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REVIEW PAPER

Nanotechnology and Protective Clothing for Defence Personnel

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ABSTRACT

Defence personnel face multiple threats from different quarters, like terrorist groups and rogue nations, who own not only advanced lethal weapons but also chemical and biological warfare weapons. The present day protective clothing system used by the defence sector is vulnerable to modern weapons and also have some inherent weaknesses like high cost, bulkiness and discomfort in wearing. Nanotechnology- based materials offer a promising future in this area due to their extraordinary physical, chemical, mechanical, and electrical properties at nano-level. This paper outlines the various developments related to the application of nanotechnology in producing lightweight and comfortable protective clothing for the military personnel and also some new developments like sensor, energy storage, conductivity, and decontaminant fabrics.

Keywords: Nanofibres, nanocomposites, nano-based yarn and fabric, protective clothing, nanoparticles

1. INTRODUCTION

Military personnel on land, sea, and in the air face many complex hazards which are deliberately aimed at maiming or killing them. Hence, it is inevitable for them to wear protective clothing like body armour, chemical and biological (C&B) protective clothing, etc. At present, textile fibres such as kevlar, nomex and nylon find immense applications in protective wear garments for military personnel. High strength, antiballistic, flame retardant characteristics are some of the vital properties that make these fibres uniquely suitable for defence and other high-tech applications. In addition to the availability of high performance fibres, specialty chemicals and coatings enhance the performance of protective fabrics. Non-woven materials such as spun-bonded and melt-blown non-woven fabrics are mainly used for the manufacture of protective wears like barrier protection and fire-retardant fabrics. The advantages of using these fabrics, as against the conventional fabrics, lie in their low cost, improved barrier properties, impermeability to particulate matter, adequate strength, and comfort properties. Recently, there is a growing interest in the use of fine fibres such as micro- and nanofibres for specialist applications. The protective clothing made up of these fibres and their composites give high performance, functionality, comfort, and larger life span with less weight, size, maintenance and cost. Nanostructures and nanocomposites are being developed for the following defence applications:

- Lightweight protective clothing
- Flexible antiballistic textiles
- Chemical and biological warfare protection and self-decontaminating nanofibre fabrics ,
- Adaptive suits like switchable fabrics for improved thermal control, switchable camouflage.

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- Microsensors for body and brain sensing, environmental and situational awareness, integrated into a smart suit or a smart helmet.
- Wearable and/or flexible displays for visual feedback auxiliary supports: Flexible/rigid textiles for additional strength, exoskeletons, and robotics to assist the human tasks.

2. NANOFIBRES

Electrospinning is a cheap and relatively simple technique to produce nanofibres. This technique, though very old, has regained interest since it enables the production of cheap nanostructures. This process (Fig. 1) mainly consists of a dc power supply used to generate high voltage in the order of 25–85 kV between a polymer solution to be drawn out into nanofibres and a grounded collector plate. The polymer solution to be drawn is stored in a syringe which has a thin capillary tube mounted at one end. The syringe is typically driven by a syringe pump at a specific flow rate. The spinning process is carried out by pumping the polymer solution to the end of the capillary tube such that it forms a small pendant or hemispherical surface. Then, a high voltage is applied between the polymer solution and the collector plate placed at a distance from the capillary tube. The electrostatic forces generated as a result of this electric field act against the surface tension and viscosity of the solution, thereby transforming the pendent like shape or the solution into a conical shape called the Taylor cone. Under further influence of the electrostatic forces, the polymer solution forming the Taylor cone stretches into a fine jet of fibre that travel towards the grounded collector plate and finally gets deposited on it. Continuous deposition of such fibres on the collector plate results in the formation of a non-woven mat having high surface area-to-volume ratio, carbon nanotubes (CNTs) can also be prepared using this process[1].

Electrospun nanofibre fabrics have several potentially attractive features. Some of these are: (i) softness potential of acting as a barrier against microorganisms and fine particulates; (ii) a potentially good strength per unit weight; and (iii) a high surface energy that indicates a potentially good vapour transmission rate.

Nanofibres can be used as nonwoven mats but can also be spun into yarn. The following applications are being developed:

- Nano filtration and absorption-catalytic breakdown (catalytic active nanofibre, or nanofibres with a catalytic coating, chemical and biological breakdown).
- As sensors, because the large surface area, are sensitive to absorption and subsequent change. for example, the electrical resistance (polymer conductive nanofibre).
- Structural applications, reinforcement fibre, e.g., for antiballistic application.
- Insulation
- Selective gas permeation (breathing, chemical and biological protective fabrics).

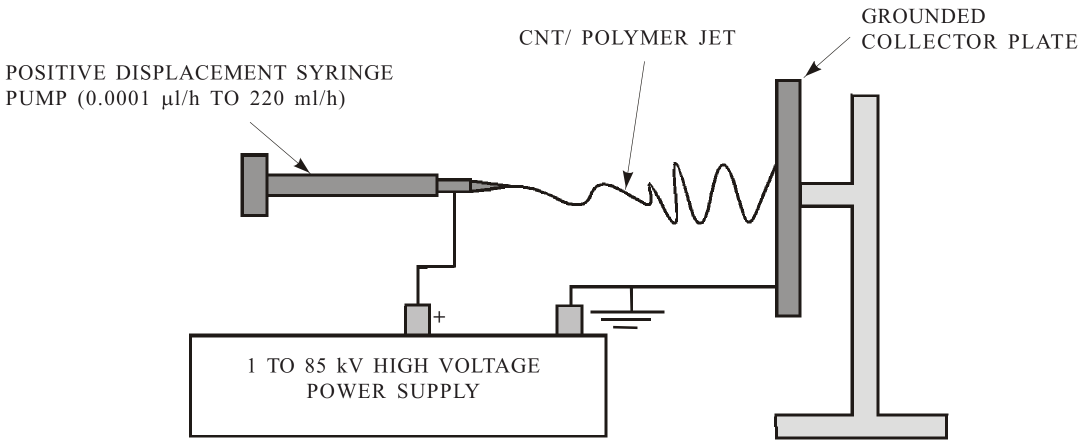

Figure 1. Schematic diagram of electrospinning unit.

- Carbonnanotube polymer composite fibre (high strength).

Experiments with non-woven mats indicate that the tensile strength increases significantly with reduction of the fibre diameter, e.g., going from a 6 µm fibre to a 60 nm fibre results in a 10-fold increase in tensile strength due to increase in number of fibre-to-fibre bonds and orientation of the polymeric molecules in the fibre-length direction. Due to small pore sizes in electrospun mats, resistance to convective gas flow is large, and hence, these are an excellent choice for protective fabrics[2].Thandavamoorthy[3], *et al.* have developed a method to produce polyurethane nanofibres which can be used to trap the toxic materials. The poly lactic-co-glycolic acid (PLGA) fibre and poly (ethylene oxide)-polypyrrole nanofibres are also produced using the electrospinning technique. These nanofibres are finding applications in electrical conductive textile material development. Tsai[4], *et al.* of University of Tennessee produced nanofibres from different polymers like polycarbonate, poly (ethylene oxide), polyurethanes, polystyrene, polycaparolactone, nylon 6, and nylon 66 and the fabrics made out of these nanofibres were studied for their barrier properties against microorganisms and chemicals.

2.1 Nanotube-based Fibres and Yarns

Nanotube-based fibres can often be prepared (Fig. 2) by dispersing single-walled carbon nanotubes (SWCNTs) in surfactant solutions followed by injecting these into a rotating bath of polymer solutions like aqueous polyvinyl alcohol (PVA), then slowly pulling the fibres from the bath, enabling aggregation and alignment of the nanotubes. The intimate inclusion of CNTs in these fibres can completely change their mechanical and electrical properties. Unlike classical carbon fibres, the nanotube fibres can be bent to maximum extent without breaking. Their obtained elastic modulus is 10-time higher than the modulus of high-quality bucky paper, a thin mat obtained by drying SWCNT[5].

Several researchers have attempted to produce CNT-polymer blends with moderate levels of alignment with nanotubes. Jalili[6], *et al.* of National Textile Centre (NTC), USA, have produced continuous yarns of up to 30 cm length of pure CNTs, with a diameter of about 200 nm, by drawing super-aligned arrays of CNTs. The process was similar to the process of production of silk from a silk cocoon. It was also reported that the tensile strength of the yarn and electrical conductivity (after the yarn was used as a filament in a vacuum chamber) were increased.

Zhu[7], *et al.* directly synthesised long ropes of nanotubes using an optimised CVD process in a vertical furnace. The process entailed the catalytic pyrolysis of *n*-hexane containing ferrocene and thiophene and was reported to produce long ropes of SWCNTs at rates of up to 0.5 g/h and a purity of up to 95 per cent. The tensile strengths of the nanotube fibres produced by this method were almost 5-time higher than those of the nanotubes produced by other methods. This would yield nanotube-based ropes that could be utilised as passive materials in fabrics with very less processing effort.

Ericson[8], *et al.* produced well-aligned macroscopic fibres composed solely of SWCNTs by the conventional wet spinning method using fuming sulphuric acid. Such neat SWCNT fibres produced, possessed good mechanical properties, with a Young's modulus of 120 ± 10 GPa and a tensile strength of 116 ± 10 MPa. The above values can be compared with laboratory-grade PBO fibres used in ballistic protection material

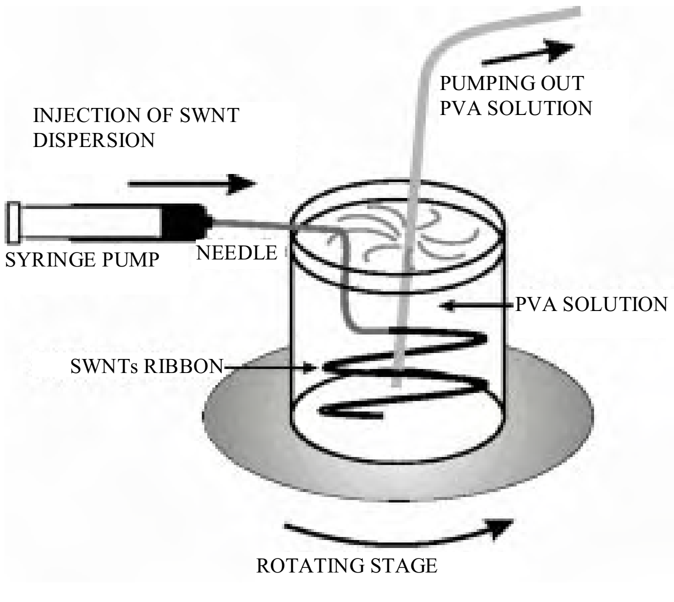

Figure 2. Preparation of nanotube-based fibres from SWCNT.

which possess a Young's modulus of 138 GPa and a tensile strength of 2.6 GPa.

The fibres produced by all the above methods possess very good electrical and thermal conductivity values apart from their interesting mechanical properties. Efforts are now being made to weave these fibres into macrostructures which can be used for a variety of applications, like actuator and sensor fabrics for the defence personnel.

3. POLYMER NANOCOMPOSITE FIBRES AND YARNS

Nanocomposites consist of a matrix material, usually a polymer, with a dispersion of nanoparticles/fibres. Several nanoparticles like carbon nonofibres, SWCNT, MWCNT, nano-TiO_2, nano-Al_2O_3, and aluminosilicate nanoclay were dispersed in a polymer matrix, instead of using conventional fillers, to produce novel composites with enhanced mechanical, electrical, and thermal properties. For example, as little as 1-5 per cent weight of nm-sized clay particles in cross-linked resins can provide big improvements in mechanical and thermal properties; reduced permeability to gases, moisture, and hydrocarbons; and increased flame resistance to textile polymers[9]. Nanocomposite materials have a wide range of applications in the fields of aerospace, ESD/EMI shielding, adhesives, paints, gas sensors, automobile seats, packaging, sporting, and tyres.

3.1 Carbon Nanotubes–Nanocomposites

Polymer matrices containing CNTs is a very active area of research and development for creating multifunctional materials. Polymers which are normally electrically insulating but have other advantages of being flexible, have low density, and are easily formed, can be combined with CNTs, 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. The most useful application areas are electromagnetic shielding, microwave absorption, ballistic protection, and chemical-sensor clothing[10]. A wide range of polymers materials such as poly(vinyl alcohol), poly(methyl methacrylate), poly propylene, polyethylene, polyethylene terephthalate, etc, have been used with CNTs to form films, fibres, and bulk composites through different spinning technologies like meltspinning, solutionspinning, and electrospinning[11].

3.2 Porous Nanocomposites

There are several types of porous nanocomposites. The simplest include foam with a homogeneous matrix containing nanometric 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 nanometric dimensions. A significant disadvantage of conventional porous polymer foams (e.g., polyurethane) is that the large surface-to-volume ratio increases the rate of heat and gas release in the case of fire. By introducing nanoparticles like clay, rate of burning can be significantly reduced. This material finds applications in defence as shock-absorbing materials, acoustic absorbents, and as vehicle seats[12].

3.3 Defence Applications of Nanocomposites

3.3.1 Smart Uniforms

This concept of smart uniform for soldiers has come up with the advent of nanotechnology. Under this concept, it is proposed to have an all-impact suit enabled by nanomaterials combined with micro- or macrofibres, offering protection against bullets, fragment of grenades, bioagents, chemical agents, and the influences in combination with the physical status of the body (insulation, ventilation, local cooling) of a soldier. Efforts are being made to produce a suit with integrated chemical and biological sensors and nanofibre networks with absorbing, deactivating, and decontaminating capacity. Likewise, efforts are also underway to use a carbon fibre and a polymer composite to produce a lightweight suit and a helmet for ballistic protection. The following developments have taken place in this concept.

3.3.1.1 Signature Reduction

This is a highly classified field of application, although it is obvious from allusions in the literature that a lot of work on developing camouflage materials based on polymer nanocomposites is being done.

Most manufacturers of CNTs mention this as one of the applications for their products. Dynamically tunable camouflage materials would be an invaluable aid to defence operations, allowing personnel and equipment to achieve highly visible or totally concealed presence, depending on the demand of the situation. Electrochromic materials offer one way towards achieving this. DeLongchamp and Hammond[13] report a high-contrast electromeric nanocomposite material based on poly (ethyleneimine) and Prussian blue nanoparticles. It is claimed that a fully switchable reflective tricolour space coating has been produced. This material has obvious applications in dynamically tunable camouflage in the visible spectrum.

3.3.1.2 Ballistic Protection

For body armour and vehicle liners, woven materials, such as kevlar, nomex, are commonly used. It is likely that electrospun nanofibres could be useful in such applications. It is reported that spun CNTs with extreme mechanical properties could be used for developing these types of materials. Lee[14], *et al.* reported a new liquid body armour based on nanotechnology. This was produced by impregnating kevlar-based conventional body armour with a stress-thickening fluid (STF) composed of colloidal dispersion of hard spherical silica nanoparticles of about 450 nm size in a polymer solution of polyethylene glycol. When this shear thickening fluid was impregnated into the conventional kevlar, the ability of the material to absorb energy was greatly improved. The ballistic performance in terms of absorbed energy is more than double so that four-layers of kevlar impregnated with the STF could absorb as much energy as absorbed by 10 layers without the STF. The mechanism proposed is that at high volume fractions, high shear stresses cause the suspended colloidal particles to form hydroclusters. Hydrocluster formation leads to a viscosity increase that can, at sufficiently high particle loading, result in a solid-like response, which is termed discontinuous shear thickening. In this line, kaolin clay platelets of about 500 nm diameter-based STF was also reported by Brian[15], *et al.* In terms of practical application, this will lead to much more flexible armour with equivalent ballistic protection and somewhat reduced total weight[16].

3.3.1.3 Fire-retardant Fabrics

Conventionally, chemical additives (halogenated hydrocarbons) are being used to reduce the flammability of fabrics but these have a number of side effects. If the fire occurs, the halogen will produce highly toxic and corrosive combustion gases and also may create several environmental problems.

Nanometer-sized clay particles (often montmorillonite) finely dispersed in selected polymer matrices are used as the reinforcement phase and provide enhancements in stiffness, toughness, tensile strength, thermal stability, gas-barrier properties, and importantly, flame-retardant character. The thermal properties of polymer nanocomposites are improved so that melting and dripping are delayed and the rate of burning is reduced by more than half. Further advantage is that the addition of the clay nanoparticles improves the mechanical properties of the fabric significantly, which can be utilised to reduce the thickness and weight. Two common types of morphologies exist for these nanocomposites: (i) intercalated, in which the polymer or monomers infiltrate the ordered array of silicate layers, and (ii) exfoliated, which results when the silicate layers are completely delaminated and finely dispersed within the polymer network. Dispersion of silicate layers in a polymer is difficult. For dispersion, compatibilising agent, a molecule constituted of one hydrophilic and one organophilic function, is commonly used[17].

3.3.1.4 Chemical/Biological Protective Nanocomposites

The protection of the soldier from exposure to hazardous chemicals, such as chemical warfare agents, is essential to mission accomplishment in today's battlefield and in that of the future. This protection is currently accomplished using an activated carbon system, using semipermeable material systems, and using impermeable barrier materials.

The activated carbon system is used in protective overgarments and affords protection by adsorbing hazardous chemicals. The impermeable barrier materials consist of rubber, coated and multilayer laminate fabrics found in gloves, boots, and for special purposes (e.g., depot storage/demolition/explosive ordnance disposal ensembles), which afford protection by acting as physical barriers to chemicals. However, these materials inherently possess either cost or logistic barriers, which make their fielding undesirable unless a catastrophic effect is eminent. A lightweight, low-cost, low-packing volume, chemical and biological protective barrier material would make collective protection feasible for conventional chemical and biological protective clothing and shelter systems, therefore enhancing the safety of soldiers during unpredictable chemical and biological attacks. Nanocomposites[18,19] based on clay, MgO[18] and TiO_2[19] have been developed which give excellent protection as well as operational advantage to the soldiers. This increase in barrier properties was accomplished without significantly changing the physical properties of the polymers.

3.3.1.5 Self-cleaning, Healing, and Decontaminating Fabrics

Self-cleaning fabrics containing TiO_2 nanoparticles have been developed based on their photocatalytic ability of oxidising dirt and other contaminants. These type of fabrics can be put to both military and civilian uses. It is reported that the textile substrates like cotton, wool, polyamide and polyester were pre-treated with RF-plasma, MW-plasma or vacuum-UV irradiation in such a way that negatively charged TiO_2 chelating groups, such as carboxylic groups, are introduced by the pre-treatment methods. Such TiO_2-treated materials showed self-cleaning activity under daylight environment[20,21]. Microbial protective clothing have been prepared by coating military garments with silver nanoparticles. These coatings in addition make the fabric self-wound healing, water-repellent, and dirt-repellent. Research is also going on to prepare the chemical and biological protective clothing with self-decontamination and drug-delivery characters. The decontaminants like nanometal oxides (MgO, Al_2O_3) along with activated carbon and antibiotics in the form of nanocoatings is being explored for this purpose[22].

3.3.1.6 Sensor and Energy-storage Fabrics

Finishing conventional textile materials with nanoparticle can convert conventional textile materials into sensor-based materials. If nanocrystalline piezoceramic particles are incorporated into fabrics, the finished fabric can convert exerted mechanical force into electrical signals, enabling the monitoring of bodily functions, such as heart rhythm and pulse, if these are worn next to the skin. The fabrics woven with CNTs can be used as energy-storing devices and can be used as next generation e-textiles. Several defence research organisations are contemplating to incorporate these technologies for developing smart soldier uniforms[23].

4. PROTECTIVE TEXTILE-BASED NANOTECHNOLOGY RESEARCH IN INDIA

In India, a larger number of research institutions are actively engaged in the nanotechnology research. The research in this particular field of protective clothing based on the above technology is limited. However, some of the nanotechnologies developed, which can be extended for protective clothing development, are summarised. Scientists at the Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore have developed several methods of producing CNTs, namely, by breaking down metallocene-hydrocarbon mixtures at high temperatures in the absence of air (a process known as pyrolysis), by *in situ* formation of metal nanoparticles from the metallocene which could act as a catalyst to produce bundles of high quality aligned CNTs and organometallic precursor routes to CNTs and their aligned bundles[24]. A CNT-based flow sensor was developed by a group of researchers at the Indian Institute of Science, Bangalore, based on the observation that a fluid flowing past a nanotube bundle gives rise to a potential difference across the bundle[25].

Scientists at the Defence Materials and Stores Research and Development Establishment (DMSRDE), Kanpur, have established CNTs Production Unit and synthesising non-aligned, quasi-aligned, and aligned CNTs with a batch size of 50 g using a fast synthesis process. The produced CNTs are being explored for applications as electro-magnetic wave absorbers, composites, gas sensors, flow monitors, field emission devices. Mukhopadhyay[26], *et al.* from DMSRDE produced microcoiled carbon fibres with high yield and good reproducibility found to have high potential for many applications, such as electromagnetic wave absorbers, electrode materials, tunable micro-devices, and so on without the addition of poisonous sulphur gas promoter.

Srivastava, [27]*et al*. of Banaras Hindu University in collaboration with Rensselaer Polytechnic Institute, USA, have developed a CNT-based filter. Using the CVD method, the scientists were able to make hollow macrotubes consisting of radial arrays of CNTs. These tubes, with a wall thickness of around 300 nm, have sufficient mechanical strength to act as filters. The filters find applications in the elimination of multiple components of heavy hydrocarbons from petroleum in a single-step filtering process, and the filtration of contaminants such as *E.coli* bacteria or the nm-sized polio virus from water. These macrofilters can be cleaned for repeated filtration through ultrasonication and autoclaving. Shrivastava[28], *et al*. of the same University reported the preparation of silver nanoparticles in the range of 10-15 nm with increased stability and enhanced antibacterial potency.

Joshi[29], *et al*. of the Indian Institute of Technology Delhi, New Delhi, prepared polyurethane/clay nanocomposite and coated there on nylon fabric to improve the gas barrier property. The coating reduced the hydrogen gas permeability by about 36 per cent at clay content of 3 per cent Wt as compared to neat polyurethane coating at the same thickness. This method of coating has military applications like coatings for hot air balloons, floating systems, and other aerial delivery systems.

5. CONCLUSIONS

Development of nanotechnology-based protective clothing for defence personnel is one of the important areas where all the major powers of the world are making efforts to do research and develop new materials. Ballistic clothing, barrier clothing against chemical and biological materials, self-decontaminant fabrics, and biomimicked fabrics based on nanotechnology are the thrust area of research in this field.

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