

Nanomaterials for footwear applications

F. Arán-Aís, M.M. Sánchez-Navarro, M.A. Pérez Limiñana, M.J. Escoto-Palacios, E. Orgilés-Calpena, M. I. Maestre and M.D. Romero-Sánchez.
INESCOP SPANISH FOOTWEAR TECHNOLOGY INSTITUTE

In recent years, aspects such as comfort, safety, health and well being are more and more in demand by footwear consumers. At the same time, they are also extremely fussy about product aesthetics. Therefore, in order to improve footwear performance and provide it with new features or functions, INESCOP is working on the development of advanced footwear materials through the implementation of innovative technologies such as nanotechnology and nanoencapsulation.

The use of novel and multifunctional materials opens the way to new and unexpected possibilities for the footwear sector, allowing manufacturers to meet a market demand and, consequently, improve their competitiveness. Nanotechnology and nanoencapsulation are considered to be key enabling technologies for the development of advanced materials with improved

performance in terms of mechanical and electrical properties, heat conductivity, lightness, durability and antimicrobial performance among others.

NANOSTRUCTURED MATERIALS

Specifically, the incorporation of carbon-based nano-fillers, such as carbon nano-tubes, nano-fibres or graphene, into polymers constitutes a new generation of nanostructured materials. In this sense, they have become very attractive materials offering a new range of innovative solutions due to their unique structure and properties on a nano-scale including high aspect ratio, high Young's modulus (the stiffness of a solid material), excellent mechanical strength and good thermal and electrical conductivity. Moreover, carbon-based nanomaterials are capable of producing numerous

changes in polymer properties just by being added in very small quantities.

In particular, the development of footwear components such as insoles with high comfort properties based on carbon-based nanofillers was investigated within the framework of the European NANOFoot project. For example, EVA micro-porous blocks for customised insoles intended for use in professional footwear, having electrical conductivity properties to protect the user from the accumulation of static charges as well as thermal conductivity to prevent heat build-up and overheating, were successfully developed. In addition, polyurethane-based adhesives with antistatic behaviour for use in the manufacture of this type of footwear, can be produced by the effective incorporation of carbon-based nanomaterials.

Nanotechnology also allows the development of footwear materials with

antimicrobial and antifungal properties to avoid the proliferation of microorganisms on the foot which, in turn, are responsible for certain infections and bad odours. To this end, mainly metallic nanoparticles, such as those of silver and gold, are being investigated as an alternative to conventional organic biocides. The antimicrobial properties of these metals, which were already well known a long time ago, have been boosted thanks to the development of nanotechnology. Nanometric-sized metal particles have proved to be highly active against a wide spectrum of bacteria and, among other benefits, have a longer lasting effect.

In this field, INESCOP has developed 'greener' synthesis routes for metallic nanoparticles in the framework of the NANOMETAL project, as an alternative to the ones currently used, thus boosting the use of natural raw materials such as amino acids, sugars, gelatine, etc. as reducing agents, stabilisers and/or catalysts, so contributing to the reduction of their environmental impacts. Furthermore, their immobilisation in inorganic microparticles, such as those from silica, reduces their marked tendency to aggregate and contributes to the improvement of their stability and dispersability in a matrix, as well as their handling and safety properties.

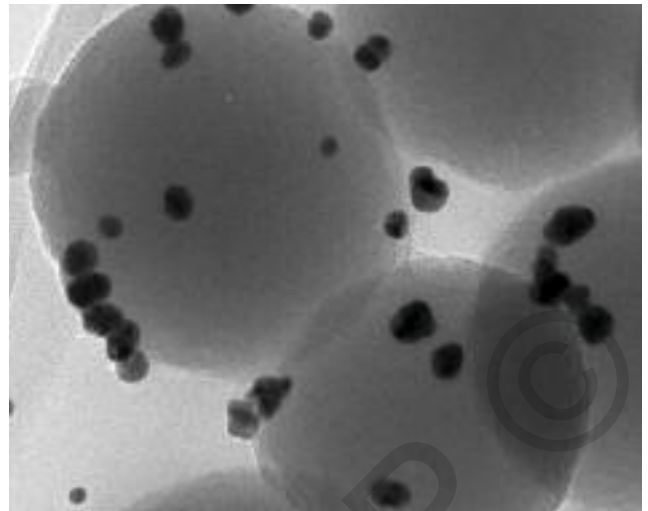
Ag@silica (silica coated silver) nanomaterials have proved effective in providing leather and other footwear materials with antimicrobial properties as well as preventing the microbiological degradation of waterborne PU adhesives. In addition, nanomaterials are also key to the functionalisation of the 3D printing of thermoplastic filaments for the manufacture of customised footwear components.

Under the TextiLeather programme, the feasibility of an innovative and eco-friendly surface treatment based on the combination of laser and plasma at atmospheric pressure is also being demonstrated to provide leathers and textiles with functional properties such as waterproofness, fire resistance, stain resistance and antimicrobial performance. The patented MLSE technology (multiplexed laser surface enhancement) being used, leads to surface enhancement based on nanoscale physico-chemical modifications to be achieved without altering touch and aesthetic properties.

NANOENCAPSULATION

The controlled release of active substances, such as natural antimicrobial fragrances and cosmetics, is a key functionality for footcare that can be achieved by nanoencapsulation technology. A timely and targeted release improves the effectiveness of the incorporated substance. Nanocapsules containing essential oils, such as limonene, eucalyptus or tea tree oil among others, can be incorporated into insole and lining materials with controlled release and acting directly in contact with the foot while the shoe is being worn to provide a long lasting effect.

One of the main problems found when using nanocapsules in footwear and other industries, however, is that high temperature and/or mechanical forces are required in certain production steps, which can damage the nanocapsules and cause the early release of the active substance involved. In the framework of the regional INORCAP project, INESCOP is working to develop nanocapsules using inorganic compounds such as silicates, carbonates and metallic oxides as shell materials with high hardness and thermal resistance in order to obtain suitable



Au (gold) and Ag (silver) metallic nanoparticles used for footwear functionalisation. 1nm (nanometre) = 1 billionth of a metre.

and biocompatible nanocapsules.

In the same way, controlled release of antibiotics at the right place and time is a key functionality that can be achieved by nanoencapsulation technology for therapeutic footwear and its components. Again, a timely and targeted release improves the effectiveness of antibiotics, broadens their application range and ensures optimal dosage. In the NANOCAB project, INESCOP focused on designing and obtaining nano/microencapsulated antibiotics from biodegradable and biocompatible polymers, as well as on their incorporation into different polymeric matrices for medical applications such as tissue regeneration or pathological footcare, which allow a controlled release on the right place to help prevent the onset of infections.

Finally, apart from the obvious benefits derived from the implementation of nanotechnology to obtain advanced materials, a safe and healthy use of the final product by consumers should be ensured. To address this within the framework of the CRONOTOX II project, INESCOP is developing *in vitro* assays on cultured human skin cells in order to test the potential cytotoxic (toxic to human cells) effect of nanomaterials and consumer goods incorporating them and also taking into account the effect of environmental factors such as UV light or atmospheric ozone. 🌀

Acronyms used in this article refer to the following research projects.

NANOFOOT – Materials, components and footwear with enhanced comfort properties based on nanotechnologies (FP7-SME-2013-606570).

NANOMETAL – Synthesis and immobilisation of silver and gold nanoparticles for antimicrobial material preparation. (CTQ2013-40927-P).

TextiLeather – Functional textiles and leathers by innovative MLSE process (TEXTILEATHER LIFE13 ENV/ES/001138).

INORCAP – Synthesis of multifunctional microcapsules with high mechanical and thermal resistance (IMDECA/2016/66).

NANOCAB – Microencapsulation of broad-spectrum antibiotics and their incorporation into different supports for sanitary applications (IMAMCK/2016/1-NANOCAB).

CRONOTOX – Study of the effects of chronic cellular exposure to nanomaterials (IMAMCK/2016/1-CRONOTOX).