

Health and safety concerns of textiles with nanomaterials

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Abstract. There is a growing concern related to the effects of nanomaterials in health and safety. Nanotechnologies are already present in many consumer products, including textiles. “Nanotextiles” can be considered as traditional textiles with the incorporation of nanoparticles. They present often functionalities such as antibacterial, ultraviolet radiation protection, water and dirt repellency, self-cleaning or flame retardancy. Nanoparticles can be released from the textile materials due to different effects (abrasion and other mechanical stresses, sweat, irradiation, washing, temperature changes, etc.). It is then expectable that “nanotextiles” may release individual nanoparticles, agglomerates of nanoparticles or small particles of textile with or without nanoparticles, depending on the type of integration of the nanoparticles in textiles. The most important exposure route of the human body to nanoparticles in case of textiles is skin contact. Several standards are being developed under the auspices of the European Committee for Standardization. In this paper, it is presented the development and application of a test method to evaluate the skin exposure to nanoparticles, to evaluate the transfer of the nanoparticles from the textile to the skin by the effect of abrasion and sweat.

1. Introduction

Recently there has been a rapid emergence of nanotechnology into several consumer products, which has led to concerns as regards the potential risk for human health following consumer exposure. There is also a concern in terms of occupational safety and health, related to the exposure of workers involved in manufacturing, processing and handling of consumer goods containing nanomaterials. Nanosafety is a growing concern: exposure to engineered nanomaterials has been associated with a number of health effects including pulmonary inflammation, genotoxicity, carcinogenicity and circulatory effects [1].

Textiles are one of the most heavily traded commodities in the world. The industry is very diverse and its products are used by virtually everybody from private households to large businesses. The textile industry is already an important user of nanotechnologies and there are a significant number of “nanotextiles” in the market, including many consumer goods, with the incorporation of nanoparticles. These include many textiles used in direct contact with the skin, such as underwear, shirts and socks but also interior textiles like cushions, blankets or mattress covers.

There is a knowledge gap between the technological progress in nanotechnology and nanosafety research which is estimated to be 20 years, and it is likely to expand. The European Agency for Safety and Health at Work has established as priority for research related to the safety and health in Europe during the period 2013-2020 the increase of knowledge on nanomaterials in occupational settings,



including new generation nanomaterials and understand their characteristics in relation to toxicity in biological systems [2].

The risk for the workers and for the consumers is linked to the characteristic properties of certain nanomaterials that make them different from their macroscale counterparts and will be determined by the chemical composition of the nanomaterial, its physicochemical properties, the interactions with the textile materials and the potential exposure levels. Ingestion exposure via the gut, airborne exposure via the lungs and dermal exposure are the most important exposure routes to be considered in a risk analysis. In addition, the increasing use of nanomaterials, including for industrial purposes, raises specific concerns regarding their disposal at the end of their life cycle with the unavoidable release to the environment that may lead to indirect human exposure.

At present, some EU Regulations already include a specific mention to nanomaterials. This is the case of food (including additives and packaging), biocides and cosmetic products. But this is still not the case of textiles.

The growing concern about the possible negative effects of nanomaterials on humans and on the environment can lead to restrictions to “nanotextiles”. In fact, for instance, the 2014 version of the ecological label GOTS (Global Organic Textile Standard) fully bans the presence of nanofinishes in textiles. Also in the recent discussion of the new version of the EU ecolabel for textiles, there were several voices to exclude nanomaterials.

In the present paper, after making an overview of the use of nanotechnology in textiles, with special emphasis on textiles for major consumer applications, the safety and health concerns related to nanotextiles are presented. The paper includes then a case study concerning the development of a test method to evaluate the skin exposure to nanoparticles, mainly directed to the transfer of the nanoparticles from the textile to the skin.

This paper does not deal with the penetration of the nanoparticles into the skin. There are many studies about this topic, related for instance to sunscreens and cosmetics, which are often based on nanomaterials. In fact, only the smaller nanoparticles seem to be able to penetrate in the undamaged skin, although in the skin is injured, larger nanoparticles can penetrate [3]. In a recent study, Larese Filon et al. [4] made a literature survey involving 129 relevant publications and concluded that the smaller nanoparticles, with dimensions smaller than 4 nm, can easily penetrate the skin, while those with dimensions from 4 nm to 20 nm, can potentially penetrate intact skin. Nanoparticles with size between 21 and 45 nm can also penetrate and permeate in damaged skin.

2. Use of nanotechnology in textiles

Often the first application of nanotechnology to textiles that comes to the minds is related to nanofibers. Nanofibers are normally produced by the electrospinning process. The polymer must previously be dissolved in a solvent. The process makes use of electrostatic and mechanical forces to spin fibers from the tip of a fine orifice or spinneret, with evaporation of the solvent. This process produces in fact a nonwoven web and nanofibers normally cannot be used in common textile processing.

Nanofibers have applications in medicine, including artificial organ components, tissue engineering, implant material, wound dressing and drug delivery. In fact, all these products are not normally considered as textile products, as they do not fully enter in the definition of the EU Regulation 1007/2011 (they cannot be processed like traditional fibres) and they are not normally present in general consumer products. This paper will not further consider nanofibers.

In this paper we will also not include the use of carbon nanotubes. In fact, carbon nanotubes pose serious health problems but, due to the present high cost, are for the moment only used in high-tech products and not in “normal” textile products.

When we speak about “nanotextiles” we refer normally to traditional textile products in which engineered nanomaterials (normally nanoparticles) are incorporated or on which a nanostructured surface has been applied. In fact, nanotechnology is already very often used in textile products and involves the incorporation of nanoparticles in textile materials or the nanostructuring of the surface, in order to obtain specific functionalities [5]. The most common effects are: water and dirt repellency

(including self-cleaning properties, also called “lotus leaf” effect), antibacterial properties, protection against ultraviolet radiation and flame retardancy.

Table 1 presents the nanomaterials that are more commonly used in the functionalization of textiles.

Table 1. Nanomaterials used in the functionalization of textiles (adapted from [6])

Nanomaterial	Function
Silver (Ag)	antibacterial (odour), electrically conductive
Titanium dioxide(TiO ₂)	UV protection
	self-cleaning
	water and dirt repellent
Zinc oxide	UV protection
	antibacterial
	self-cleaning
Silicon dioxide (SiO ₂)	abrasion resistance, stiffness
	water and dirt repellent
	abrasion-resistant, reinforcement
	improved dyeability
Aluminium oxide (Al ₂ O ₃)	abrasion resistance
	flame retardant
Nanoclays (e.g. montmorillonite)	abrasion resistance
	flame retardant
	support of active ingredients

Nanomaterials can be incorporated in textiles in two different ways: during fiber production or during textile finishing.

During fiber manufacturing, nanoparticles can introduced by mixing in the polymer, before fiber spinning. The nanoparticles are evenly distributed inside the fiber volume. We can speak in this case of a “nanocomposite” material. The content of nanoparticles in the fiber can be as low as 0.1% to obtain a sufficient functionalization [7]. When the incorporation is done by this process, the nanoparticles are firmly incorporated in the textile fiber and the effect is highly durable. The nanoparticles are inside the fiber and normally can only be released by means of abrasion. This fact poses low risk in terms of safety and health both for the workers involved in the subsequent textile processing and for the consumers.

The incorporation of nanoparticles is in most of the cases made during fabric finishing. It can be obtained by traditional processes like dipping (exhaustion process), padding, printing or coating. To assure a good adhesion of the nanoparticles to the textile surface, organic polymers are normally used.

In this case, there are further concerns for the safety and health of the workers involved in the fabric finishing processing, due to the manipulation of the chemicals containing nanoparticles and of the textile itself. There must also be a concern for the workers in the garment manufacturing processes, which will be manipulating the textiles containing nanoparticles in all the cutting, sewing, pressing and packaging operations.

Most of the nanotextiles present in the consumer products are based on the application of nanoparticles by means of the fabric finishing process. The release of nanoparticles during the daily use is a safety and health concern, which will be dealt in the next section.

3. Safety and health concerns related to nanotextiles

There can be a variation in how tightly bound the nanoparticles are into the textile material, depending on the manufacturing processes. It is these factors and the use to which the textile is subjected that determine whether and to what extent nanoparticles can be released from it.

Depending on the location of the integration of nanoparticles in the textile, they can be more or less heavily exposed to external influences. In addition, there can be different degrees of binding of the nanoparticles to the textile material (covalent bonding, ionic bonding, hydrogen bonding, Van der Waals bonding). The strength level of bonding depends primarily on the following factors [7]: type of nanoparticle (chemical composition, shape, etc.); type of fabric; ageing of the nanoparticle functionalization (e.g. photo-oxidative reactions on the nanoparticle surface can cause the destruction

of functional groups and the covalent bond to the fabric); process engineering parameters during production; previous and subsequent finishing treatments of the textile fabric.

The stability (durability) of the nanoparticles present in the textile is not only dependent on their binding to the fabric, but also on the impacts on the fabric during its life cycle (production, use, recycling / disposal), which can damage the textile material or the bond between the nanoparticle and the fibers: abrasion, mechanical stress (such as strains, pressure), ultraviolet radiation, body fluids (sweat, saliva, urine), water (rain, washing), solvents (during textile processing or dry cleaning), detergents (either in textile processing or during laundry) and temperature changes; high temperatures (up to 225° C in textile finishing).

It is known that textiles can lose between 5% (in the case of continuous filaments) and up to 20% (in the case of staple fiber loose materials) of their mass during use as a result of abrasion, mechanical influence, irradiation, water, sweat, washing detergents or temperature variations. Even if the nanoparticles remain attached to the fibers, they will be released from the textile material to the environment (either to the human body, air, water, soil) together with the fibers. In fact, nanotextiles may release individual nanoparticles, agglomerates of nanoparticles or small particles of textile with or without nanoparticles.

For instance, in the case of textiles containing nano-silver, there are several studies concerning the release of silver nanoparticles during washing [8]. Some investigations that have been made show that some products can lose up to 35% of the silver in the washing water after only one wash; nevertheless, some suppliers of silver-based antibacterial finishes claim that there is practical no release during washing and that the finish remains effective after more than 50 washes.

Safety and health concerns related to nanotextiles should consider all the life cycle of the materials: safety for the workers during all the manufacturing stages, especially in the case of the application of nanostructured materials in the fabrics, as mentioned in the previous section, safety for all the people involved in the trade phases (distribution and retail), safety for the consumers. Nanoparticles released from textiles to the air, to the water and to landfill must also be taken into consideration, as they can directly or indirectly affect humans.

The nanoparticles can interact with the human body via three different ways of contact or penetration: inhalation, ingestion and skin contact. Although all the three pathways can be related to textiles, skin contact is of course the most relevant. This topic will be discussed in the next section.

4. Case study: development of a test method for skin exposure to nanoparticles

The European Commission has recently issued a mandate to the European Standardization bodies to develop standards for testing methods and tools for the characterization, behaviour and exposure assessment of nanomaterials. The exposure takes into account aspects of health and safety of workers as well as of consumers and the environment itself.

This mandate is being handled by the Technical Committee CEN/TC352 – Nanotechnologies. A roadmap identified 45 standardization projects in the field of "characterization of and exposure to nanomaterials" and "health, safety and environment". An extensive standardization programme has been prepared and is being developed, with conclusion foreseen for 2018.

One of the possible exposures of humans to nanomaterials is skin exposure. As this topic can be very relevant for textiles, the Technical Committee CEN/TC248 (Textile and Textile Products) is developing a test method named: "Guidance on measurement techniques relevant to different exposure routes to nanoparticles – Skin exposure".

In order to evaluate the migration of nanoparticles from textiles to the skin, a possible test can be based on the use of an artificial perspiration solution under physical stress. Artificial perspiration solutions (acid and alkaline) are described in standard EN ISO 105-E04 (Textiles – Tests for colour fastness – Part E04: Colour fastness to perspiration). The artificial perspiration acid solution is already used in the following standard: EN 16711-2 (Textiles – Determination of metal content – Part 2: Determination of metals extracted by acidic artificial perspiration solution).

In the standard EN ISO 105-E04, there is a simulation of contact with the skin of the textile to be tested, together with white standard adjacent fabrics, during 4h at 37°C, but there is no mechanical stress. A possible alternative is to use a test similar to the test EN ISO 105-C06 (Textiles - Tests for colour fastness - Part C06: Colour fastness to domestic and commercial laundering), by immersing the textile to be tested in the artificial sweat solutions, under mechanical agitation in a thermostatic bath at 40°C. Test is made both with the acid (pH 5.5) and with the alkaline (pH 8.0) artificial sweat solutions, with separate test specimens. The treatment is carried out during 30 minutes and involves the use of acrylic plastic balls to simulate physical stress. Nanoparticles, as well as their aggregates and agglomerates that can release nanoparticles, are then analysed in the extract solution.

This method has been developed by von Goetz et al [9]. These authors have tested commercially available textile products intended for sports or outdoor activities (shirts, pants trousers and socks, for adults and also for children) which included finishes based on nano-silver (antimicrobial effect) and nano-titanium dioxide (UV protection). The content of nanomaterials in the tested textiles was up to 183 mg Ag / kg of textile and 8543 mg Ti / Kg of textile. The tests show a significant release of nano-silver, which reached up to 14%. These results are much higher than other reported in the literature and contradict the producers that the claim that there is practically no release of nano-silver during the use of textiles and that the finish is permanent. In the case of titanium dioxide, no relevant release has been detected.

Another test, which is also foreseen to be included in the standard test method under development, is the release from the textile by mechanical action, through a “linting” mechanism. This test is based in the method mentioned in the standard EN ISO 9073-10:2004 (Textiles - Test methods for nonwovens - Part 10: Lint and other particles generation in the dry state).

Recently a pilot study involving the detection of silver in skin layers after dermal exposure to a functionalized textile has been published [10]. This study involves in vivo tests with human volunteers wearing sleeves functionalized with silver nanoparticles, during 5 days, 8h a day. The content of silver nanoparticles was measured in the skin cells and also in urine. This study is interesting for research but the method cannot be used for regular quality control of textiles. The proposed method under development at CEN/TC248 can be easily used by textile testing laboratories to measure the transfer of nanoparticles to the skin, serving as a basis for an appropriate health risk assessment of nanotextiles.

5. Conclusions

Nanomaterials have the potential to improve the quality of life and to contribute to industrial competitiveness in Europe. However, the new materials may also pose risks to the environment and raise health and safety concerns. The Scientific Committee on Emerging and Newly Identified Health Risks has concluded that, even though nanomaterials are not per se dangerous, there is still scientific uncertainty about the safety of nanomaterials in many aspects and therefore the safety assessment of the substances must be done on a case-by-case basis. In the case of textiles, there are still very few studies on the possible health risks involved with “nanotextiles”.

The release of nanoparticles from textiles is particularly relevant when the incorporation is made by fabric finishing. It can occur by different mechanisms. In this paper, the release resulting from skin contact, involving abrasion and sweat, has been analysed more in detail, involving a possible standard test method. The studies made up to now involve silver and titanium dioxide nanoparticles, which are present in the most common nanotextiles in the consumer market. Nevertheless, there are still a lot of discussions on if these nanoparticles can really penetrate into the different skin layers and on the negative effects on human health.

In the case of titanium dioxide, it is very commonly used in sunscreens, the nanoparticles being deliberately spread over a large surface of the skin. Comparatively, the dermal exposure coming from textiles is much lower, so the relative relevance of skin exposure coming from textiles can be questioned.

Also in the case of nanosilver, it is used in deodorants, deliberately put on the skin, food packaging or even in toothpastes. Again the relevance of the silver nanoparticles from the textiles to the human body can also be questioned.

Further research work involving experts in the area of textiles, of safety and health and of toxicology is needed before the emergence of any regulation concerning nanotextiles.

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