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S.J. Savage

Defence applications of nanocomposite materials

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This report briefly describes and discusses relevant properties of polymer-based nanocomposite materials, and gives examples of the actual and potential use of nanocomposite materials in defence applications.

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Försvarstillämpningar för nanokompositmaterial

Sammanfattning (högst 200 ord)

Rapporten beskriver och diskuterar relevanta egenskaper hos polymer-baserade nanokompositmaterial, och ger exempel på aktuella och potentiella användningsområden för dessa material i försvarstillämpningar.

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Introduction

This report presents a “popular scientific” overview of the applications for nanocomposite materials and nanocomposite technology in defence materiel and systems.

Nanocomposite science and technology is a large and rapidly growing field, driven mainly by the obvious commercial potential of these materials in civilian applications. The large volume of information available precludes including more than a very limited selection in this report, which will however attempt to present a reasonably representative cross-section of applications relevant for defence materiel. *The main objective of this report is to give the reader a qualitative overview of the field, and to illustrate some defence applications.*

Nanocomposite science and technology is a young field, having its origins in the Toyota Research Laboratories in Japan in the 1980s. As is almost always the case, initial interest focuses on basic research, and so much of the literature concerning nanocomposites relates to manufacture and/or characterization of these materials. This area will not be covered in this report. The interested reader is referred to some of the excellent books and reviews published, including the book: *Polymer-clay nanocomposites* by Pinnavia and Beall [1], and the review recently published by Harris [2].

Nanocomposite technology has now reached the stage where basic research is being applied towards material and process development, aimed at specific products or semi-finished materials. A number of new products are appearing on the market (automotive components, sports equipment, consumer goods); and existing processes are being improved with the application of nanocomposite technology and materials. Nanocomposite technology has reached a critical mass and it is likely that many new materials and products will be developed in the next few years.

It is relevant to emphasise the difference and similarities between convectional composites (carbon-fibre and glass-fibre reinforced polymers), nanocomposites, and conventional polymers containing fillers. The dimensions of conventional carbon and glass fibres are in the micrometer range, i.e. considerably larger than the nanotubes/fibres mentioned below. While fibre dimensions are relevant in terms of manufacturing processes, what is much more relevant is the dramatic enhancement in mechanical and physical properties obtained in carbon nanotubes, and the related but less expensive nanofibres.

Many polymers are today compounded with fillers to modify their properties. This is usually done to improve mechanical properties such as stiffness, or improve environmental stability against ultraviolet degradation. In addition, various other additives can be used to modify the performance (colour, transparency, magnetic properties, reflectivity, etc) of a polymer. Some particle additives (aluminium compounds) are added to improve fire resistance. In most, if not all cases these additives are of conventional particle size, typically in the 10 to 100 micrometre range. Often relatively large volumes of additives are required to obtain the desired property, which results in density increases (most additives have a density much greater than the polymer host, and a reduction in flexibility and fracture toughness of the polymer.

There are usually disadvantageous side effects to using conventional additives, mainly the effect on mechanical properties. While elastic modulus may be increased, fracture toughness and tensile/bend strength are negatively affected. A major advantage of using nanoparticles additives is that mechanical properties are not negatively affected, and in fact tensile strength is usually improved, often significantly. An additional benefit of nanoparticles additions is that they can be combined with conventional carbon- and glass-fibre reinforcement, and conventional process technology (resin transfer moulding, injection moulding, etc) can be used. This is not possible with conventional (micrometre-size) fillers.

Definition

The term nanocomposites as used in this report is taken to mean polymer-based materials containing particles (equiaxed or elongated), or fibres with at least one dimension in the 1 to 200 nanometre range. The particles or fibres may be inorganic (metal or ceramic, including semiconductors) or organic (e.g. polymer). This definition excludes metal-matrix nanocomposites, and similarly ceramic-matrix nanocomposites. This is not to suggest that these fields are unimportant, merely that they are not covered in this report.

Defence applications of nanocomposites

In the field of materials technology there are relatively few examples of materials, including nanocomposites, which are developed specifically for defence applications. In contrast to the situation during the period of the Cold War where the need for materials for weapons systems and aerospace provided the driving force for much materials research and development, the situation today is that commercial forces almost exclusively provide the driving force. Only in areas such as signature management, where there are in principle no civilian applications, does defence needs motivate a dedicated effort.

This is very much the case in the field of nanocomposite technology – although much research is being done in defence organisations, both in Europe and the USA, the vast majority of basic research is funded by civilian sources, (there is some exception in the USA, where defence funding for basic research is orders of magnitude greater that in the rest of the world).

In the short discussions which follow it is assumed that the informed reader will be able to understand the defence applications for the materials and properties described. At the end of each discussion an example of a particular defence application is added for clarity.

Examples of applications

Fibre/textile applications

The discovery of carbon nanotubes by Iijima in 1991 [3] has aroused great interest due to the extraordinary properties of these materials [4]. From a very simplified perspective nanotubes can be compared to conventional carbon fibres, but with much smaller dimensions and orders of magnitude better mechanical properties. In addition, carbon nanotubes have a wide range of extreme thermal, electrical, semiconductor and optical properties, which can be used to modify and improve the functional properties of polymer matrices.

A considerable disadvantage is that the first attempts to produce nanotubes resulted in very small quantities of tangled nanotubes, which however has created interest in these materials as non-oriented mats. Further development had also led to techniques for spinning nanotubes into fibres in a polymer matrix, which is of special interest for mechanical and electronic textile applications [5, 6]. By infiltrating nanotube mats or woven fibres with a polymer, continuous sheets or films of a nanocomposite can be produced. The nanotubes will contribute to the mechanical properties (strength and stiffess) of the film, as well as the electrical conductivity. Practical applications of this type of nanocomposite include electrostatic painting of automotive parts, and electromagnetic and radio-frequency shielding [7, 8].

The production of polymer fibres was until recently limited to extruding fibres of relatively large (micrometer diameter) sizes. Recently, an electrospinning technique has been shown to be effective to produce pure polymer and polymer nanocomposite fibres with diameters in the range 200 to 300 nanometres [9]. Perhaps more interesting is that in the nanocomposite electrospun fibres, the nanoparticles were found to be highly aligned. The effect of this on optical and mechanical properties is likely to be significant, although no results were reported.

For non-woven fabrics, some method of bonding the fibres may be required to produce a material which can be handled, or to selectively bond fibres in a pattern, for example to achieve a particular electrical conductivity. A very simple and flexible method has been reported, where the non-woven mat is exposed to a high intensity light source (e.g. from a flash tube), which results in immediate welding of fibres at cross-over points of contact. By using a mask, the fibres can be welded in any desired pattern.[10].

Example of defence applications: woven or non-woven fabrics for fabrics, electrically conductive textiles, sensors, mechanical reinforcement, electromagnetic shielding, microwave absorption, electrical energy storage (capacitors), actuators, and materials for micro-UAVs.

Carbon nanotube-nanocomposites

Polymer matrices containing carbon nanotubes is a very active area of research and development, due in the main to the potential for creating multifunctional materials. Polymers, which are normally electrically insulating but have other advantages of being flexible, low density and easily formed, can be combined with carbon nanotubes, which have excellent electrical conductivity, extreme mechanical strength and high thermal conductivity. By combining these two materials, a nanocomposite with extremely useful properties can be obtained.

One of the most useful application areas is electromagnetic shielding, as the electrical conductivity and dielectric losses can be tuned by varying the concentration and orientation of the nanotubes additions. In addition, there are a variety of treatments which can be applied to nanotubes, either during or after manufacture to optimize their electrical properties for various applications. Glatowski et al have been awarded a patent [8] in this area, covering a wide range of thermoplastic and thermosetting polymer matrices, containing oriented nanotubes. The main application of this patent seems to be microwave absorption. Particularly relevant is that only low levels of nanotubes need be added to the polymer (a few weight percent) to achieve useful properties.

Nanotubes have exceptional mechanical strength, but as yet can only be produced in relatively short lengths (about 40 mm at present, although processes to manufacture longer tubes are rapidly improving). A method to utilise at least some of the potential for mechanical strength in fibre form is to disperse nanotubes in a polymer, and then extrude the polymer into a fibre. The nanotubes are aligned parallel to the fibre axis during processing, and can result in polymer nanocomposite fibres with greatly improved strength. These fibres can then be used and woven into textiles in the conventional way [11].

Example of defence applications: multifunctional materials for electrical energy storage (condensers) integrated into load-carrying structures for UAVs, high strength nanotube-reinforced polymer fibres for energy absorption (ballistic protection), electromagnetic shielding (microwave signature management).

Refractive index tuning

In many optical applications, including micro-optical components for use in telecommunications and optical computing (connectors and switches) it is essential to adjust the refractive index of the connecting optical fibre. In many cases it is attractive to use polymer optical fibres (due to ease of mass production and low cost). To minimise losses due to mismatch between the refractive index of the optical fibre and e.g. a semiconductor device or a silica optical fibre it is essential to raise or lower the refractive index of the polymer fibre respectively. This can be done in various ways, including addition of nanoparticles with various refractive indices to the polymer. Böhm et al [12] report additions of nanoparticle zirconia, alumina and silica to poly(methyl methacrylate), and were able to both increase and decrease the refractive over a range sufficient to allow the nanocomposite polymer produced to be used as a waveguide. Levels of up to 10 wt% were used. Difficulties were reported in introducing the nanoparticles into the polymer matrix, and it is clear that surface treatment of the nanoparticles must be optimized in this respect. Nonetheless the technique promises to be a cheap method to control the refractive index of polymer optical fibres. Tuning the refractive index of surface coatings is also important in signature management. An additional benefit is that the damage resistance (abrasion and scratching) of the fibre is likely to be improved by the addition of the ceramic nanoparticles.

Example of defence applications: optical connectors, optical fibres and switches, signature management

Solid lubricants

Polymers are attractive due to their ease of forming and low density. However, they are known to have poor wear and friction properties when rubbing against other materials. It is also common to impregnate porous bearings with an oil/grease based lubricant to reduce friction in low cost bearings found in huge numbers in e.g. electric motors. It is possible to produce “inorganic fullerene-like” (IF) nanoparticles of e.g. tungsten sulphide (WS_2), which have a characteristic structure like a hollow onion, i.e. they are hollow spheres with multiple shells. Recent reports indicate that adding these IF nanoparticles to polymers can greatly reduce the friction between a polymer and a metal. In addition, the fracture toughness of the polymer tested was improved. Rapoport et al [13] have reported that by adding small quantities of (WS_2) nanoparticles (about 100 nm diameter) to two common polymer matrices: epoxy and polyacteal (Delrin®), it was possible to reduce the coefficient of dry friction between the polymer and a steel disc (standard pin-on-disc method) to less than half, in both cases. In addition, if a simple lubricant was present the friction coefficient was further reduced significantly. Secondary advantages include improvements in the fracture toughness of the epoxy, and reduced wear on the steel disc. It is likely that the materials can be further improved, by improving the distribution of the nanoparticles in the polymer matrices.

Example of defence applications: all forms of rotating and sliding bearings, all areas where two surfaces slide across each other and where a reduction in friction or the need to supply lubrication is desirable. The reduction in friction is likely to be less temperature dependent than conventional grease lubrication.

Chemical sensors, pressure sensors

There are many examples of polymer-based nanocomposite chemical sensor materials. One recent report illustrates the advantages of combining carbon nanotubes with a conducting polymer matrix, which led to improved sensitivity and greatly reduced power consumption. An et al [14] used an in-situ polymerization of pyrrole and single-wall nanotubes to produce a nanocomposite porous material consisting of nanotubes dispersed in a conducting polypyrrole matrix. The porosity of the nanocomposite allowed rapid diffusion of the gas to be detected (nitrogen dioxide, a common atmospheric pollutant), and the large surface area/volume ratio of the nanotubes gave a sensitive sensor. Addition of the nanotubes improved the sensitivity of the composite by a factor of approximately 10, compared to the polymer alone. The authors note difficulties in synthesis of the nanocomposite, which suggests that further improvement in sensitivity may be achievable if the synthesis process can be optimized. This type of sensor can be tuned to detect many specific chemical substances (normally in the gas phase), by suitable coatings on the nanofibres.

A further type of chemical sensor consists of a number of different polymers containing nanofibres which are exposed simultaneously to an unknown substance. Most solvents are easily absorbed in polymers, and lead to swelling of the polymer, which gives a direct and easily measurable change in electrical resistance. By using a matrix of different polymers a wide range of chemicals can be detected. Similar types of material can be used as simple pressure sensors, e.g. in “artificial skin” for interface between humans and machines (e.g. “active gloves”)

Example of defence applications: detection and identification of gases, including atmospheric pollutants, flammable gases, solvent vapours, etc. Touch sensors for interaction between operators and machines.

Porous nanocomposites

The range of porous (foamed) polymers is enormous, and is growing rapidly. It seems likely that only the very surface of (nano)porous polymer nanocomposites has been touched upon, and that much more remains to be done. Applications include smart membranes, textiles, fuel cells, reflective displays, sensors, soft or hard foams for seats/furniture and filter materials.

There are several ways to consider a porous nanocomposite. The simplest include foam with a homogeneous matrix containing nanometre pores, i.e. a *nanoporous* material, whereas more complex materials may include nanoparticles or nanotubes dispersed in a matrix which may contain pores of conventional or nanometre dimensions. The addition of nanoparticles can also serve to improve the foaming properties of a polymer, as reported by Siripurapu et al[15], who used additions of nanoparticles silica to act as nucleation sites for nanopore formation using carbon dioxide as a blowing agent.

A significant disadvantage of porous polymer foams (e.g. polyurethane) is that the large surface / volume ratio increases the rate of heat and gas release in the case of fire. This is especially important in the many applications of polymer foams in furniture, vehicles and similar applications where a soft and deformable shock absorbing material is required. By introducing nanoparticles with a flake-like morphology, the rate of burning can be significantly reduced. Little has been publicly reported in this area, probably due to intellectual property right issues, but some success in this direction has been achieved [16]. There are indications that nanoporous polyurethane is being considered for automotive seat applications.

Example of defence applications: shock absorbing materials, acoustic absorbents, vehicle seats (with the advantage of reduced flammability).

Microwave absorbers

Nanocomposites as microwave absorbers are receiving much attention, both as magnetic lossy materials and electrical lossy materials. Although little is published openly, there are a few reports which give some indication as to the types of nanocomposites being studied. Nguyen and Diaz report [17] a method to synthesis polypyrrole nanocomposites containing of 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. No microwave properties were given. Glatkowski et al have been awarded a patent describing the use of carbon nanotubes, both randomly and non-randomly oriented in a polymer matrix, for electromagnetic shielding[8].

Example of defence applications: microwave absorbers in aerospace and other applications.

Aerospace applications

Aerospace is a field which demands optimum properties, and in particular optimized *property combinations*, due to the substantial weight savings (which translate directly to cost benefits in reduced fuel consumption). Njuguna and Pielichowski [18] briefly review aerospace applications, focussing largely on nanotubes-containing polymers and methods to produce these materials. Schmidtke and Brandt [11] from EADS (European Aerospace and Defence Systems) have recently presented an overview of aerospace applications, covering applications ranging from materials for aeroplane interiors with improved fire retarding properties; materials with improved elastic modulus **and** improved impact properties (property improvements which are normally mutually exclusive) to transparent polymers with improved scratch resistance and higher mechanical strength without loss of transparency. The application of nanocomposites in microwave absorbers is also clearly relevant in military aerospace.

Example of defence applications: impact/damage resistant carbon fibre-reinforced polymers; transparent materials (canopies), surface coatings for signature management, corrosion protection.

Electrostatic charge dissipation - space

Many of the applications for nanotube-containing nanocomposites in the form of thin films are related to electrical conductivity. Dissipation of static charge on spacecraft is a severe problem, which requires a material with not only sufficient electrical conductivity but is also stable to the space environment (intense ultraviolet radiation, charged particle irradiation, atomic oxygen, rapid and severe temperature changes). Smith et al of NASA [19] report that conductivities sufficient to eliminate static discharge could be achieved in a polyimide nanocomposite containing as little as 0.03 wt% nanotubes.

Resistance to radiation of a styrene-butadiene-styrene / clay nanoparticles nanocomposite has been investigated by Zhang et al [20]. It was found that the nanocomposite was virtually unaffected when exposed to γ-radiation. This unexpected stability was attributed to two effects arising from the nanoparticles additions. Firstly, the flake-like clay particles act in a passive mode to shield the polymer from the radiation, and secondly the nanoparticles act as active sinks for broken polymer chains, which are grated onto the nanoparticles surfaces.

Example of defence applications: anti-static coatings for components and systems especially in space systems), anti-static coatings in aerospace, lightning protection for aerospace structures and systems.

Ultraviolet irradiation resistance

Common polymers are not stable under ultraviolet irradiation, and will after a period ranging from weeks to months begin to degrade. Mechanical properties such as strength and fracture toughness are drastically reduced, and the polymer becomes brittle. Conventional carbon fibre/epoxy composites, frequently used in space applications suffer from the space environment. Jiang et al have studied the effect of modifying the epoxy matrix often used in space applications [21]. By adding nanoparticles titanium dioxide to the epoxy matrix in a carbob fibre composite, it was found that resistance to degradation by ultraviolet irradiation could be reduced by approximately half, and at the same time mechanical properties (measured by interlaminar shear strength) could be improved by 80 %. If such materials were to be used it is likely that the material improvements could result in enhanced effective load, reduced outgassing and extended lifetime.

Example of defence applications: components and coatings exposed to sunlight, space coatings, textiles exposed to sunlight, paint and other surface protection.

Existing industrial applications

There are a number of industrial applications where the improved electrical conductivity of nanocomposites is already being used in production, including the North American automotive industry. Plastic components (wing mirrors, bumpers, door handles, etc) are frequently manufactured from injection moulded plastic, which must be painted. This is normally done by electrostatic spray painting, but for this to be effective the (insulating) plastic component must first be coated in a conducting layer. Previously this was achieved by dipping in a conductive paint, which had disadvantages including the thickness required and lack of mechanical strength. Recently a coating made from a dispersion of nanotubes in a polymer has been developed, and is now used in production. Bearing in mind the extreme cost-consciousness which exists in the automotive industry this must be taken as an indication that this new technology offers a “total solution” which provides real cost/performance benefits [22]. An additional advantage is that the thinner coating required to achieve adequate electrical conductivity results in improved surface quality and smoothness.

Under 2004 the American automobile manufacturer General Motors has released information that a nanocomposite is used in a production application, as various components on a van. The benefits quoted include:

Weight savings of 3 to 21%

Lighter weight reduces cost and requires less adhesive for attachment

Improved Appearance

- Improved Knit Line Appearance
- Improved Colorability & Paintability
- Sharper Feature Lines & Grain Patterns
- Improved Scratch/Mar Performance

Large Processing Window

- Consistent Physical and Mechanical Properties
- Elimination/Reduction of Tiger Striping

Reduced Paint Delamination

Retains Low Temperature Ductility

Improved Recyclability

Lower Flammability

Example of defence applications: functional and lightly loaded components, presently made from plastics or light alloy (handles, fasteners, components of portable weapons systems, especially where injection moulded plastic can replace metal components)

Signature reduction

This is a field of application surrounded in secrecy, although it is obvious from allusions in the literature that much work on developing camouflage materials based on polymer nanocomposites is being done. Most manufacturers of carbon nanotubes mention this as one of the applications for their products. Eikos [23] is a company claiming to have research and development programmes in:

- Composites for tailored electromagnetic radiation shielding
- Conformal coatings
- Electrostatic discharge film
- Infrared electromagnetic shielding using carbon
- Electrostatic dissipative polymers (canopies)
- Non-metallic compliant conductive materials for airframe electrical conductivity

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 demands of the situation. Electrochromic materials offer one way towards achieving this. DeLongchamp and Hammond report a high-contrast electrochromic nanocomposite material based on poly(ethyleneimine) and Prussian Blue nanoparticles [24]. 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.

Example of defence applications: all systems and platforms requiring signature management.

Ballistic protection

There are few reports of ballistic testing polymer nanocomposites. This is likely to be due in part to the secrecy associated with such materials, and in part due to the lack of suitable forms of nanocomposite materials. For light protection (body armour and vehicle liners) woven materials such as Kevlar® are commonly used. It is likely that electrospun nanofibres could be useful in such applications, but at present the quantities of materials available are too limited to allow realistic testing. However, it should be noted that very recently there have been reports of spun carbon nanotubes, which would be expected to have extreme mechanical properties [25], combined with extreme elastic properties, which would make them very suitable for such applications.

Ostermayer et al have reported measurements of the V_{50} behaviour of one of the first nylon 6-clay nanocomposites, using a fragment simulating projectile [26]. The results, which appear to be superficial, showed that the ballistic limit of the nanocomposite was lower than the unreinforced polymer (which would not be considered to be suitable as an armour material).

There are several reports [27], [28-30] of a promising application of what may be termed a nanocomposite in body armour. Shear thickening fluids consist of a fluid, containing a dispersion of particles. When the fluid is sheared rapidly by an external force it stiffens and resists deformation. Reports from the U.S. Army Research Laboratory [31] indicate very 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) is more than doubled, so that 4-layers of Kevlar® impregnated with the shear thickening fluid absorbed as much energy 10 layers without the shear thickening fluid. It terms of practical application, this will lead to much more flexible armour with equivalent ballistic protection, and somewhat reduced total weight. It is expected that this type of armour will be field tested during 2005 [32].

Example of defence applications: body/personal armour where flexibility of movement is required, in particular protection against blunt weapons (stones, sticks and bars) for arms and legs which today are unprotected because of the need for flexibility present armour cannot provide.

Fire retardation

One of the first and still most significant properties of nanocomposites which was discovered is their fire resistance. Polymers are well known for their lack of fire resistance. If ignited, most polymers will burn very well, releasing large quantities of heat, toxic gases (carbon monoxide), and soot. In addition, the polymer, due to its low melting temperature melts, and drips, spreading burning droplets which serve to increase the size of the fire, and encourage it to spread. It many defence applications a fire will have disastrous results, particularly on board ships, submarines, aircraft and ground vehicles. The problem is compounded by the (usually) very restricted space available to introduce fire limitation partitions. Chemical additives have been widely used to reduce the flammability of polymers (halogenated hydrocarbon additions), but these have a number of disadvantageous side-effects. If a fire occurs, the halogen (chlorine or bromine) will result in highly toxic and corrosive combustion gases. In addition, when released into the environment these compounds have been show to accumulate in fish and animals, and ultimately in the human food chain. It is certain that halogenated fire retardants will be forbidden by environmental legislation within the next few years.

Polymers containing small (a few weight percent) additions of nanoparticles clays have greatly improved fire resistance in several ways, as reported by Gilman et al [33]. The thermal properties of the polymer nanocomposite are improved, so that melting and dripping are delayed (which reduces the rate of spread of a fire), and the rate of burning is greatly reduced (by more than half). The exact mechanisms of this are not yet entirely clear, but it appears that the presence of the (flake-like) clay nanoparticles reduces the diffusion of polymer decomposition volatiles (the fuel) to the burning surface, and reduces diffusion of air (the oxidant) into the polymer. In addition a protective crust forms on the surface which protects the unburnt polymer from radiative heating. A further advantage is that addition of the clay nanoparticles improves the mechanical properties of the polymer significantly, which can be utilised to reduce thickness/weight, or to improve the component load-carrying capacity. The effect has been observed in all common thermosetting and thermoplastic polymers. Similar improvements have also been noted in polypropylene/carbon nanotube nanocomposites, which is somewhat unexpected since the high thermal conductivity of carbon nanotubes might be expected to increase heat input into the polymer, and enhance the rate of burning. Kashawagi et al report that this is not the case [34].

Example of defence applications: reduction of fire risk in enclosed spaces in vehicles, submarines, aeroplanes, etc. Surface vessels (ships) in particular can benefit from replacement of existing polymers, e.g. epoxy and vinyl ester in glass- and carbon-fibre reinforced composites, without loss of mechanical properties.

Corrosion protection

Corrosion protection of metals and alloys is normally achieved by a surface coating 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. More recently, the need to provide corrosion protection has broadened greatly, to include e.g. electronic circuits. This is becoming more important in view of the increasing use of commercial of the shelf components (COTS) in defence applications, and the increasing demand for robustness and reliability on the ever increasing number of small, portable electronic devices used in defence systems.

Polymer nanocomposites have a number of potential advantages, although it seems that this application area is as yet poorly studied. Polymer nanocomposites have improved scratch and abrasion resistance, due to their higher hardness combined with improved elastic modulus. Nanocomposites also show improved performance as a diffusion barrier, a property useful in packaging materials. Reduced diffusion of water and other solvents into a protection coating is therefore an advantage. Gentle and Baney report 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 [35].

Example of defence applications: corrosion protection in aerospace (at normal or low temperatures, not suitable for temperatures above about 150 °C), corrosion protection of electronic circuits.

Actuators

The need for actuators in defence systems is increasing rapidly, as the use of autonomous systems increases. This trend is expected to continue for some time to come. The actuators required are often rather small, which limits the use of the traditional actuator – the electric motor. Electric motors in addition require high power levels, and in addition there is often a need to convert the rotary motion from a motor to a linear motion, which requires some form of gearbox. Nanocomposite-based actuators have been reported which offer some advantages, in the form of reduced power requirements and linear motion directly. Koerner et al have dispersed a small amount (<5 volume percent) carbon nanotubes in a polyurethane thermoplastic polymer (Morthane) and found that the resultant nanocomposite could store (and release when required) 50 % more strain energy than the unreinforced polymer . In addition, the addition of carbon nanotubes allowed indirect (infrared) or direct (Joule heating) activation. Compared to conventional additives (e.g. carbon black), considerable lower additions of carbon nanotubes was required, in addition to he nanocomposite having improved properties.

Shape memory polymers already exist, and are being used in some applications. However, they are still insufficiently strong (low recovery stress) to find wider application. By adding a mechanical restrain in the form of inert silicon carbide nanoparticles to a commercial shape memory polymer Gall et al [36] were able to increase the recovery stress by up to 50 %, without degrading other properties.

Example of defence applications: actuators in UAVs, especially micro-UAVs.

Diffusion barriers

One of the first new and unique properties to be discovered in nanocomposites is their resistance to penetration by light molecules (gases and volatile solvents). This is attributed to the presence of the nanoparticles, which themselves are impenetrable by the diffusing molecules. It is also suggested that the polymer chains directly connected to the nanoparticles are more rigidly bound than chains at a distance from the nanoparticles, which leads to an *effective* size of the particle which is larger than the nanoparticles. Only a few weight percent nanoparticles is required to generate a significant improvement in barrier properties.

Improved barrier properties influence the suitability of a material for a number of widely different applications. In one commercial application, a rubber-based nanocomposite is used as a gas-tight lining for tennis balls, to replace the conventional unreinforced rubber lining. Wilson the manufacturer claims that the pressure inside the improved tennis ball is maintained for more than twice as long as a conventional ball.

Food packaging is an application very dependent on preventing diffusion of gases and odours from diffusing into or out of air-tight 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. Water vapour which is lost from the food can lead to “drying-out”, alternatively water vapour diffusing into the food can lead to loss of crispness. The U.S. Army is field-testing individual ready-to-eat food portions packaged in a nanocomposite container. The food is claimed to remain “fresh” for three years.

Also linked to barrier properties are other applications where a gas or liquid barrier is required, including the fire resistance of nanocomposites presented elsewhere in this report, and nanocomposite corrosion protection layers.

Example of defence applications: food containers, fuel containers, gas-tight containers which are presently made of rubber or similar elastomers.

Discussion

Some general comparisons can be made between polymer-based nanocomposites and the corresponding unmodified polymer matrix. An important difference is that while functional properties (electrical, optical, magnetic) of ordinary composite scan be varied by adding various particle fillers, this invariably degrades the polymer’s mechanical properties. This is not the case for additives in the form of nanoparticles, and in fact some improvement in mechanical properties can frequently be expected.

1. Nanocomposites have improved mechanical properties, including:
   - Increased stiffness without loss of fracture toughness
   - Improved tensile and bend strength
   - Improved interlaminar strength (in fibre reinforced composites)

2. Nanocomposites have improved thermal properties, including:
   - Higher softening temperature
   - Higher thermal conductivity
   - Higher glass transition temperature

3. Nanocomposites (e.g. containing carbon nanotubes) have improved electrical properties, including:
   - Higher electrical conductivity
   - Can be used to store electrical charge (condensers)

4. Nanocomposites have greatly improved fire resistance.
5. The magnetic and optical properties of nanocomposites can be varied over a wide range, and optimized for a particular application.

As can be seen above, there are numerous possibilities to employ polymer-based nanocomposites in a wide range of defence applications. In some cases defence applications already exist (packaging for “ready-to-eat” food rations), and in others field testing is planned within less than one year (shear-thickening fluid impregnated Kevlar body armour). In both cases significant improvements in performance are expected. One can also see signs of convergence in what are apparently very different technologies. One example of this is to use the ultraviolet protection capability afforded by aluminium oxide and silicon dioxide nanoparticles to protect the Kevlar® fibres in body armour [37]. The manufacturer claims to extend the life of the armour from 5 years to 10 years.

It is likely that other applications will emerge in the next few years. In particular, mention should be made of the research (under contract to the U.S. Army Research Laboratory) being done at the Institute of Soldier Nanotechnologies at Massachusetts Institute of Technology [38]. While this is directed towards all forms of advanced technology of potential use to the future soldier (“Land Warrier”), much is directed towards polymer-based nanomaterials for personal survival, which includes not only armour against projectiles and other weapons, but sensors integrated into clothing and textiles for:

- electrical power generation and storage
- condition monitoring (the physical and mental health of the soldier)
- communication (integrated optical/wireless communication)
- camouflage, including dynamic camouflage
- "climate control" i.e. materials to protect against heat and cold, rain and wind
- recognition "friend or foe"
- active armour, i.e. stiffening and providing protection when required

Practically all these materials are polymer based, and many will be nanocomposite polymers.

When comparing the properties and performance of new materials with those of existing materials cost is a factor which should be taken into account. It is rare that a new material will be available at a lower cost than an existing material, simply due to the investment in process equipment which must be made. There are however exceptions to this, when production of the new material can be achieved using existing equipment and processes. Polymer nanocomposites may be one example where existing process technology can be modified and used to manufacture new materials. For example, it has been shown that conventional resin transfer moulding (injection of epoxy resin into a fibre lay-up) can be done even with epoxy containing additives of nanoparticles. When evaluating costs, the overall cost-performance equation must be examined. If additional functionality can be "added" to a material, it may be possible to eliminate another material or component, or the overall combination of properties may enable previously impossible performance. It is relevant to note the increasing use of nanocomposites in production automobiles, an industry which is extremely cost sensitive. Actual cost figures are of course not available, but we can safely assume that the overall cost-performance is beneficial.

There are a number of areas of nanocomposite technology which are not yet fully understood, and where further research and development will be required to achieve the full potential. These include:

- surface functionalisation of the reinforcing nanoparticles and nanofibres, to optimize the interface between particle/fibre and the polymer matrix
- conversion of nanofibres to woven or non-woven mats and textiles
- micromechanical modelling of the interface between nanoparticle/fibre and the matrix polymer

Swedish activities

Research in nanocomposite technology in Sweden is concentrated in the following groups:

- Prof. U. Gedde, Dept. Fiber & Polymer Technology, KTH
- Prof L. Berglund, Dept Aeronautical & Vehicle Engineering, KTH
- Dr M. Krook, STFI-Packforsk (R & D into packaging)
- FOI activities at the Dept of Functional Materials

Summary & Recommendations

Nanocomposite technology is a rapidly growing technology, with a wide range of actual and potential applications, in defence and civilian components and systems. Most of the basic research and development is driven by civilian and industrial forces, but there are a number of specific defence applications, including camouflage which is not addressed in this way. There are also a number of unexplored avenues, which will not be presented here. Further details of specific applications in these areas can be obtained from the author.

The full potential of nanocomposites will be obtained in applications which require a combination of properties, where the overall performance outweighs one particular property.

There are several application areas where nanocomposites can make an impact in defence systems, of which two deserve particular attention. These are nanocomposites in heavily integrated multifunctional materials for unmanned aerospace vehicles (UAVs), and in materials to enhance the functionality and survivability of the individual soldier. It is recommended that these two application areas be investigated in greater depth.

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