Nanotechnology in textile applications: research @ Centexbel

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Introduction

In spite of the textile and clothing industry being perceived as more traditional, the field of nanotechnology is being actively researched.
Nanotechnology in combination with textile materials typically falls within one of the following three topics [1]:

- *Nanofibers*: the production and application of fibres that have a diameter which is much smaller than the one of conventional fibres.
- *Nanoadditives for extrusion*: adding nanoparticles to the polymer compounds used for filament extrusion
- *Nanoscale coating*: this is possible in a direct way (deposition of nanoscale coatings onto the textile) or indirect way (mixing nanoparticles (NP) into 'traditional' coating or finishing products).

Slightly more generalised, we distinguish the four main topics, as shown in Table 1 below.
A key factor for success of nanotechnology in textile applications is that besides offering one or more novel functionalities, it should not compromise the inherent favourable textile properties, like processability, exibility, washability or softness. Of course, also the safety aspect is critical, but this will not be further discussed here.

Here, we will focus on the extrusion and coating approach. Both aspects are explained in more detail. Afterwards, some examples of research performed at Centexbel will be introduced, focussing on the potential of the application, the challenges and the pitfalls.

Extrusion approach

Direct way

Nanofibres can be produced via different methods. One of the most versatile processes is the relatively simple technique of electrospinning [2]. It relies on electrostatic forces obtained by applying an electrical field between the tip of a nozzle and a collector. When the electric field is strong enough, the electrostatic forces overcome the surface tension of the polymer solution at the nozzle tip and a jet starts. The jet elongates and the so produced nanofibres are deposited in a random structure on the collector.
Because nanofibres are so small, they have a very high surface area and enable structures with small pore sizes, making them interesting for a wide range of applications, e.g. for use as filters or sensors. This topic is not further dealt with in this article.

	Extrusion	Coating/ Finishing
Direct	Nanofibre spinning	Specific deposition techniques: evaporation, sputtering, ALD, plasma coating,…
Indirect	NP added in compounds for 'traditional' extrusion	NP added in 'traditional' textile coating formulations

Table 1 Overview of how to integrate nanotechnology in textile materials.

Indirect way

Using nanosized fillers is one of the most common approaches to generate nanostructured composite fibres. This means that nanoparticles are added to the polymer used for extrusion of filaments. A major challenge for the preparation of such polymer compounds with nano-fillers is the dispersion of the nanosized material. Due to the large surface area the nanoparticles tend to interact differently with the polymer matrix than the bulk materials. Other nanoparticles, like for example carbon nanotubes (CNTs), show a strong tendency to aggregate. Breaking up these aggregates is challenging, but required for fully utilizing the specific properties of the nano-materials. Formation of aggregates may also strongly interfere with the processing of compounds and yarns.
At Centexbel many of such applications have been studied, including CNTs and nanoclays. See also further.

Coating approach

Here, two methods need to be distinguished: the *direct* and *indirect way*.

Direct way

This includes the direct application of a layer with thickness in the nanometre range onto the textiles. This can be achieved via more advanced coating methods, eg vacuum deposition techniques like evaporation, magnetron sputtering or Atomic Layer Deposition (ALD). Alternatively, methods like atmospheric pressure plasma coating or sol-gel deposition can be used.
A main challenge here is the textile substrate itself. When looking at a textile substrate from the nanoscale range, it appears as a very rough surface and it has to be considered as a 3-dimensional structure. In addition, processing additives may stay behind and contaminate the surface. As such, coating nano thick layers on textiles becomes a real challenge.

Indirect way

This option refers to the addition of nanoparticles to the traditional polymer based (textile) coatings and finishes. This research topic is less common then the extrusion way, especially for systems using water-based dispersions. Nevertheless, this can also be a valuable approach.
One of the major challenges when working with nano-additives in coating and finishing applications is to obtain a good pre-dispersion of the nanoparticles, which then can be added to the standard coating and finishing products. These nanoparticle dispersions are often not commercially available or not tailored to textile products. For this reason, research into the preparation of coating and finishing formulations containing nanoparticles additives is a strong priority at Centexbel.

Applications

In the following paragraphs, some examples of applications are highlighted.

Carbon nanotubes - CNTs

For several years now, CNTs have been the subject of extensive research, especially as additives in polymer matrices. Due to the superior properties of CNTs with respect to electrical and thermal conductivity as well as mechanical strength, this material is envisioned as a replacement of carbon black as conductive polymer filler. One advantage is that far less CNT additive (about 1/5th to 1/10th) is needed compared to carbon black, to achieve comparable results.

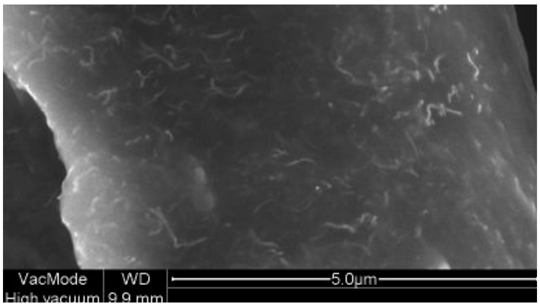

Figure 1 Coating of textiles with a CNT containing formulation: if aggregation of CNT occurs, this becomes visible as micrometer-sized dark spots (up): if well-dispersed these spots are prevented and via SEM analysis the individual CNTs can be seen (down).

CNTs can be introduced at extrusion level by adding them into the compound or by adding them to coating formulations [3]. At Centexbel the use of CNTs as conductive additive has been studied and the results have shown that it is possible to prepare textile coatings with a final resistivity of 1 kΩ/sq with an addition of less than 5 wt% CNTs in the coating formulation. The idea behind using CNTs in conductive coatings is not only to replace the use of metal fibres for antistatic textile applications, resulting in lighter weight and better resistance to corrosion. A new direction is that of *smart textile* or *electronic textile*, where the components are directly deposited onto the textile substrate instead of integrating the finished components or devices into the textile product as is done nowadays. The advantage of the former approach is that the character of the textile (being stretchable and flexible) can be retained, which nowadays is not really the case. At Centexbel conductive bottom electrodes are being developed for devices as photovoltaic (PV) cells or piezoelectric acceleration sensors.

Another important aspect when using nanoparticles to prepare textile coatings is to ensure a good dispersion. Due to their small size, the surface properties of nanoparticles become very important and due to their low weight electrostatic attraction forces play a major role. As a result, nanoparticles show a strong tendency to agglomerate so that actual particle sizes can easily be on the order of several μm, as illustrated in Figure 1 (left). If this happens, the initial advantages of the nanoparticles are lost. One of these advantages is the possibility to achieve a finer dispersion of the additive in the coating and thus reduce the total amount of additive needed. The other advantage is the ability to produce more stable fluid dispersions of the additive in the coating or finishing formulation to be used: The smaller the particle size the less sedimentation occurs. In order to facilitate this, dispersants need to be used that keep the nanoparticles well separated. Centexbel has obtained very good results for CNT dispersion in textile coatings and finishes, as can be seen from Figure 1 (down).

Nanosized oxides

Another group of materials of interest are nanostructured metal oxides such as ZnO and TiO_2, which possess photocatalytic abilities (photo-oxidizing capacities against chemical and biological species) and UV absorption properties. Others like MgO, Al_2O_3 and SiO_2 can increase the mechanical strength, abrasion resistance or fire retardance of textile materials.

On the one hand, nanosized oxides can be introduced as additives for extrusion or traditional coating mixtures. On the other hand, they may be directly deposited on textile materials by for example magnetron deposition [4] or ALD deposition. Regarding ALD, deposition of Al_2O_3 was performed on PET non woven, the research focus was on characterisation of the penetration of the coating into the non woven [5].

Clay nanoparticles

Another important class of materials are clay nanoparticles or nanoflakes, which are composed of several types of hydrous aluminosilicates. Clay nanoparticles possess electrical, heat and chemical resistance and an ability of blocking UV light. For example, nanoparticles of montmorillonite are one of the most commonly used clays. Centexbel has performed research evaluating the added value of nanoclays in extrusion applications, like increasing strength and fire retardance.

Nanosized silver

Antimicrobial properties can be obtained by the addition of nanosilver. Silver nanoparticles are so small that they are virtually 100% surface area. Since the surface of silver is active against bacteria (via release of Ag^+ ions), the activity of a silver particle increases with its surface area. Nanosilver particles show antimicrobial properties in concentrations as low as 0.0003 - 0.0005 %. For antimicrobial applications, these low concentrations compensate for the material cost of silver. Because of its effectiveness against a broad range of germs, even in small concentrations and over long periods of time, it is very interesting to incorporate nanosilver, which is non-toxic for higher life forms at these low concentrations, into textile materials (e.g. medical applications and packaging material). Centexbel is currently studying the incorporation of nanosilver into different textile materials for antibacterial applications, both via extrusion and coating (indirect way).

Sol-gel layers

In this case, a thin SiO_x- layer is applied on the textile via the sol gel method. This method stems originally from deposition on ceramic substrates but by modifying the chemistry, systems which can be cured at temperatures compatible with the most common polymers could be developed.

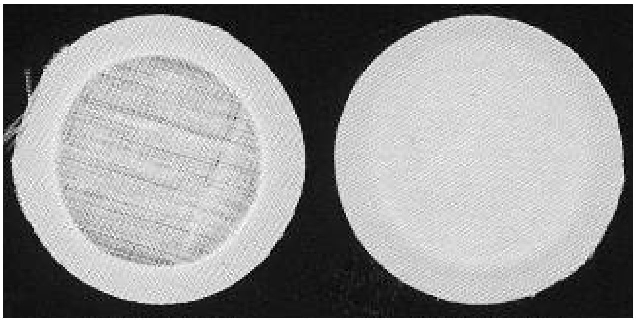

Figure 2 Coating of textiles with sol gel can improve the abrasion resistance as can be seen by comparing the result of Martindale Testing (EN ISO12947 - part 2) after 100.000 cycles on an untreated (left) and treated (right) woven PES substrate.

Tests on textile reveal that sol gel layers can be deposited with a thickness of typically around 100nm and with a nanoporous structure. This type of coatings can improve the abrasion resistance of the textile material significantly as shown in Figure 2. Further, the sol gel formulation can also be functionalised, e.g. to improve the hydro- and oleophobic properties [6].

Nanocapsules

Recently, the synthesis of nanosized phospholipid vesicles filled with an antibiotic (sodium azide – NaN_3) has been reported [7]. Only when exposed to toxins released by pathogenic bacteria, these nanovesicles open up and release their content. Within the Bacteriosafe research project [8], this smart response of the nanocapsules is being investigated to see how it can be used for a novel type of antibacterial wound dressings.

Immobilising similar types of smart nanocapsules that are specifically triggered clearly opens a lot of new possibilities for textile functionalisation.

Conclusion

Introducing "nano" into textile applications can be realised via several methods: nano-fibre spinning, mixing in nano-additives during extrusion, deposition of nanolayers or including nanoparticles into existing coatings.

Some examples of promising potential applications were highlighted, some of which are already extensively researched (e.g. use of CNTs), others are emerging in the textile industry (e.g. smart nanocapsules).

Irrespective of the method followed or application targeted, it is crucial that the typical textile properties (flexibility, washability, softness) for that application are not negatively influenced.

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