

## REVIEW PAPER

## Advancement in Textile Technology for Defence Application

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### ABSTRACT

The early development of textiles involved use of natural materials like cotton, wool and flax. The advent of the new technology revolutionized textiles which enables to develop synthetic fibers like lycra<sup>®</sup>, a segmented polyurethane-urea, which has exceptional elastic properties, Kevlar<sup>®</sup>, which has ultra high strength properties and is used as bulletproof vest. For the improvement of personal mobility, health care and rehabilitation, it requires to integrate novel sensing and actuating functions to textiles. Fundamental challenge in the development of smart textile is that drapability and manufacturability of smart textiles should not be affected. Textile fabrics embedded with sensors, piezoelectric materials, flame retardant materials, super hydrophobic materials, controlled drug release systems and temperature adaptable materials can play major role in the development of advanced and high-tech military clothes. Advancement in the textile materials has the capacity of improving comfort, mobility and protection in diverse hostile environment. In this study, the advancement in energy harvesting textiles, controlled release textiles and engineering textiles are presented.

**Keywords:** Piezoelectric fabrics, controlled release fabrics, engineering fabrics

### 1. INTRODUCTION

In recent times, intelligent textiles have been a topic of vast interest to academic field as well as industrial field. Smart textile or intelligent clothes are defined as the textiles which sense and react to environmental conditions or stimuli from mechanical, thermal, chemical, electrical, or magnetic sources. New fiber techniques, functional fabrics, smart materials, advanced microelectronics and artificial intelligence technology together with biosensor and conducting fabrics have enabled the implementation of usable intelligent clothes.

Performance of defence personnel much depends on the comfort, mobility and protection provided by the particular textile material. Defence personnel clothing became extremely complex due to unprecedented threats by ballistics, chemical biological, thermal and hazardous environment. Protective clothing for defence personnel should have unique characteristics to perform under diverse hostile conditions and wide range of threats. In the future, soldier's clothing will be capable of recording, analysing, storing, sending and displaying data, and also be able to provide protection of the individual combatant, whilst maintaining full operational effectiveness. It can be used for protection in a wide array of environmental conditions including chemical/biological, ballistics, noise and visual enhancing devices, insects and micro organisms in all-weather conditions.

In this paper, the advances in energy harvesting textiles, controlled release textiles and engineering textiles are presented. After reviewing details of recent developments in these textiles, the possibility of incorporating these materials in the defence clothing has been studied.

### 2. ENERGY HARVESTING TEXTILES

#### 2.1 Piezoelectric Fibers

Modern military devices such as sensors, actuators, communication devices and sighting system rely heavily on electrical energy. This energy is provided by means of batteries, which add extra weight to the soldiers which in turn affect their mobility. To overcome this problem, piezoelectric devices, super capacitors, solar cells, lithium ion batteries and other energy harvesting devices can be directly incorporated into the uniform of the soldiers. In this review we will primarily discuss the advancement in piezoelectric devices and super capacitors.

Piezoelectric devices are devices which are able to convert mechanical work into electrical energy and vice versa. In the field of polymers, poly (vinylidene fluoride) (PVDF) was the first discovered piezoelectric polymer material<sup>1</sup>. PVDF consists of four phases, among which  $\beta$ -phase showed strong piezoelectric effect. So, numerous efforts have been carried out to form  $\beta$ -phase content in PVDF by incorporating clay<sup>2</sup>, carbon nano tube<sup>3</sup>, mechanical stretching<sup>4</sup> and electrospinning<sup>5</sup>. A comparative study on electrospun PVDF blend fiber with polar matrix (poly acrylonitrile) and non polar matrix (polysulfone) and also studied the synergistic effect of electrical poling, mechanical stretching, and dipolar interaction on the  $\beta$ -phase formation<sup>6</sup>. In their study, it has been observed that PVDF with polysulfone is not able to persist its ferroelectric properties after removal of mechanical stretching by melt recrystallization process. By dip coating method, solid piezoelectric film consisting of PVDF, acetylene black and  $BaTiO_3$ <sup>7</sup>. But when compared to the solid piezoelectric film, porous piezoelectric

polymeric membrane can be a prominent candidate in applications like hydrophone devices and power sources for wearable electronic devices. In addition, He<sup>2</sup>, *et al.* developed porous poly (vinylidene fluoride-trifluoroethylene) copolymer membrane by electrospinning and further hot pressing<sup>8</sup>. Results showed very high value of dielectric constant ( $d_{33} = 24.7$ ) when compared to electrospinning, due to tight contact between the fibers in hot pressing.

Lead zirconate titanate (PZT) is another promising piezoelectric material because of its high electromechanical coupling coefficient, high dielectric constant and high piezoelectric response. Dharmaraj<sup>9</sup>, *et al.* fabricated lead zirconate titanate fiber, diameter ranging from 200-300nm. Xu<sup>10</sup> *et al.* investigated mechanical properties of individually electrospun PZT nano fiber and it showed elastic modulus of 42.99 Gpa. Lead is toxic to our environment so great effort has been put to develop synthetic lead free piezoelectric material. In this regard, vanadium doped ZnO nano fiber is fabricated by electrospinning technique. Liao<sup>11</sup>, *et al.* prepared  $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$  nano fiber by sol-gel and electrospinning technique.

Mimura<sup>12</sup>, *et al.* fabricated barium titanate ( $BaTiO_3$ ) nanoparticle/poly (2-hydroxyethyl methacrylate) (PHEMA) hybrid from in-situ synthesized  $BaTiO_3$ /polymer hybrid nanofibers by electrospinning technique<sup>12</sup>. The effective  $d_{33}$  value was observed as 6.7 pm/V for hybrid nanofiber with 20% PHEMA in their study. Further increase in PHEMA content indicated reduction in effective  $d_{33}$  value.

Recently, phase change materials have attracted great interest for the thermal energy storage. Fatty acids acquired considerable attention as a promising candidate for phase change materials (PCM) due to its non-toxicity, high capacity of latent heat and good thermal and chemical stability. But PCMs have problem of encapsulation which increase its operating costs. To overcome this limitation, different polymer matrices such as polymethylmethacrylate, polyethylene oxide<sup>13</sup> have been investigated to support PCMs. Chen<sup>14</sup>, *et al.* prepared polyethylene glycol (PEG)/cellulose acetate (CA) composite

fiber by electrospinning process. In their study, PEG was used as PCMs and CA as supporting polymer matrix.

## 2.2 Solar Energy

Solar energy is another topic which is being extensively studied in recent years as fossil and mineral energy resources are approaching inevitable exhaustion. Device which converts solar energy directly into electrical energy through photovoltaic effect is called a solar cell. Dye sensitized solar cells are the new class of thin film solar cells, in which a dye sensitized n-type semiconductor oxide film is deposited on a transparent conducting glass substrate which is called working electrode or photo anode. A platinum coated glass substrate placed parallel to photo anode, acts as counter electrode<sup>15</sup> as shown in Fig. 1.

For the fabrication of electrode by the use 1D nanowires, nanobelts, nanofibers and nanotubes for DSSCs application, different techniques such as metal organic chemical vapour deposition<sup>16</sup>, hydrothermal synthesis<sup>17</sup>, vapour transport<sup>18</sup>, and electrospinning<sup>19</sup> have been reported. Among them, electrospinning is proved to be the most effective and versatile technique, but lack of adhesion of electrospun fibre on fluorine doped tin oxide (FTO) substrate limits its application in DSSCs. To improve the adhesion of electrospun fiber on FTO substrate, Sining Yu<sup>20</sup>, *et al.* employed seed layer before the deposition of Al doped ZnO composite nanofibre on FTO substrate. There was great improvement in total energy conversion efficiency of 0.54% - 0.55% after seed layer treatment of the FTO as compared to substrate without seed layer treatment. Francis<sup>21</sup>, *et al.* fabricated rutile  $TiO_2$  nanofibers/rods by electrospinning followed by sintering and hot pressing. Result showed energy conversion efficiency of 4.17% - 4.56% for  $TiO_2$  nanorods and 1.51% - 1.76% for  $TiO_2$  nano fibers. To avoid hot press pre-treatment in the formation of nano fibers upon sintering, Nair<sup>22</sup>, *et al.* proposed simple method for the efficient  $TiO_2$  nano fiber based DSSCs.  $TiO_2$  nano fibers were fabricated to nano rods and mixed with polyester, after sonication, pachini type paste was formed. After polymer evaporation, a highly porous and dense film of nano rods is produced on the FTO substrate. Resultant nano rods showed energy conversion efficiency of 4.20 per cent.

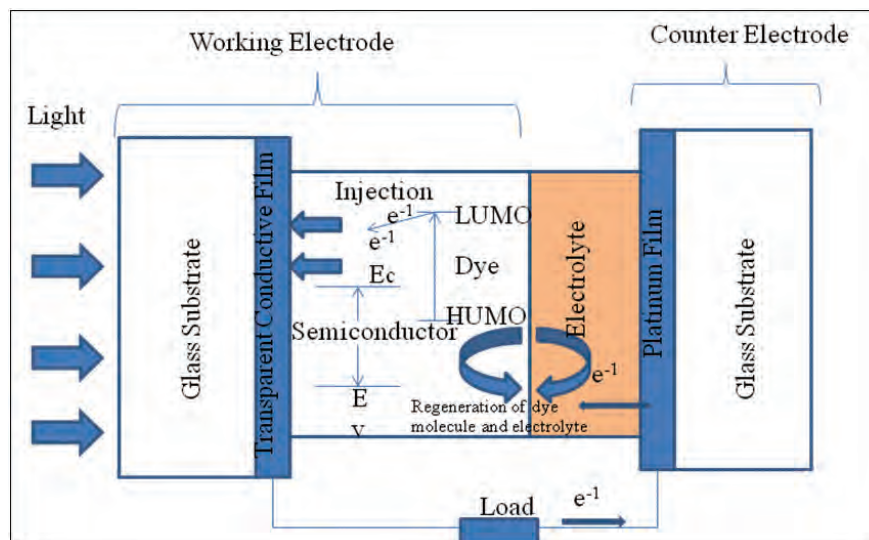


Figure 1. Outline of a dye sensitized solar cell<sup>15</sup>.

### 3. CONTROLLED RELEASE TEXTILES

Most textile materials currently used in military are vulnerable to diseases caused by microorganisms. These infections are mainly caused by Gram positive *Staphylococcus aureus* (*S. aureus*), *Bacillus subtilis* (*B. subtilis*), and Gram negative *Pseudomonas aeruginosa* (*P. aeruginosa*) and *Escherichia coli* (*E. coli*). To avoid infections, antimicrobial properties can be imparted to textile material by incorporating functional agents on to fibers and fabrics. Usually, drug loading into textile material can be achieved by incorporating drug during the preparation of the textile material or after the formation of it by incubating the drug with them.

Silver ions have long been known to exhibit strong inhibitory and antibacterial activity. Fu Chu Yang<sup>23</sup>, *et al.* studied antibacterial properties of bamboo charcoal supported silver (*BC/Ag*) and titanium dioxide supported silver fabric (*TiO<sub>2</sub>/Ag*) by activation and chemical reduction. Obtained results in their study demonstrated, killing of 100% Gram-positive *S. aureus* strain after 1 h of incubation by non woven blank reacted with *BC/Ag* while non woven blank reacted with *TiO<sub>2</sub>/Ag* showed same result after 2 h of incubation. Cyril Ringot<sup>24</sup>, *et al.* elaborated a new antibacterial material by grafting mesoerythroporphyrin on cotton fabric by the means of cellulose azidation followed by click chemistry reaction with acetylenic porphyrin and result showed final number of *E. coli* and *S. aureus* accounts for only 20% of the original count after 24 h of incubation. It is hypothesized that incorporating antibacterial agent directly into spin dopes, leads to low antibacterial efficacy. Introducing antibacterial functionality onto nanofiber surface after the nanofibers were produced is potential solution to overcome this problem. Lifeng Zhang<sup>25</sup>, *et al.* prepared PAN nano fibrous membrane by electrospinning and treated nanofibrous membrane with hydroxylamine aqueous solution to form amidoxime nano fibrous membrane, which was coordinated with  $Ag^+$  ion. Subsequently the coordinated  $Ag^+$  ions were converted into silver nano particle. They have demonstrated that coordinated membrane with  $Ag^+$  and with silver nano particle exhibit excellent antibacterial property against *S. aureus* and *E. coli* and capable of killing tested microorganisms in 30 min. In addition, Pant<sup>26</sup>, *et al.* successfully embedded silver nano particles in electrospun *TiO<sub>2</sub>/nylon-6* composite nano fiber through the photocatalytic reduction of silver nitrate solution under UV-light irradiation.

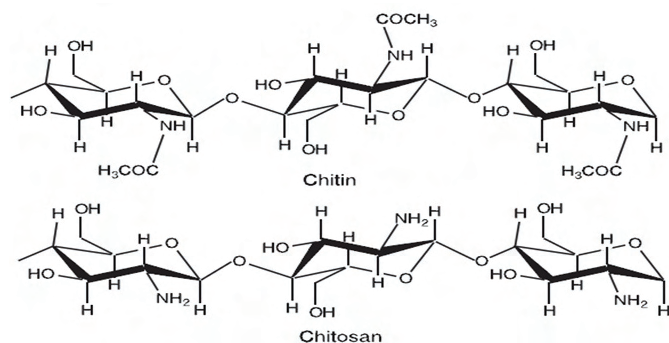


Figure 2. (a) Chitin (b) chemical structure of chitosan<sup>27</sup>.

Recently, researchers have extensively focused on chitosan because of its favourable physicochemical and biological properties such as biocompatibility, non toxicity and antibacterial property. Drug release for chitosan system follows three mechanisms

- drug release from the surface
- drug release due to surface erosion
- diffusion through the swollen matrix.

Mechanism of drug release from the surface indicates that adsorbed drug dissolves on contact with the release medium. Release due to surface erosion also follows drug release mechanism. Diffusion mechanism takes place in three step

- release system absorbs water
- matrix swells and become rubbery
- diffusion of drug through swollen matrix<sup>27</sup>.

Ritger and Peppas proposed an empirical (1),  $M_t/M_\infty = kt^n$  for diffusion controlled matrix, in which early release data is used to obtain the diffusion parameter<sup>28</sup>. Where  $M_t/M_\infty$  is the fractional drug release at time  $t$ ,  $k$  is a constant characteristic of the drug-polymer interaction and  $n$  is an empirical parameter of drug release mechanism or diffusion exponent.

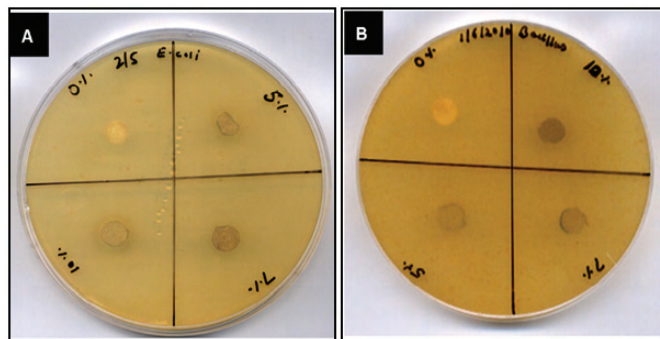


Figure 3. Optical images agar plate showing zones of inhibition after 12 h of incubation for (a) *E. coli* and (b) *B. subtilis*<sup>29</sup>.

To study the antibacterial property of copper nano particle, Sheikh<sup>29</sup>, *et al.* fabricated polyurethane nanofibers containing copper nano particle and studied the anti bacterial property against *E. coli* and *B. subtilis*. Figure 3 showed clear inhibition zone for 12 h of incubation in their study.

The treatment of wounds restores integrity of the injured tissues and prevents organisms from deregulation of homeostasis. An ideal dressing aimed to maintain a moist environment at the wound interface, allow gaseous exchange, act as a barrier to microorganisms and remove excess exudates. It should be non-toxic, non-allergic, non-adherent and easily removable without trauma. Schematic presentation of required properties of a wound dressing material<sup>30</sup> has been shown in Fig. 4.

In this regard, Shalumon<sup>31</sup>, *et al.* developed sodium alginate and PVA composite nano fiber mat through electrospinning technique, by incorporating ZnO nano particles with different concentration of 0.5%, 1.0%, 2.0%, and 5.0%. Results showed, among the entire nano fibrous mats, 0.5% ZnO containing mat exhibited best cyto-compatibility for wound

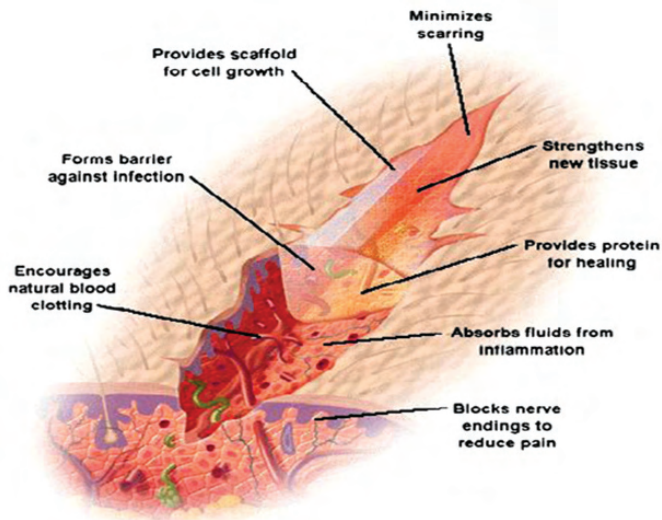


Figure 4. Representation of required properties of wound dressing material<sup>30</sup>.

dressing. The properties of alginate can be tuned by changing chemical composition and molecular weight of polymer.

Each kind of drug has its own biological half life and is effective only when their concentrations in the blood are above their minimum effective level. Increasing dose of the drug will turn itself into the toxic response region, whereas, having selected dose of drug during a period of time is not convenient for the patient. So controlled drug release has become a prerequisite to achieve therapeutic efficacy and avoid adverse side effect over conventional drug dosage forms. Recently many researchers have been investigating many controlled drug release systems such as films, micelle, hydrogel, and microparticles. Li<sup>32</sup>, *et al.* generated core-sheath nanofibers containing poly ( $\epsilon$ -caprolactone) (PCL) and silk fibro into study controlled drug release. They have conducted in vitro fluorescein isothiocyanate (FITC) release study to evaluate sustain release potential of core-sheath nanofibers. Long time release study<sup>32</sup> showed in Fig. 5. The core-sheath fiber had continuous release kinetics ( $62.2 \pm 4.2\%$  within 80 h) of FITC compared to pure PCL ( $49 \pm 1.8\%$  within 80 h).

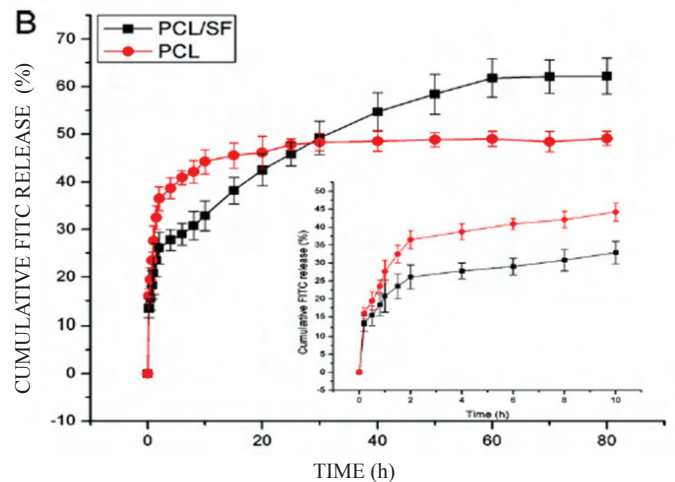


Figure 5. Long term release behaviour of FITC from electrospun PCL and core sheath nano fibrous scaffolds<sup>32</sup>.

#### 4. ENGINEERING FABRICS:

Performance of military personnel can be improved by controlling environmental conditions. These conditions can be tailored by providing them such dresses which is waterproof, flame retardant, chemically protected, thermally insulated, and embedded with sensors and electromagnetic shielding materials. In this section we primarily discuss the advancement in superhydrophobic fabrics, temperature adaptable fabrics, flame retardant fabrics, fabrics for body armour and fabrics embedded with sensors.

##### 4.1 Super Hydrophobic Surfaces

In recent years research groups have focused extensively on superhydrophobic surfaces with the contact angle (CA) of  $150^\circ$  for the application in protective coating, self cleaning surfaces, anti-icing/anti-snowing and micro fluidic systems. Some superhydrophobic surfaces are available in nature which can cause water and even oil to roll-off leaving little or no residue and carry away all the surface contaminations. Lotus leaf is the best known example of self cleaning surface. The SEM images of lotus leaf<sup>33-34</sup> have been shown in Fig. 6.

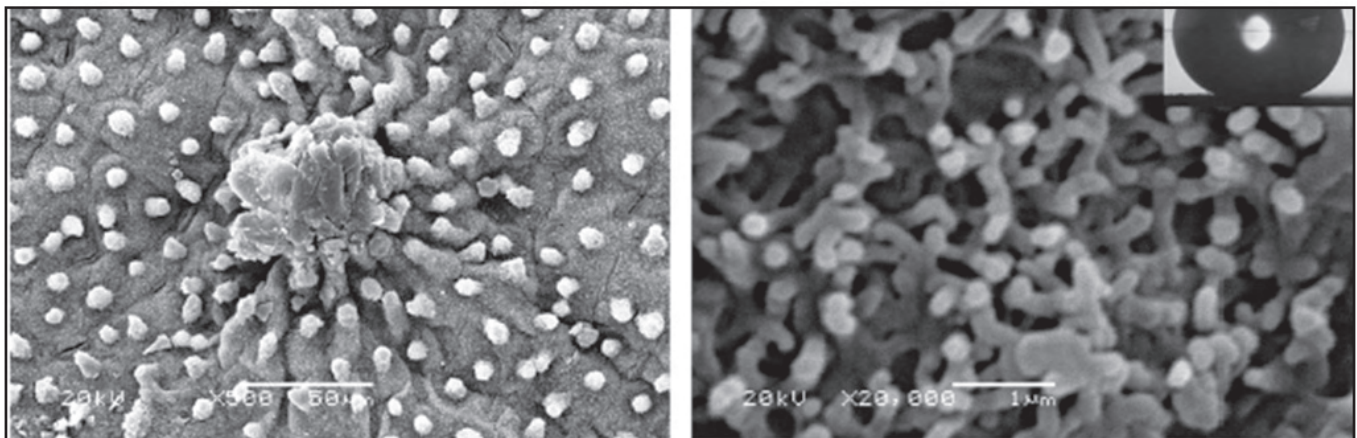


Figure 6. SEM images of lotus leaf with low and high magnification respectively<sup>33-34</sup>.

To realize superhydrophobicity from various substrates, many elegant methods such as wet chemical reaction<sup>35</sup>, hydrothermal reaction<sup>36</sup>, electrochemical deposition<sup>37</sup>, layer-by-layer<sup>38</sup>, chemical vapour deposition<sup>39</sup>, and polymerization reaction<sup>40</sup> have been employed. For instance, Ci<sup>41</sup>, *et al.* developed vertically aligned large diameter double walled carbon nanotube arrays. Results showed that when thickness of catalyst Fe was fixed about 3 nm by water-assisted chemical vapour deposition process then obtained surface exhibited water CA of 170°.

Ogawa<sup>42</sup>, *et al.* developed superhydrophobic membrane surfaces through electrostatic deposition of a rough layer-by-layer coating on electrospun cellulose acetate nanofibrous membrane and then modified the surface by fluoroalkylsilane (FAS). In this study they were able to achieve water contact angle (CA) of about 140°. Further, Lifang Wang<sup>43</sup>, *et al.* developed superhydrophobic thermoplastic polyurethanes (TPU) mat modified with hydrophobic nanosilicas by solution immersion route. The electrospun TPU mat exhibited improved hydrophobicity with the contact angle of 139.2° compared with flat TPU mat prepared through spin coating (CA is about 74°).

A durable superhydrophobic surface has been developed by Wang<sup>44</sup>, *et al.* In their study super hydrophobic surface was obtained by electrospinning PVDF, mixed with epoxy-siloxane modified  $SiO_2$  nanoparticles.  $SiO_2$  nanoparticles were introduced into PVDF precursor solution to obtain rough surface and achieved contact angle was 161.2°.

#### 4.2 Thermal Resistant and Phase Changing Material

Defence personnel are exposed to various thermal environments, from which their body needs protection. For efficient protection of the body, protective clothing requires balance between different properties such as, thermal resistance, hygroscopicity, water transfer, water vapour (WP) permeability, control of dynamic temperature and moisture in the clothing skin microclimate. To maintain constant temperature of the body is essential to homeostasis, because most enzymes are sensitive to temperature and function only in narrow temperature range. In hot conditions, heat must be continuously dissipated and regulated to maintain normal body temperature. Therefore, thermal protective clothing is needed to protect defence personnel against climatic influences. In this regard BO-an Ying<sup>45</sup>, *et al.* analysed the physical mechanisms of heat and moisture transfer through textiles with phase change materials (PCM) and studied thermal regulating capability, thermal psychosensor intensity (TPI) and static thermal insulation performance of textile<sup>45</sup>. Results were demonstrated that there was no change in thermal regulating capability with the change in PCM level while heat flux transfer and TPI were increased with increase in PCM level.

Polyimide (PI) is now a widely used material in high temperature application because of its excellent fire retardation and outstanding thermal stability. Porphyrin rings, rare earth compounds and hemicyanine dye<sup>46-47</sup> was introduced to PI matrix for enhancing its properties. Interaction between organic and inorganic phases can be obtained by two methods either by physical blending<sup>48</sup> or by chemical reaction<sup>49</sup>.

Cheng<sup>50</sup>, *et al.* prepared PI/europium nanofiber electrospinning. Chemical coupling sites between PI and europium was directly introduced by the simultaneous formation of europium gel and imidization of polyamic acid (PAA). Similarly, Im<sup>51</sup>, *et al.* fabricated polyurethane fibers using electrospinning process with aluminium hydroxide and multi-walled carbon nano tubes as flame retardant additives for enhancing its thermal oxidation stability. In this study, multi walled carbon nano tubes (MWCNTs) were modified by oxyfluorination to improve its dispersivity in the polyurethane fibers and aluminium hydroxide were used as energy storage tank. Figure 7 exhibited sharp peak due to incorporated aluminium hydroxide additives.

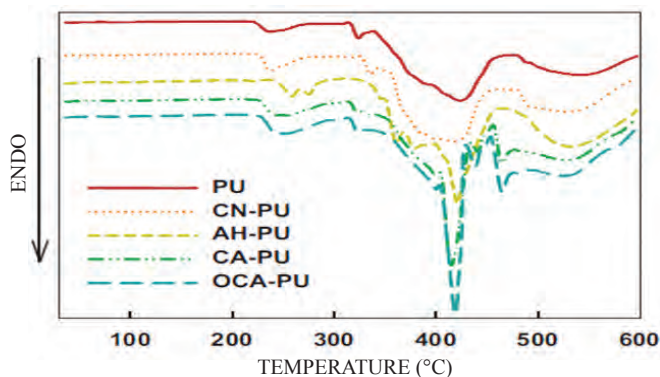


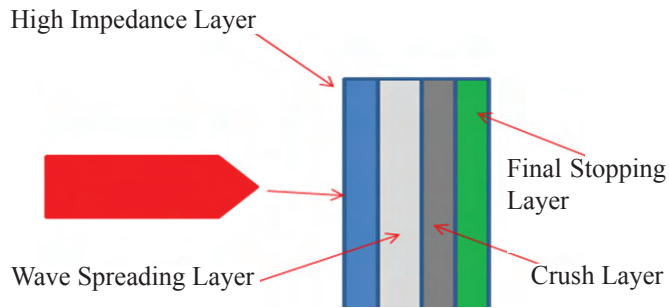
Figure 7. DSC curve of electrospun PU fibers containing MWCNTs and aluminium hydroxide<sup>51</sup>.

#### 4.3 Armour Design

Armour materials<sup>52</sup> are used to provide protection against ballistics as well as fragments of ballistics and armour itself. Energy required for projectile to penetrate is a function of specific modulus, density, tenacity, specific tenacity and extension to break. Basic body armour includes ballistic vest and plate which provide protection against bullet and fragmentation above the velocities of 244 m/s. Development of armour materials involved history from raw steel, alloys to the high performance fibers like aramid fibers, ultra high molecular weight polyethylene fibers, liquid crystal polymer matrix fibers and so on<sup>53</sup>. But the most marketed body armour materials are Kevlar®, Spectra®, Dyneema® and Zylon®, in which Kevlar was the first concealable body armour developed by DuPont<sup>54-55</sup>.

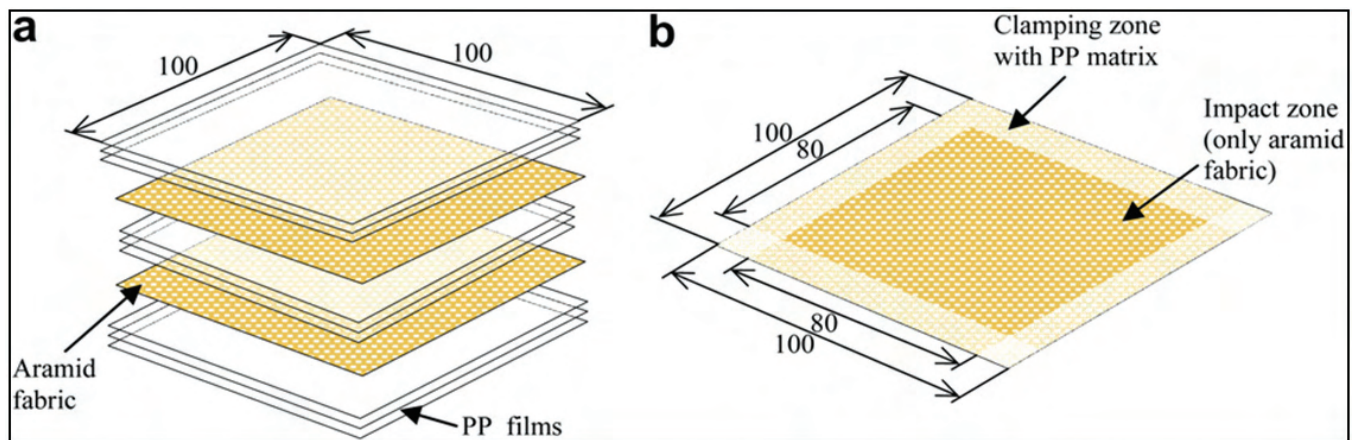
Recently research groups are emphasising on the development of new armour layering concept. This layering concept based on the combination of four layers which consists very hard 1<sup>st</sup> layer to deform and fracture the projectile, 2<sup>nd</sup> layer to slow down the shock wave propagation, a 3<sup>rd</sup> porous layer to absorb the shock and 4<sup>th</sup> layer to provide restriction to the porous medium as shown in Fig. 8. Based on this concept, Ong<sup>56</sup>, *et al.* developed composite plates comprising alumina ceramics as 1<sup>st</sup> layer, Dyneema® HB25 as 2<sup>nd</sup> layer, porous polyurethane as 3<sup>rd</sup> layer and this porous layer was confined by aluminium. Live firing result showed 24 % reduction in target deformation against projectile velocity of 475 m/s.

Feli<sup>57</sup> *et al.* investigated finite element analysis of the ballistic perforation of ceramic/composite target in which



**Figure 8. Graphical illustration of armour layering concept<sup>56</sup>.**

ceramic was made of 99.5 % of alumina and back up plate of ceramic was composed of Tawron fibers of 50 layers with 0.4mm thickness. In their study, brittle failure, effect of high pressure, high strain rate and large deformation was considered to describe the fragmentation of ceramic plate under high velocity impact by using Johnson-Holmquist continuum based plasticity model. Carrilo<sup>58</sup>, *et al.* studied the ballistic behaviour of multi layer aramid fiber/polypropylene (PP) composites laminates and compared with the multi layered aramid fiber without PP which is shown in Fig. 9. The contribution of PP matrix to the system ballistic resistance was also discussed.



**Figure 9. (a) Multi layer aramid fiber with PP (b) layered aramid fiber<sup>58</sup>.**

Result exhibited that three layer aramide fiber with PP matrix was able to clear all tests compared to plain layered aramide fiber. Result also showed that increment in permanent deformation for both the configuration was the function of number of layer before the projectile was stopped.

## 5. CONCLUSIONS

Development of smart textiles may affect many aspects of defence personals lives. New materials integrating novel technologies enables smart fabrics to retain its necessary wearable and flexible characteristics, which we expect from our daily clothing. By integrating these technologies to the fabrics will also improve its mechanical, thermal and electrical properties. The major problem in wearing computing, sensors, actuators, biomedical garments and etc is the durability, flexibility and washing cycles for a long period of time. For

the defence personnel, development in textile technologies and fabrics will be able to enhance battle uniforms, suits, ballistic protection systems and survivability of the army personnel. Smart fabrics will help to develop lightweight and high durable fabrics with very high strength simultaneously these fabrics will be embedded with antibacterial additives, small and massive storage devices, microprocessors, super capacitors, high resolution displays and water purifiers etc. These advanced technologies enable army personnel in striking improvement in the battlefield.

Smart textiles include interdisciplinary research areas like materials research, sensor technologies, engineering, electronics, computer applications, biosciences and etc. This topic covered a large range of applications starting from very specialized application of the generally available products. So with the current pace of development in smart textile will form a ubiquitous part of defence lifestyle. Their clothing will become contextually aware and will be able to adjust to the change in the environment.

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