TEXTILES / CLOTHING AND NANOTECHNOLOGY

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1. INTRODUCTION

Nanotechnology is a technology which has tremendous opportunities. Important users of nanotechnology relate to the medical world, cosmetics, consumer electronics, sports equipment, and … textiles. It all started half a century ago when an American scientist Richard Feynman said: "there is plenty of room at the bottom". In the world of nanotechnology a lot is to be discovered when dimensions of 1.0 to 100 nanometer are coming into the picture. How small this is can be demonstrated by the following comparison : the ratio of a football to our world is about the same as the ratio of a nanoparticle to a football. Another comparison can be made with a human hair: a human hair is, on average, one thousand to ten thousand times larger / thicker than nanoparticles used in nanotechnology. One is really working with groups or agglomerates (aggregates) of individual atoms. So, atoms in the *individual* state are not considered as structures in the nanotechnology area : clusters of atoms however do fit in nanotechnology.

2. NANOTECHNOLOGY : SPECIAL FORCES AT WORK

For almost two decades now, textiles welcome the remarkable impact and power of nanotechnology. The power is based on special forces which become active at sizes / dimensions around, e.g., 20 nanometer. At these dimensions bulk characteristics are being oppressed as a result of specific electronic or electromagnetic forces not fully active at large (bulky) dimensions, nor at atomic level. At real nano level (clusters of atoms) forces attain the maximal strength and are not overruled because of a large mass in which many particles cannot exercise their full potential as they are blocked by surrounding particles, or as a result of being too small (individual atoms). In the latter state, particles as individual entities do not exercise enough impact / power. So, at nanolevel, the size of material is achieved for almost maximal strength! Quantum-mechanics do apply and any material should be considered as having a *dual* characteristic.

3. NANOTECHNOLOGY : DEFINITION

There is a lack of consensus about a precise definition of nanotechnology. A rather simple definition can be as follows : a technology that enables the manipulation of matter with a size range between 1 nm and 100 nm. More complicated definitions do exist. In addition, it is understood that a nanomaterial should have properties different from those of the bulk material with the same chemical substance. Nanomaterials show quantum-like behaviour.

4. NANOTECHNOLOGY AND TEXTILES

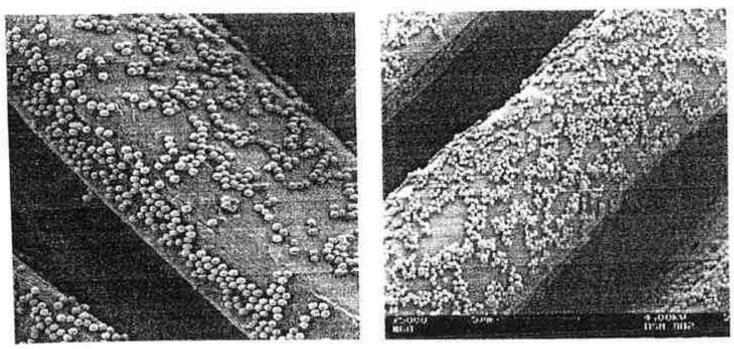
Nanotechnology can be a blessing for textiles, textile products and apparel / clothing. Either *nanofibres* are coming into being or nanolayer coatings (nano-coatings) based on (homogeneous) layers of *nanoparticles*.

Nanofibres have dimensions which are roughly 50 to 100 times smaller than the usual fibres known today : wool, cotton, silk, polyester, … fibres. These nanodimensions give the nanofibre completely new characteristics : they may become (extremely) strong, have enormous surface areas per mass (e.g. over 1000 m^2 per gram), the so called specific surface area, resulting in an extreme absorption capacity of interest for filter materials. Mouth masks can be manufactured using these very thin fibres and these masks acting as filters are able to stop (block) bacteria and viruses present in the air (protection!). Also medical applications are being developed : renewal of the human skin (after skin damage to a fire), cartilage in the human body and as carrier for cultivating cells and human tissue.

Several techniques are known to produce nanofibres but "electrospinning" actually likely is the way to guarantee reliable and realistic nanofibre production in addition to "Forcespinning". Electrospinning uses an electric force on a polymer solution or melt to produce fibres in the "nano-range", i.e. 100 to 500 nm, by stretching the solution or melt as it solidifies. These nanofibres are collected resulting in various structures of which a nanofibre web and nanofibre veil are the most attractive ones. Webs can be used as filters because of the small pores (open pore structure), but with a weight of about 5 g/m^2 and a few nanometers in thickness the membrane type webs are applicable in performance sportswear : windproof, breathable and water resistant clothing. In addition, these webs are nanosized versions of an interlining, also contributing to overall comfort in textiles. Nanofibre veils (or generally nanofibres) recently introduced in the market are outperforming other types of *toughening* particles applied in composite materials. Impact strength, delamination resistance and fatigue life of composites are (strongly) improved by using either individual nanofibres or nanoveils! As nearly any polymer can be turned into a nanofibre by electrospinning, this technology has a great potential.

Nanoparticles are very promising when being used in textiles (clothing) or in the fibres composing the textile material. A large number of (inorganic) particles (metal oxides, …) is being tested and sometimes already industrially applied : it is about TiO_2 (anatase or rutile), SiO_2 (silica), Al_2O_3, MgO, copper based molecules, ZnO (UV-protection and antibacterial) and CeO_2 (catalyst), and many others like nanoclays (for flame retardancy, …), indium-tinoxide, … . Often so called hybrid structures are preferred : they are half inorganic and half organic with many remarkable properties (POSS, …). Nanoparticles (for example present as a very thin, i.e. 20 nanometer, multilayer on a textile) generate antimicrobial activity, UV resistance (sun cream and cosmetics), catalytic self cleaning (stain release) and thus avoid washing, increase wrinkle resistance, give superhydrophobicity (repel water and oils), flame retardancy (self extinguishing) as a result of using non toxic inorganic products like clays (montmorillonite, sepiolite, …) mostly replacing the actual (toxic) flame retardant products, give personal protection (antiballistic: carbon nanotubes), enhanced conductivity (use of graphene), improved dyeability, etc.

Nanocoatings and finishes modify the surface properties of (textile) materials. A padding process (highly automated), so mostly pad dry-cure technology, and layer-by-layer deposition techniques are applied in order to achieve surface modification, often following a special pretreatment, e.g. (low-temperature) plasma or corona to improve effectiveness. In *padding* a fibre or fabric is passing through a pad (a tank) in which a liquid (solution, sol or colloidal suspension) wets the fabric or fibres. A thermal treatment transforms the liquid (nanosol, …) absorbed by the fabric / fibre into a film or nanocoating. This technique functionalizes in various ways a textile material, e.g. provides flame retardancy, antimicrobial properties, (super)hydrophobicity, stain-resistivity, … and is well known.



Polyester fibres (17 micrometer diameter) with a (homogeneous) layer of nanoparticles (metal oxides) on top

In *layer-by-layer technology* (multi-step adsorption) nano-modification of a surface is realized by an alternating adsorption of charged cationic and anionic species resulting in a (functionalized) multilayer film (of nanoparticles). Some automated industrial-scale processing is available. Durability of the obtained (surface) coating may still be a problem and must be optimized.

Titanium dioxide (titania) is a cheap and abundant material able to accelerate a chemical reaction under UV-irradiation (photocatalyses). Such photo-catalytic (or self-cleaning) properties can be imparted to a cotton fabric by TiO_2 colloid padding including a binder like SiO_2 (silica), leading to an organized structure of highly dispersed TiO_2 particles on cotton after thermal treatment at 150 °C, and with the titania particles surrounded by the amorphous silica with silica bound to a cotton fibre. Thickness of the nanolayer is about 20 – 30 nanometer and this layer discolours (oxidizes) for example red wine with high efficiency. Particularly the anatase crystalline structure of TiO_2 is suitable. Recently this self-cleaning action was optimized into the *visible light* by applying N-doped TiO_2 nanolayers loaded with AgI particles on the surface (synergetic effect : narrowing band gap). In 2012 Clariant (Switzerland) secured a patent in respect of photocatalytically active textiles for air purification under visible light and / or ultraviolet irradiation.

The ability of TiO_2 nanoparticles to act as a chemically stable UV-blocker by absorption is well known. Blocking of UV is determined by measuring direct and diffuse transmission of a fabric across the wavelength range 280 – 400 nm (UV-B and UV-A). UV-blocking is also possible applying nano-ZnO. In addition, nano-ZnO (an n-type semiconductor) can be applied to catalysts, gas sensors, piezoelectric devices, varistors, etc.

Recently a study was ordered by the European Commission to find out about the toxicity of titania (and related substances such as iron oxides, zinc oxide, …) for the human body. There are indications that titanium dioxide has negative effects and that TiO_2 should be classified as a category 2 carcinogen by inhalation! By 2020 the toxicity aspect of titania should become clear.

A very special group of products are the carbon nanotubes (CNT). These extremely small cylindrical structures (based on graphene) possess or introduce many interesting characteristics, i.e. strength, stiffness, conductivity, … and are really amazing and challenging structures belonging to the fullerene carbon family. Graphene (a conductor) itself was recently applied for the first time in a dress showing the power of wearable technology. The highly conductive transparent graphene can be used to create designs acting as screens showcasing digital imagery! In the year 2017 a collection of ski jackets was revealed by the company "Directa Plus" (Italy) in which graphene is introduced onto the fabric in order to guarantee an even body temperature to the wearer during physical activity leading to top sporting performance. The general idea is to incorporate graphene into customized protective clothing, workwear and uniforms where the dissipation of antistatic charges and heat management (homogeneous distribution) are required. A higher level of protection and comfort is aimed at!

Notwithstanding the interest for graphene, a one-atom-thick, two-dimensional (2D) material is high, graphene largely remains a substitute material. There is no robust supply chain and any certification of an end-product that contains the graphene is still missing; real commercial sales are exceptional but research efforts at academic level continue to be high seeking for industrial applications based on a continuous process.

A lack of compatibility between carbon nanotubes and textiles is still limiting their application in the textile industry. CNTs can introduce conductivity (fabrication of intelligent clothing), may act as filter material for wastewater, are fire retardant, give repellency, crease resistance, etc., but will become important once properly assembled into nanoscopic fibres or yarns.

More examples of nanotechnology are the use of chromic materials in fashion, shape memory materials based on special alloys (Ni-Ti / Cu-Zn, …), heat flux adjusting fabrics (comfort!), shear thickening fluids (STF) for impact protection (military, protective clothing = PPE), etc. Macromolecules such as dendrimers, dendrons, … offer several unique properties and could be of great importance for inkjet printing, coatings, etc. Self-assembly nanomaterials based on lipids, metal oxides, … have potential in personal care products but may represent a significant concern as a result of undesirable entry and inappropriate reassembly in the body!

Nanotechnology is to some or possibly to a large extent the technology which creates the fundamentals for smart, intelligent (or interactive) textiles. Smart textiles do interact with the environment around the person wearing the smart textile material or smart clothing. Computers are becoming part of a textile material or even more : nanotechnology based textile material allows to communicate as if it were a computer. Textiles are *software* and *soft wear*. Textiles do measure heart rate, blood pressure, the physical status of the body, give warnings if needed and are able to heat or cool the body according to the external conditions. So an amazing number of properties will be stored in “simple” textiles and this is because (safe?) nanotechnology confers specific benefits to textile fibres.

Important however is the *toxicity* of nanoparticles and nanofibres. Nanostructures are able to penetrate the body through the skin and accumulate in organs like livers, lungs, the brain, etc. Nanostructures (particularly in the range ± 20 nm passing rather easily through the cell membrane) do indeed interfere with human cells as a reaction with specific cell proteins. Intensive research is going on about that phenomenon. At this moment it cannot be stated that nanoparticles are really safe although skin by the epidermis proves to be a rather “good” protector notwithstanding nanoparticles can cross biological (lipid) membranes. So far mainly lungs are (mostly) being affected as a result of inhalation of nanoparticles present in the air. Cytokine-mediated inflammation, fibrosis and granuloma formation are noticed. Oxidative stress-related cellular death responses are observed. Particularly single walled carbon nanotubes might be problematic and possibly the widespread silver (Ag) nanoparticles of which the body effect is not fully clear yet, although intensive research is going on.

Nanosized silver (Ag) particles indeed do require special attention as they are used in commercial textile products because of their antibacterial (biocide), antistatic and other interesting properties. There are however reports that nano-silver may accumulate in the cell and deactivate its critical physiological functions showing a toxic effect in the human body. Also silver being rubbed off or after repeated laundering of clothing, is (very) toxic for the environment and damages ecosystems. So, dilemmas regarding the safety of silver for humans and the environment are still present. In order to deal with these challenges specific “microsilver” systems have been developed in which silver particles of 8 – 10 micrometer (microparticles) instead of particles between 100 – 250 nanometer, are applied. That kind of silver is also used in combination with a “binder” to guarantee wash fastness (up to 50 normal washes), being less problematic to the environment.

5. CONCLUSION

Nanotechnology is changing the properties of textiles and consumer products in a remarkable way and may have enormous economic impact. Society starts to notice the way “nano” is affecting daily life. In general specific advantages (comfort, …) can emerge by using nanotechnology and numerous nanoscale research is going on. Some negative effects however cannot be excluded at this very moment. Therefore in 2014 GOTS (Global Organic Textile Standard) fully banned the presence of “nano” in textiles. A permanent follow up and an appropriate approach of the risks of using nanotechnology may turn nanotechnology into a “blessing” for modern society, but it is wise to presume that no nanoparticle (actually a synthetic product!) is safe until proven otherwise. Although being around for about 25 years, nanotechnology is still like the early days of radio-activity when the knowledge of its risks is concerned! So, many issues still have to be addressed : quality control, test devices, overall safety, … .

6. REFERENCES

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