars) for arms and legs.

#### 3.3 Microwave Absorbers

Nanocomposites as microwave absorbers are receiving much attention. Nguyen and Diaz<sup>78</sup> have reported a method to synthesize polypyrrole nanocomposites containing iron oxides ( $\gamma$  and  $\alpha$ ), tin oxide, tungsten oxide and titanium dioxide. Pyrrole containing a dispersion of nanoparticle metal oxides was polymerised *in situ* and the magnetic properties reported.

The electrical conductivity and dielectric losses can be tuned by varying the concentration and orientation of the nanotubes additions. Glatowski<sup>72</sup>, *et al.* have been awarded a patent in this area, covering a wide range of thermoplastic and thermosetting matrices containing oriented nanotubes. Only a few weight per cent of nanotubes need be added to the polymer to achieve useful properties. Efforts have been made to utilise CNTs for developing economical microwave (in the range 8 GHz to 24 GHz) absorbers<sup>103,104</sup>. These materials have wide applications in electrical energy storage (condensers) integrated into load-carrying structures for UAVs, high strength CNTs-polymer fibres for energy absorption, electromagnetic shielding, etc.

### 3.4 Refractive Index Tuning

In many optical applications such as telecommunications and optical computing, polymer optical fibres are very attractive to adjust the refractive index of the connecting optical fibre (due to ease of mass production and low cost). This can be done by the addition of nanoparticles with various refractive indices to the polymer. Bohm<sup>79</sup>, *et al.* reported additions of nanoparticle zirconia, alumina, and silica to poly (methyl methacrylate) and they were able to adjust the refractive index over a sufficient range. Levels up to 10 Wt % loading were reported. Tuning the refractive index of surface coatings is important in signature management. Damage resistance (abrasion and scratching) of the fibre is likely to be improved by addition of ceramic nanoparticles.

### 3.5 Solid Lubricants

It is possible to produce inorganic fullerene-like (IF) nanoparticles of tungsten sulphide (WS<sub>2</sub>), which have a characteristic structure like a hollow onion. Rapoport<sup>80</sup>, *et al.* have reported that by adding small quantities of WS<sub>2</sub> nanoparticles (about 100 nm dia) to two polymer matrices: epoxy and polyacetal, it was possible to reduce coefficient of dry friction between polymer and a steel disc to less than half in both the cases. If a simple lubricant was present, friction coefficient was further reduced significantly. Fracture toughness of the epoxy was also improved. These lubricants may be used for rotating and sliding bearings.

### 3.6 Porous Nanocomposites

The additions of nanoparticles can serve to improve the foaming properties of a polymer as reported by Siripurapu<sup>81</sup>, *et al.* who used additions of silica nanoparticles to act as nucleation sites for nanopore formation using carbon dioxide as a blowing agent. A disadvantage of porous polymer foams (e.g., polyurethane) is their large surface-to-volume ratios, which increase the rate of heat and gas release in case of fire. By introducing nanoparticles with a flake-like morphology, the rate of burning can be significantly reduced. Nanoporous polyurethane is being considered for automotive seat applications. Other applications include shock-absorbing materials, and acoustic absorbents, etc.

### 3.7 Electrostatic Charge Dissipation in Space Environment

Dissipation of static charge on spacecraft is a severe problem, which requires a material with not only sufficient electrical conductivity but also must be stable to the space environment (intense ultraviolet radiation, charged particle irradiation, atomic oxygen, rapid and severe temperature changes). Smith<sup>82</sup>, *et al.* working at NASA reported that the conductivity sufficient to eliminate static discharge could be achieved in a polyimide nanocomposite containing as little as 0.03 Wt % CNTs.

Resistance to radiation of a styrene-butadiene-styrene/clay nanoparticles nanocomposite has been investigated by Zhang<sup>83</sup>, *et al.* The nanocomposite was virtually unaffected

when exposed to  $\alpha$ -radiation. This unexpected stability was attributed to two effects arising from nanoparticles additions. Firstly, flake-like clay particles act in a passive mode to shield the polymer from radiation and secondly, nanoparticles act as active sink for broken polymer chains, which are grafted onto the nanoparticles surfaces.

Recently Charati<sup>97</sup>, *et al.* revealed a method for manufacturing conductive composites. They first sonicated an organic polymer precursor (e.g., poly(arylene ether)) with SWNTs in an ultrasonicator to disperse the SWNTs and then polymerised the organic polymer precursor using shear and elongational forces. They claimed that in this way, at least a portion of the CNTs could be functionalised either at the side wall or hemispherical ends.

### 3.8 Ultraviolet Irradiation Resistance

Common polymers are not stable under ultraviolet irradiation and will begin to degrade after few weeks. Strength and fracture toughness are drastically reduced and the polymer becomes brittle. Jiang<sup>84</sup>, *et al.* studied the effect of modifying the epoxy matrix by adding nanoparticles of titanium dioxide to epoxy/carbon fibre composite. They found that resistance to degradation by ultraviolet irradiation could be reduced by approximately half and mechanical properties (measured by interlaminar shear strength) could be improved by 80 per cent.

### 3.9 Fire Retardation

Polymers have poor fire resistance. If ignited, most polymers will burn quickly, releasing large quantities of heat, toxic gases, and soot. Polymers containing a few weight per cent of nanoparticle clays have greatly improved fire resistance as reported by Gilman<sup>85</sup>, *et al.* The thermal properties of the PNC are improved, melting and dripping are delayed, and rate of burning is greatly reduced (by more than half). The presence of flake-like clay nanoparticles reduces the diffusion of polymer decomposition volatiles (the fuel) to the burning surface and reduces diffusion of air into the polymer. Further, addition of clay nanoparticles improves mechanical properties significantly. Similar improvements were noted in polypropylene/CNTs nanocomposites. High thermal conductivity of CNTs might increase heat input into polymer and enhance rate of burning. However, Kashawagi<sup>86</sup>, *et al.* contradict this observation in CNTs. Examples of applications include reduction of fire risk in enclosed spaces in vehicles, submarines, aeroplanes, and ships.

### 3.10 Corrosion Protection

Corrosion protection of metals and alloys is normally achieved by a surface coatings which must resist both mechanical damage (scratching, impact, abrasion) and chemical attack (salts, acids and bases, solvents). It should also not be damaged (cracked) by having a coefficient of thermal expansion greatly different from the metal to be protected. PNCs have improved scratch and abrasion resistance, due to their higher hardness combined with improved elastic

modulus. Gentle and Baney<sup>87</sup> reported preliminary experiments using a silica-reinforced silicone nanocomposite coating deposited to protect aluminium surfaces and electronic circuits. A significant improvement during salt fog testing was obtained with survival rates improved by up to 100 times<sup>87</sup>. Corrosion protection in aerospace (at normal or low temperatures, not suitable above 150 °C) and corrosion protection of electronic circuits demand such materials.

### 3.11 Signature Reduction

This is a field which is surrounded in secrecy. Dynamically tuneable camouflage materials would be an invaluable aid to defence operations, allowing personnel and equipment to achieve a highly visible or totally concealed presence depending on the situation. DeLongchamp and Hammond report a high-contrast electrochromatic nanocomposite based on poly (ethyleneimine) and Prussian Blue nanoparticles<sup>87</sup>. It is claimed that a fully switchable reflective tri-colour space coating has been produced. This material has obvious applications in dynamically tuneable camouflage in the visual spectrum.

### 3.12 Diffusion Barriers

Food packaging is dependent on preventing diffusion of gases and odours in airtight packets. Many 'tetra-pack' and similar liquid containers consist of several layers, including a layer of aluminium as an impervious barrier to prevent carbon dioxide or oxygen spoiling the contents. The US Army is field-testing individual ready-to-eat food portions packaged in a nanocomposite container<sup>108</sup>. The food is claimed to remain fresh for three years. Also linked to barrier properties are fire resistance and corrosion protection of nanocomposites. Food containers, fuel containers, gas-tight containers which are presently made of rubber or similar elastomers.

### 3.13 Sensors

Kong<sup>99</sup>, *et al.* demonstrated chemical sensors based on individual SWNTs. They found that electrical resistance of a semiconducting SWNT changed dramatically upon exposure to gas molecules such as  $NO_2$  or  $NH_3$ . The existing electrical sensor materials including carbon black polymer composites operate at high temperatures for substantial sensitivity whereas the sensors based on SWNT exhibited a fast response and higher sensitivity at room temperature.

Ajayan<sup>100</sup>, *et al.* developed a controlled method of producing free-standing nanotube-polymer composite films that can be used to form nanosensor, which contains at least one conductive channel comprising an array of aligned CNTs embedded in a matrix (e.g., poly (dimethylsiloxane)). This material can be used to determine a real time physical condition of a material, such as that of an airplane wing or chassis while the airplane is in flight<sup>87</sup>. Such materials may be used for detection and identification of toxic gases such as chemical warfare agents, flammable gases, solvent vapours, etc., touch sensors for interaction between operators and machines.

### 3.14 Actuators

Nanocomposite-based actuators have reduced power requirements and linear motion directly. Koerner<sup>109</sup>, *et al.* dispersed a small amount (<5 vol per cent) CNTs in a polyurethane thermoplastic polymer (Morthane) and found that the resultant nanocomposite could store (and release when required) 50 per cent more strain energy than the unreinforced polymer. The addition of CNTs allowed indirect (infrared) or direct (Joule heating) activation. Compared to conventional additives (e.g. carbon black), considerable lower additions of CNTs was required.

Existing shape memory polymers are insufficiently strong (low recovery stress) to find wider application. By adding a mechanical restraint in the form of inert silicon carbide nanoparticles to a commercial shape memory polymer, Gall<sup>88</sup>, *et al.* were able to increase the recovery stress by 50 per cent, without degrading other properties. Courty<sup>101</sup>, *et al.* reported a novel actuator response driven by an electric field due to the presence of MWNTs in nematic elastomer, polysiloxane. They produced a composite material with embedded and aligned CNTs with an effective dielectric anisotropy, many orders of magnitude higher than in the usual liquid crystals. Ounaies<sup>102</sup>, *et al.* developed technique for making actuating composite materials with polarisable moieties (e.g., polyimide) and CNTs. UAVs, especially micro-UAVs, may demand such actuators.

## 4. PRACTICAL EXAMPLES AND DEVELOPMENTS

With regards to coatings and camouflage, BASF polymer researchers<sup>89</sup> are looking into nanoparticles with highly branched polyisocyanates. These coatings will offer superior abrasion resistance, anti-reflection, tailored refractive indices, protection from corrosion, and self-cleaning surfaces. All these properties are of immense interest to the defence arena.

Toyota started using nanocomposites in their bumpers making them 60 per cent lighter and twice as resistant to denting and scratching. Likewise, the Chevrolet Impala makes use of polypropylene side body mouldings reinforced with montmorillonite. These novel nanomaterials save on weight but enhance the hardness. Oxonica, are commercialising cerium oxide to improve the combustion efficiency. Savings in fuel use, storage are a vital asset in military scenarios.

Kodak is producing organic light emitting diodes (OLED), colour screens (made of nanostructured polymer films) for use in car stereos and cell phones.

In medical field, Angstro Medica has produced a nanoparticulate-based synthetic bone (Human bone is made of calcium and phosphate composite called Hydroxyapatite). By manipulating calcium and phosphate at the molecular level, the firm has created a patented material that is identical in structure and composition to a natural bone. In addition, the combination of nanotechnology and genomics will lead to the development of new vaccines and treatments for genetically-based illnesses. M/s. Smith & Nephew markets an anti-microbial dressing covered with nanocrystalline silver. The nanocrystalline coating of silver rapidly kills



a broad spectrum of bacteria in as little as 30 min.

Nanocubes made of organometallic network materials, currently being analysed by BASF researchers, could prove a suitable storage medium for hydrogen. Their three-dimensional lattice structure has numerous pores and channels, making nanocubes an ideal storage medium.

## 5. INDIAN SCENARIO

India has initiated focused efforts on nanotechnology only in 2001, i.e., 5-7 years after countries like USA, EU, Japan, Korea, and Taiwan started their own programmes. The application-oriented research in India in the last few years has focused primarily on energy, environment, and health-related areas.

The invention of flow-induced electrical response in CNTs has direct relevance in biological and biomedical applications<sup>90</sup>. Indian Institute of Science (IISc) has transferred the exclusive rights of this technology to an American start-up to commercialise the gas-flow sensors. Nanocrystalline gold triangles developed by a group at National Chemical Laboratory (NCL), Pune has been shown to be useful for cancer treatment by hyperthermia, where irradiation of the cancer cells is carried out by infra-red radiation<sup>91</sup>. These materials are used in insulin delivery for advanced diabetics.

A research Group at Banaras Hindu University, has developed a novel method to produce a membrane out of CNTs for treating contaminated drinking water<sup>92</sup>. Eureka Forbes, in collaboration with IIT Madras, Chennai; has come out with a nanosilver-based water filter for the removal of dissolved pesticides in drinking water<sup>93</sup>. International Advanced Research Centre Powder Metallurgy and New Materials (ARCI), Hyderabad has the synthesis facilities to produce a wide range of metallic, ceramic and cermet nanopowders in large quantities. ARCI has developed the low-cost nanosilver-coated ceramic candle for disinfection of drinking water<sup>94</sup>. It has developed the lightening arresters based on ZnO microcrystalline powders<sup>95</sup>.

Though, the speed of scientific research has increased considerably over the years<sup>96</sup> in terms of number of quality publications in technical journals, India still lags behind countries like Korea, China, and Taiwan, leave alone the leading countries like USA, Japan, and Europe. In application development and commercialisation of nanomaterials-based technologies, India is far behind even when compared to countries like Singapore. Both the government and industry need to ramp up their efforts in this area dramatically and immediately.

## 6. CONCLUSIONS

It may well be predicted that PNCs in the mid- and longer-term will pervade all aspects of life, similar to the way plastics did in the last century. Clearly a diverse range of sectors such as aerospace, automotive, packaging, solar cells, electrical and electronic goods, household goods etc. will profit substantially from a new range of materials. In the short term (<5 years), the commercial impact may include inkjet markets, nanoparticles in cosmetics, and

automotive applications such as body moldings, engine covers and catalytic converters, batteries, computer chips. In the medium-term (<10 years), memory devices, biosensors for diagnostics, advances in lighting are all possible. The time-scale for automotive, aerospace, bio-nanotechnology is a long-term prospect (>15 years).

To create macroscale materials, many issues surrounding the incorporation of nanotubes into a matrix, strategies for property improvement and the mechanisms responsible for those property improvements still remain critical. Since only a moderate success has been made over the last 20 years, researchers must continue to investigate strategies to optimise the fabrication of nanotube-enabled materials to achieve improved mechanical and transport properties. Defence needs to do a dedicated effort in areas such as signature management. Two major thrust areas in defence are nanocomposites to be used in heavily integrated multifunctional materials for UAVs and materials that enhance functionality and survivability of the individual soldier.

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## Contributors



**Mr R.V. Kurahatti** obtained his ME (Production Technology) from Visvesvaraya Technological University, Belgaum in 1999. Presently, he is working as Senior Lecturer in Basaveshwar Engineering College, Bagalkot (Karnataka) and pursuing PhD in the Dept of Metallurgical and Materials Engineering, National Institute of Technology Karnataka, Surathkal.



**Dr A.O. Surendranathan** obtained his PhD from Mangalore University, Karnataka in 1994. Presently, he is working as Professor in National Institute of Technology Karnataka, Surathkal. His research areas are superplasticity, batteries, corrosion, powder metallurgy, electroplating, welding, heat treatment, polymers, composites and nanotechnology.



**Dr S.A. Kori** obtained his PhD from IIT, Kharagpur in 2000. He joined as teaching faculty in Basaveshwar Engineering College Bagalkot in 1987. Presently, he is Registrar (Evaluation) in Visvesvaraya Technological University, Belgaum. He has published 25 research papers in international journals and 60 papers in international and national conference proceedings. He has received University Grants Commission fellowship of Indo-Hungarian faculty exchange programme in 2005.



**Dr Nirbhay Singh** obtained his MTech and PhD from IIT, Kanpur. Presently, he is working as Scientist 'G' (Additional Director) in DMSRDE (DRDO) Kanpur. His research areas are metallic corrosion and its prevention, fatigue and fracture studies of metallic and non-metallic materials, failure analysis of aircraft components, polymer nanocomposites. He has published 70 papers in national and international journals/conferences.



**Dr A.V. Ramesh Kumar** obtained his MSc (Physical Chemistry) from School of Chemistry, Andhra University and PhD (Applied Chemistry) from Kanpur University. He joined DMSRDE, Kanpur as Scientist 'C' and worked there till May 2009 and currently is posted in Naval Physical and Oceanographic Laboratory (NPOL), Kochi. He has filed 4 patents and published 4 technical reports.



**Mr Saurabh Srivastava** obtained his BTech (Mechanical Engineering) from Institute of Engineering and Technology, Lucknow. He worked with M/s L&T before joining DRDO as Scientist. Currently, he is working as Scientist 'C' in DMSRDE, Kanpur.