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NANOTECHNOLOGY FOR BALLISTIC MATERIALS: FROM CONCEPTS TO PRODUCTS

NANOTEHNOLOGIJA ZA BALISTIČNE MATERIALE: OD IZHODIŠČ DO PROIZVODA

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The main trends and materials in protection technologies are briefly reviewed, emphasizing the properties and limitations of p-aramid fibres, widely used in armour systems, particularly in terms of their susceptibility to UV radiation, humidity and chemical attacks. Then, a novel nanotechnology capable of effectively diminishing these effects is described, as well as its application for an actual commercial ballistic vest.

Keywords: nanotechnology, ballistic materials, aramid fibres, bullet-proof materials, nanoparticles, degradation

Podan je pregled glavnih usmeritev in materialov v tehnologijah zaščite s poudarkom na lastnostih in omejitvah p-aramidnih vlaken, ki se uporabljajo v oborožitvenih sistemih s poudarkom na njihovo občutljivost za UV-sevanje, vlago in kemični napad. Nato so opisane nove nanotehnologije, ki so sposobne zmanjšati te vplive, kot tudi njihova uporaba pri dejanskem komercialnem balističnem telovniku.

Ključne besede: nanotehnologija, balistični materiali, aramidna vlakna, neprebojen material, nanodelci, degradacija

1 INTRODUCTION: THE WORLD OF PROTECTIVE MATERIALS

Protection represents an important industry, both economically and socially speaking, that includes, in the broad sense, industrial, laboratory, home and, of course, military protection, with an enormous variety of products, from simple plastic gloves to sophisticated and confidential military armour. It is considered a "fragmented industry", in spite of the high volumes involved, for literally thousands of manufacturers of raw materials, producers of finished goods, distributors at all scales, consultants, etc., operating worldwide with a steady growth rate of around 3 % annually.[1–10] In particular, the materials that may be used for personal garment have attracted a great deal of attention in the past few decades. In fact, in December (2003), U.S. Attorney General John Ashcroft instructed the National Institute of Justice to implement a new initiative *"to address the reliability of body armour...and to examine the future of bullet-resistant technology and testing…"*[2,11–17]

In the particular area of protective materials, thanks to the technological breakthrough of the 1960s that will be discussed later on, the share of the market for high-performance fibres for garment applications of one single company (Dupont) is 60 %, whereas Honeywell has 30 % and Toyobo, with the most recent technologies, has 5 %.[3–17]

Nanotechnology is already a subject taught not only at universities but also at the industrial level, while the capacities of creating new nanomaterials have been explored only in part.[18–32]

In the sections below we will focus, among all the ballistic conceivable materials, on those intended for personal protection, particularly on the ballistic vests and related gadgets.

2 MODERN TRENDS IN BALLISTIC MATERIALS

Today's generation of body-armour systems can provide protection at various levels designed to defeat most common low- and medium-energy handgun rounds. However, currently the highest-threat-level ballistic needs in the market are fulfilled by special, high-performance ceramics that tend to be very costly, fragile for standard handling, extremely heavy and very difficult to shape to the requirements of an ergonomic design.[3–5] The search for novel polymer-based armour materials dates back to the invention of synthetic macromolecules. Accordingly, some companies have recently publicized some nanofibre-reinforced systems that are expected to provide very attractive weight/protection relationships not only for personal equipment, but also for belly plates for motor vehicles and even aircrafts[5], exposed to the impacts caused by dust, birds and other objects, not necessarily by combat conditions, offering an interesting potential market for novel ballistic materials.

From the military point of view and according to a recent report[3], nanotechnology offers two important advantages: first, the potential to achieve high degrees of miniaturization, which will be reflected in the weight of the equipment and second, the possibility of finding unexpected effects at the nanoscale, which not only will represent a strategic advantage over the enemy, but will also include a possibility of concealing the technology behind a given effect.

According to this view, a list of potential applications of nanotechnology for equipping the soldiers of the XXIst century is limited only by imagination, at least according to the Massachusetts Institute of Technology's Institute for Soldier Nanotechnologies, which includes 56 specific projects divided into 7 work teams,[3] one of them dedicated to energy-absorbing materials, an area of obvious relevance for the use of nanoparticles and nanostructured composites, in addition to "smart" materials, of course[4].

3 KEVLAR: A TRUE TECHNOLOGICAL REVOLUTION

The modern history of ballistic polymers begins with Stephanie Kwolek's 1966 patent on Kevlar, a para-aramid, invented while working with Dupont.[6] Chemically speaking, the "para" configuration allows the formation of fibres, as opposed to the "cis" one that is sterically hindered due to the large aromatic groups of the structure. Thus, the discovery of the properties of this molecular configuration has led to the development of a whole family of high-performance polymeric materials: the so-called p-aramids. In particular, Kevlar certainly represents a technological revolution not only for armour materials, but for many other important applications, from brake lining to space vehicles, including boats, parachutes, building materials, etc. From the chemistry standpoint, Kevlar is an aromatic polyamide, produced with a condensation reaction of para-phenylenediamine and terephthaloyl chloride, yielding a product with a chemical composition of poly-para-phenylene terephthalamide (PPD-T), having the technical name of Kevlar. It is known that aromatic and amide groups of the type contained in the structure of PPD-T provide a high mechanical and thermal strength. One of the important, and not very well known, facts about Kevlar is that it constitutes a type of liquid crystalline polymer. Indeed, when PPD-T solutions are extruded to produce an actual fibre, the liquid crystalline nanodomains align themselves according to the flow, thus producing a highly anisotropic material, capable of withstanding very high impact energies. For example, the tensile modulus of Kevlar 29, a high-toughness variant used for ballistic vests, is of around 60 GPa, which can be further increased to 130 GPa (Kevlar 49) with thermal treatments under tension, increasing the anisotropy of the crystallites in the material[7]. The aromatic rings in the structure of Kevlar provide a high thermal stability, since the corresponding decomposition temperature is nearly 430 °C.[8] After the success of the original Kevlar formulation, Dupont and a number of other companies have developed a whole family of p-aramids that, along with the other special polymeric materials (e.g., ultra-high-molecular-weight polyethylene –UHMWPE), nowadays constitute the core of the ballistic vest industry.

One very important limitation of Kevlar, however, is its susceptibility to degradation due to UV exposure, environmental humidity and the chemicals contained in perspiration (sweat), the conditions that cannot be avoided during in-field operations. A report by the U.S. Lawrence Livermore Laboratory[9] reveals that Kevlar "is susceptible to photo-degradation from UV light sources". Photo-degradation is a phenomenon, in which the tensile strength of the fibres is reduced as a result of exposure to UV light sources such as sunlight and fluorescent light. Photo-degradation leads to reduced abrasion and tear resistance in aramid fibres such as Kevlar. This problem is so serious that, for example, the User Instruction, Safety and Training Guide provided to the customers by Lion Apparel (Dayton, Ohio, U. S.) gives the following warning:

"Exposure to ultraviolet light (found in the sun's rays and fluorescent light) will severely weaken and damage the fabrics in your protective clothing after only <u>A FEW DAYS</u>. *This is especially true for fabrics of the following aramid materials: Hoechst Celanese Pbi, Dupont Kevlar, Dupont Nomex, Dupont Nomex Omega, Dupont Nomex IIIA, Lenzing P84, Southern Mills Advance, and BASF Basofil."*

4 NOVEL BALLISTIC FIBRES

One of the most promising recent advances in polymeric materials for protection garments is the Japanese fibre Zylon[10], a poly(p-phenylene benzobisoxazole) (PBO), which has a tensile strength of around twice that of Kevlar and similar commercial p-aramids, such as Twaron (by Teijin Twaron Co.). The amazing properties of Zylon have allowed super light, very comfortable (and very expensive!) vests. However, recent studies[9-12] reveal inherent limitations in terms of its degradation under visible light, heat and, particularly, when exposed to humidity and the chemicals commonly found in sweat, which can lead to a 65 % strength loss over a period of only six months.[10] Sealing the fabric into some thermoplastic does not improve much this effect, even at room temperature, due to the capillarity behaviour of the Zylon fibre.[12] These important limitations, along with the price, have severely limited the use of an otherwise attractive material.

5 STRATUM nanoPROTEC^{TM}: NANOTECHNOLOGY IN ACTION

In the above context, armour industry faces an interesting conundrum: the availability of very strong polymeric materials that are highly sensitive to standard working conditions. A number of solutions have been proposed and tested so far, from protective coatings, to the use of irradiation[13–16] to change the molecular configuration of polymeric materials such as HIPS, Nylon, Kevlar and Zylon and make them less susceptible to the environment, to the humidity coming from both the ambient and, particularly, from the bearer of the vest (i.e., the sweat). The problem is not simple at all, because the treatment or coating must not only preserve the ballistic properties of the system, but also allow a good deal of comfort that can be affected by stiffening the fibres through crosslinking or surface layers of various kinds. The challenge is, thus, too great for the standard technology of ballistic materials, as it can be corroborated by the fact that the leading industries in the field have spent years and enormous amounts of money to produce an environmentally stable garment to no avail.

An opportunity for nanotechnology is then to find a solution using the unique characteristics of nanoscale systems. Indeed, ceramics are known to have a very high resistance to UV degradation, as compared to polymers.[17–30] Their brittleness and specific density, however, prevent their use in a garment. By chemically attaching suitable ceramic nanoparticles to the surface of the fibre, one is able to effectively shield the material against UV without changing any other property. This can be done with a proper reaction between the nanoparticles and the previously modified Kevlar 29 fibre, using an organic coupling agent for the fibre and the particles.[31–34]

The problem of humidity is a more complicated one, since the common paradigm is to offer a *physical* barrier to the water molecules. The obvious difficulty is to ensure, at a molecular level, that the barrier keeps its integrity during the use, enduring bending, shear and all the typical abuses of a military garment. Chemically functionalized nanoparticles linked to organic structures offer a possibility of presenting a *chemical* barrier to water molecules. This has a number of unique advantages: first, no need to have a 100 % continuous coverage of the surface; second, no danger of detachment as with a coating, and third, no change in the other relevant physical and chemical properties of the fibre.[34]

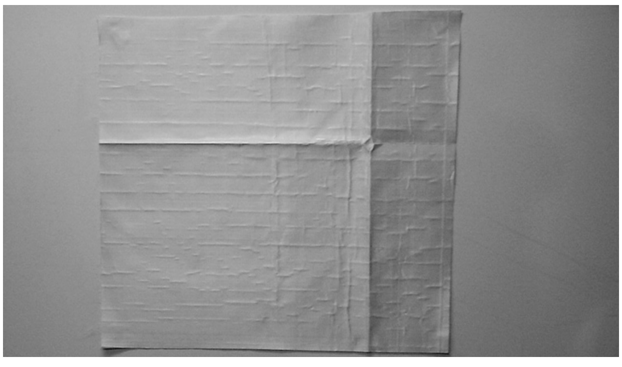

Figure 1: Overview of Kevlar-based STRATUM nanoPROTEC™ fabric
Slika 1: Videz tkanine STRATUM nanoPROTEC™, ki temelji na kevlarju

Figure 2: Detail of the fibres
Slika 2: Detajl vlaken

The above hypothetical scheme has been applied to an actual armour vest, first commercially produced by Parafly, S. A.,[17] under the trade mark of STRATUM nanoPROTEC™, and currently by QUANTICORP.[33] The proprietary technology includes a multicomponent network, which uses, among other materials, Kevlar 29, to which chemically modified nanoparticles were attached during the fabrication process. Photographs of the modified Kevlar 29 fabric can be appreciated in **Figures 1** and **2**.

In the case of STRATUM nanoPROTEC™, the Kevlar fibres were thermally treated to become ribbon-like fibres that changed, after the weaving, into a cloth with a better resistance to bullet penetration. This improvement is essentially due to an increase in the resistance to fibre openings in the fabric as a bullet penetrates the vest. **Figure 3** displays a photograph of a standard

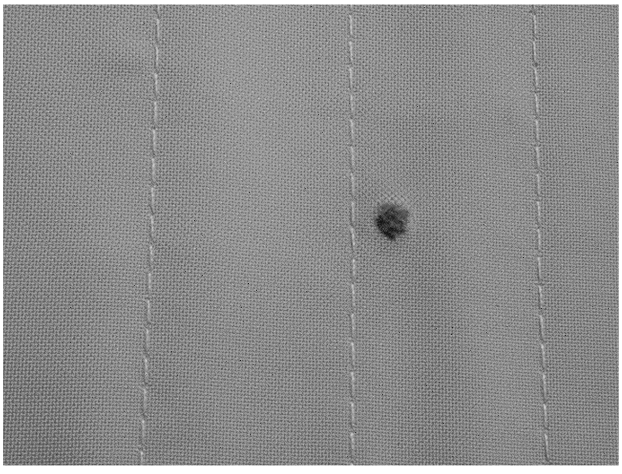

Figure 3: Detail of a standard Kevlar fabric using threads with a cylindrical shape
Slika 3: Detajl navadnega kevlarskega tkanja z uporabo niti z valjasto obliko

Figure 4: Photograph of a STRATUM nanoPROTEC™ ballistic vest
Slika 4: Posnetek balističnega telovnika STRATUM nanoPROTEC™

Kevlar fabric employing threads with a cylindrical shape, where a clean hole produced by a projectile 9 mm is clearly observed.

STRATUM nanoPROTEC™ is then one of the first commercial examples of an effective use of nanotechnology in armour devices. Nanotechnology added very significant UV and chemical resistance to the ballistic performance of the vest, which fulfils the international regulations in the area, being a unique garment. **Figure 4** shows a photograph of a STRATUM nanoPROTEC™ vest.

6 CONCLUDING REMARKS

Today, the area of materials for various types of protection represents a unique opportunity for nanotechnology, though perhaps not to develop brand new systems with amazing properties in a short term, but to overcome some of the serious limitations of the current technologies discussed above. Some other desirable features for armour garments can be achieved with current techniques available to many groups working in nanosystems throughout the world. In particular, the development of adequate variations of the nanotechnology products described above, specifically Zylon and other high-performance ballistic fibres,[35] is currently under way and will be reported separately.

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