ADVANCED TEXTILES MANUFACTURING INDUSTRY
Learning unit 2
Lesson 2

Raw materials for active textiles

HACKTEX
Innovative smart textiles & entrepreneurship

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Raw materials for active textiles

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Content

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Introduction

This lesson about *Raw materials for active textiles* (LU2.2) is enclosed in the Learning Unit 2, which corresponds to *Raw materials and components for functional and smart textiles*.

The previous lesson reviewed raw materials that can provide passive functions to the smart textiles, it is to say, for obtaining textiles that can sense environmental conditions and in which the interaction with the surroundings is limited.

This lesson focuses on raw materials for the development of active smart textiles smart textiles which can both sense and react to environmental conditions, and hence, can be considered both sensors and/or actuators. To this end, the fundamentals about chromo-active materials, phase change materials (PCMs), shape memory materials and energy harvesting materials focused on textile applications will be revised in this lesson.

1. Chromo-active textiles

Chromic responsive materials react to changes on the environmental conditions providing a colour change. The external stimuli that trigger the change can be: the temperature, an electromagnetic radiation, a mechanical pressure or deformation, a change on pH, a solvent's polarity, or an electric charge. However, the most extended for their use in chromo-active textiles are *thermochromic* and *photochromic* materials.

1.1. Thermochromic materials

Thermochromic materials are those that react to a change on the temperature by changing their colour. Thermochromic systems can be classified into two types: *intrinsic systems* where colour change depends only on heat, and *indirect systems* where the heat changes the environment and this change on the environment generates the colour change. In the particular case of textiles, the thermochromic effect is mainly achieved by two approaches: *liquid crystals*—that are an intrinsic system— and *leuco dyes*—that are an indirect system—(Christie, 2013).

Liquid crystals

Liquid crystals are organic materials remaining in an intermediate state between a solid and a liquid. In that stable state, the molecules of liquid crystals of the cholesteric type present a certain helical arrangement. In fact, the molecules organize themselves in this helical arrangement so their orientation changes gradually (Figure 1a). The distance to complete one full helical rotation is known as the "pitch length" (Van Der Werff et al., 2013).

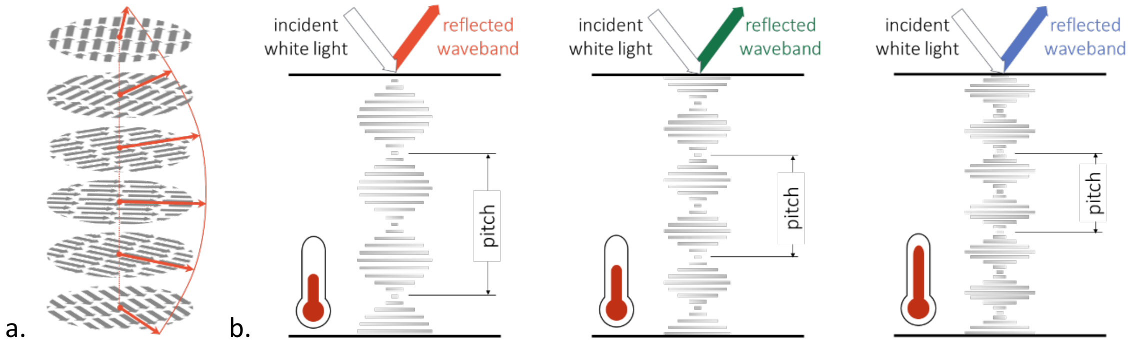

Figure 1. Helical arrangement in liquid crystal cholesteric phase (a). Colour changes with pitch length in a liquid crystal from red to green and to blue (b).

When light interacts with the material, the light with a wavelength of the pitch length is reflected whereas the all other wavelengths are transmitted. Therefore, the colour will depend on the pitch length, but pitch length is temperature dependant (Figure 1b), so the colour of the material reveals a colour gradient depending on the temperature distribution.

Leuco dyes

Leuco dyes base their colour change on molecular rearrangements of organic compounds. They are, typically, pH sensitive dye-based indirect systems that change pH value due to heating, typically. These systems require the microencapsulation of three components altogether to ensure their interaction: an organic colour former (the leuco dye), a developer that acts as proton donor, and an organic solvent of low-melting point (Figure 2).

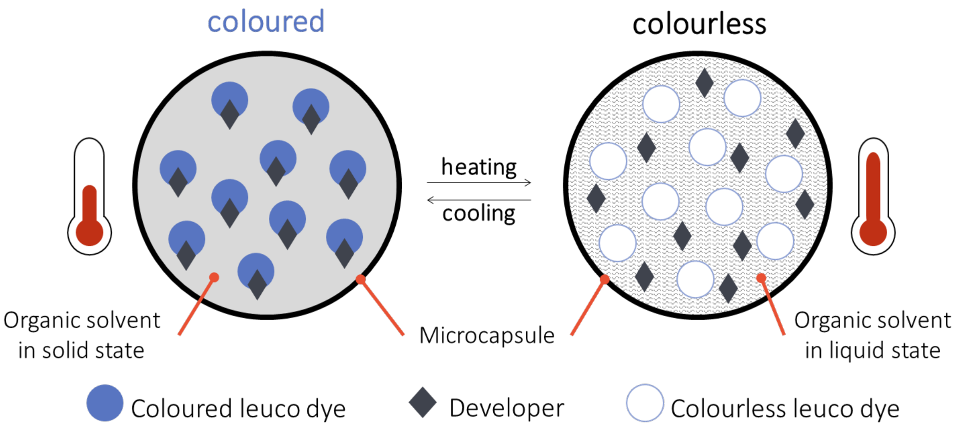

Figure 2. Scheme of the composition of a leuco dye thermochromic microcapsule and its working principle.

When heated, the organic solvent melts allowing a change in the interaction between the colour former (leuco dye) and the developer, leading often to a colour loss. On cooling, the solvent solidifies and the system reverts to its original state and colour (Chowdhury & Joshi, 2014).

1.2. Photochromic materials

Photochromic textiles present a reversible colour change as a consequence of their interaction with light. In this case, photochromic materials are chemical compounds that change between two forms with different absorption spectra: a thermodynamically stable form A, and an induced form B (Figure 3). The reaction from A form to B form is always triggered by light, but the reverse reaction from B form to A form can be induced by temperature (T-type) or light (P-type) (Chowdhury & Joshi, 2014).

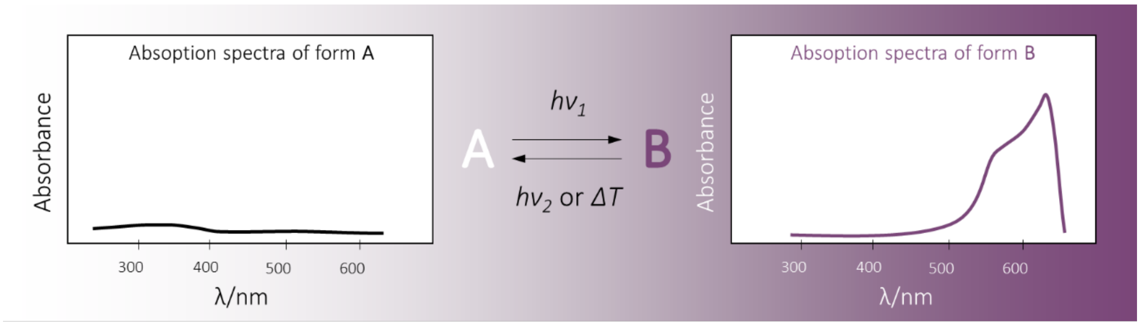

Figure 3. Schematic explanation of the photochromic effect

Moreover, photochromic substances can be classified as positive, when the stable form A is colourless and the induced form B is coloured or negative, when the stable form A is coloured and the induced form B is colourless.

Want to learn more about this topic?

In the research papers *Photochromic and Thermochromic Colorants in Textile Applications* (Chowdhury & Joshi, 2014), *Thermochromic Silks for Temperature Management and Dynamic Textile Displays* (Wang, Ren, Ye, Pei & Ling, 2021) and *Multifunctional Resistive-Heating and Color-Changing Monofilaments Produced by a Single-Step Coaxial Melt-Spinning Process* (Laforgue, Rouget, Dubost, Champagne & Robitaille, 2012) you will find information about thermochromic textiles.

In the research papers:

- *Screen-Printed Photochromic Textiles through New Inks Based on SiO2@naphthopyran Nanoparticles* (Pinto et al., 2016)
- *Screen-Printed Photochromic Textiles with High Fastness Prepared by Self-Adhesive Polymer Latex Particles* (Yang, Mintee, & Fu, 2021)
- *Preliminary Exhaustion Studies of Spiroxazine Dyes on Polyamide Fibers and Their Photochromic Properties* (Lee, Son, Suh, Lee & Kim, 2006)
- *Photochromic Cotton Fabric Prepared by Spiropyran-ternimated Water Polyurethane Coating* (Bao, Fan, Wang & Yu, 2020)
- *High Tri-Stimulus Response Photochromic Cotton Fabrics Based on Spiropyran Dye by Thiol-ene Click Chemistry* (Fan et al., 2020)

and PhD dissertation *Ink Jetting of Photochromic Ink: Towards the Design of a Smart Textile Sensor* (Seipel, 2020), you will find information about photochromic textiles produced with different technologies (screen printing, inject printing, bath exhaustion and supercritical carbon dioxide).

In the research paper *Novel cellulose and polyamide halochromic textile sensors based on the encapsulation of Methyl Red into a sol–gel matrix* (Van Der Schueren et al., 2012) and *Smart Cotton Fabric Screen-Printed with Viologen Polymer: Photochromic, Thermochromic and Ammonia Sensing* (Sun et al., 2020) you will find information about other chromo-active textiles.

2. Phase Change Materials (PCMs)

A Phase Change Material (PCM) is a substance that can store and release thermal energy by changing its physical state, typically from solid to liquid and back again. When a PCM is heated above its melting point, it absorbs heat to pass from solid to liquid, storing thermal energy. When the PCM is cooled below its melting point, it releases heat and changes from liquid back to solid, releasing thermal energy (Figure 4). Due to this, PCM can be applied to textiles for thermal regulation of temperature peaks.

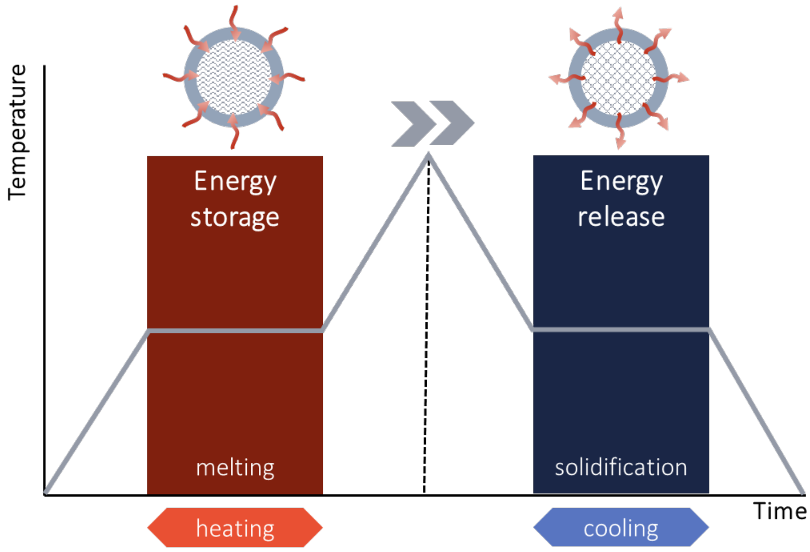

Figure 4. Working principle of PCMs.

Image credits: Adapted from the original by Pazrev - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=36477085

Although there are different phase change materials that can change temperature in different ranges from below to above 0 ºC (Sarier and Onder, 2012), the most suitable for textiles are the ones composed for polymers like paraffin or waxes which change phase by 20-40 ºC. These paraffin polymers are microencapsulated to allow the transformation from solid to liquid and liquid to solid without releasing the PCM (Figure 5).

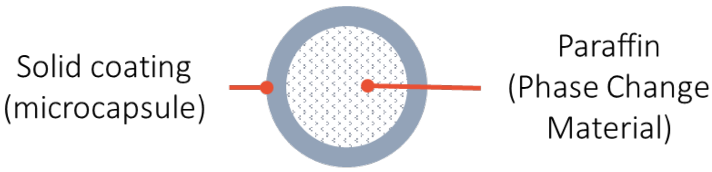

Figure 5. Schematic of a microcapsule containing a PCM

In textile applications, PCM are used for thermo-regulation, mainly in clothing—such as outdoor jackets, gloves, sooks or special clothing among others—and home textiles—such as covers for pillows or mattresses—, but also in other technical applications in which an improvement of thermo-regulation is necessary. The temperature and time of thermoregulation depends on the type and content of PCM in the textile. In this case, the microcapsules can be applied directly in the fibres through compounding. However, the most efficient way to apply an enough amount of PCM microcapsules in textiles is the coating technology.

Want to learn more about this topic?

In this the research article *Review: incorporation of organic PCMs into textiles* (Yang et al. 2022) you will find information about the recent research work related to PCM textiles.

In the following link, you will find commercial applications of phase change materials in textiles:

- Outlast technology: https://www.outlast.com/en/thermo-technology/application-methods

3. Shape memory effect

Shape memory materials are able to recover a pre-defined shape as a reaction to a certain stimulus that is, typically, heat. In this group, we can find to types of shape memory materials with applicability to smart textiles: the shape memory alloys and the shape memory polymers (SMPs).

3.1. Shape memory alloys (SMAs)

Shape memory alloys base their working principle in their intrinsic ability to endure phase transitions between austenitic and martensitic phases in favourable temperature ranges. Nickel-titanium alloys are the most widely known SMAs. When the alloy is subjected to a certain stress, the plastic deformation induces this transition, allowing a retention of the deformed shape. However, the induced phase is not stable under room conditions, so it can be reversed by heating. This also releases the plastic deformation retained, recovering the original shape. Due to this, SMAs can be used as actuators in smart textiles (Figure 6).

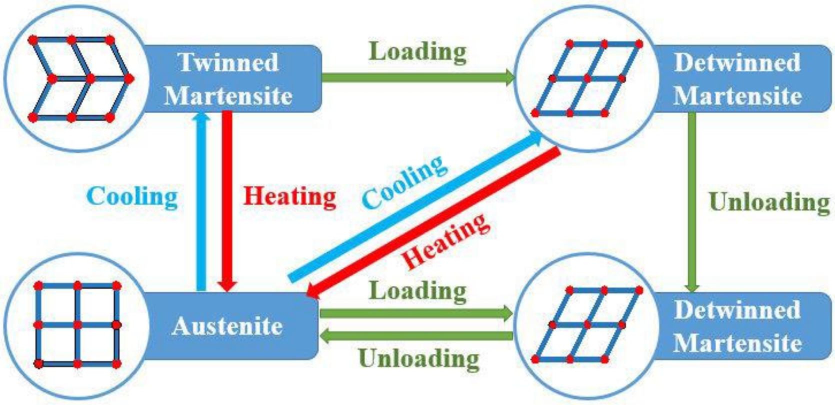

Figure14.

Figure 6. Phase transitions in SMAs that are induced by temperature or stress

Image credits: By Ying-qi Jia, Zhou-dao Lu, Ling-zhi Li, Zhen-li Wu, CC BY 3.0, (Jia, Lu, Li, & Wu, 2018)

3.2. Shape memory polymers (SMPs)

On the other hand, shape memory in polymers is not an intrinsic property, so it requires the programming of a temporary deformed shape. Their most common trigger is also temperature, although there are SMPs that react to light. In this case, in shape memory polymers we talk about two kind of segments instead of phases. The hard-segments are those capable of retaining the original shape, whereas the switching (soft-)-segments fix the programmed temporary shape by glass transition, crystallization, or reversible bonds (Behl, & Lendlein, 2007). Therefore, SMPs are able to shift from the temporary shape to the original shape when heated, since the switching segments are deactivated so the hard segments can act.

The thermomechanical deformation process of shape memory polymers is presented in Figure 7. As can be seen: firstly is necessary to heat and further deform the SMP above its transition temperature T_{trans}; then, cool down the SMP below its T_{trans} and remove the applied force. At this point, the temporary shape is fixed. To recover the original shape, the pre-deformed SMP has to be heated above the T_{trans}, and then cool the SMP below the T_{trans} in its original shape to keep it (Wang, Liu, Guo. Sun & Xu, 2017).

SMPs can be used as actuators in smart textiles.

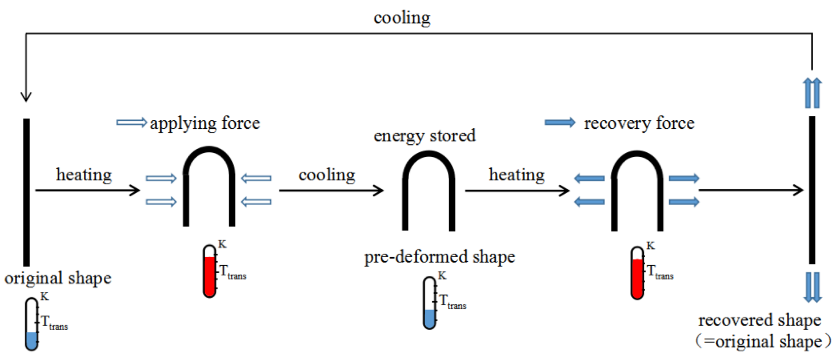

Figure 7. Schematic of thermomechanical deformation process of shape memory polymers
Image credits: By Zhenqing Wang, Jingbiao Liu, Jianming Guo, Xiaoyu Sun and Lidan Xu, CC BY, (Wang, Liu, Guo. Sun & Xu, 2017)

Want to learn more about this topic?

In the review paper *Application of shape memory materials in protective clothing: a review* (Ma, Lu, He & Dai, 2019), you will find an overview on the application of shape memory materials both thermal and cold protective clothing.

In the following links and videos, you will find information and application examples about shape memory alloys (SMAs):

- *Shape Memory Alloys for Controllable Compression Textiles and Garments*, MIT Technology Licensing Office. TECHNOLOGY #17392 https://tlo.mit.edu/technologies/shape-memory-alloys-controllable-compression-textiles-and-garments
- ▷ *How do shape metal alloys work?*, by MIT-k12videos (2012) https://www.youtube.com/watch?v=s62PL5vmfNw
- ▷ *Shape Memory Textiles,* design by Mariëlle Leenders (2008) https://www.youtube.com/watch?v=HdRRy7hItgI
- ▷ *3D shape memory weft knitted fabric* (2011) https://www.youtube.com/watch?v=iLIVn8x1tBU

In the research papers *Suit-type Wearable Robot Powered by Shape-memory-alloy-based Fabric Muscle* (Park & Park, 2019), *Development and assessment of a knitted shape memory alloy-based multifunctional elbow brace* (Jung, Lee, Ahn & Park, 2022) and *Functional textiles driven by transforming NiTi wires* (Heller, Janouchová, Šittner & Vokoun, 2015) you will find information about the development and behaviour of SMA textiles.

In the book chapters *Shape Memory Polymers for Smart Textile Applications* (Thakur, 2017) and *Polyurethane: A Shape Memory Polymer* (Thakur and Hu, 2017) you will find general information about SMPs and their applications.

In the research papers *Shape memory behavior of SMPU knitted fabric* (Liu, Chung, Hu & Li, 2007), *Recent progress in shape memory polymer: New behavior, enabling materials, and mechanistic understanding* (Zhao, Qi & Xie, 2015), *Design and characterization of reversible thermodynamic SMPU-based fabrics with improved comfort properties* (González, Ardanuy, González, Rodriguez & Jovančić, 2023) and *Polyurethane shape memory filament yarns: Melt spinning, carbon-based reinforcement* (González, Ardanuy, González, Rodriguez & Jovančić, 2022), you will find information about development and behaviour of SMP textiles.

4. Energy harvesting

The energy-harvesting concept implies the collection of energy that is produced from renewable sources and easily found on our surroundings such as sunlight, heat, wind, vibrations, pressure, etc.

Energy harvesting materials are active materials that respond to external stimuli by converting it into electrical energy. The main examples are:

- The photovoltaic effect, which uses solar radiation as external stimuli
- The pyroelectric effect, which acts when heated or cooled
- The thermoelectric effect, that is obtained when there is temperature difference between two sides of the structure
- The piezoelectric effect, that generate electricity when a mechanical stress is applied, where this mechanical stress can provide from the wind, rainfall, waves, footsteps or body movements, among others
- The triboelectric effect, generated when two materials with dissimilar electrical potentials enter into a friction-based contact

From all those, *piezoelectric* and *triboelectric* materials present a higher independence of the environmental conditions, hence are an interesting solution for their application in smart textiles.

On the other hand, before selecting the materials for energy harvesting, it should be taken into account that for wearable energy, it is important than has to be integrated without affecting the comfort of the user and that has to provide long term life (fastness and durability) and has to be cost effective. In this sense, the polymer-based structures the most suitable for textile applications. On the other hand, for low power electronic devices or sensing are most suitable piezoelectric materials and for higher power consumption triboelectric ones.

4.1. Piezoelectric materials

Piezoelectric materials can generate electricity when a mechanical stress is applied, where this mechanical stress can provide from the wind, rainfall, waves, footsteps or body movements, among others. For textile applications, the group of polymeric-based piezoelectrics is of a greater interest due to their low density and high flexibility. The most known piezopolymer is polyvinylidene fluoride or PVDF (Zaszczynska, Gradys & Sajkiewicz, 2020).

Due to its atomic distribution, PVDF presents electrical dipoles that, with a certain doping and induction, can adopt the β-phase responsible of the piezoelectric effect. This can allow generating sensors for the development of smart textiles. PVDF polymer can be incorporated to textiles basically through yarns composed by PVDF fibres or in the form of nanomembranes produced through electrospinning. The β-phase in melt-spun fibres can be induced by a high stretching (Magniez, Krajewski, Neuenhofer & Helmer, 2013) of the polymer or by a stretching followed by a poling (Nilsson, Lund, Jonasson, Johansson, & Hagström, 2013)—a process in which the dipoles are aligned subjecting the PVDF fibres to a high voltage under contact or non-contact mode—. In the case of nanomembranes the β-phase is favoured by the electrospinning process and the use of doping agents (Shao et al., 2017).

4.2. Triboelectric materials

The **triboelectric effect** occurs at the friction interface between two different materials. To achieve it, the materials have to be widely separated from the triboelectric series (Figure 8), which rank the materials according to their ability to gain or lose electrical charges. Due to the friction, the electrical charges transfer from one material to the other, producing a certain voltage. With this approach is it is possible to obtain a triboelectric generator, which can be easily placed in certain areas of smart garments for energy harvesting.

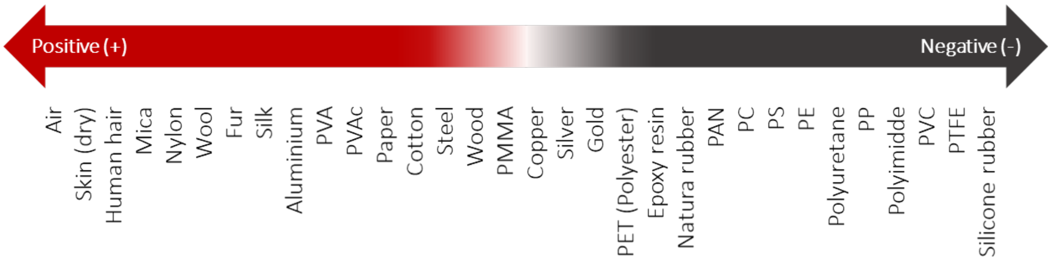

Figure 8. Triboelectric series

In the literature, it is possible to find several approaches to produce textile wearable triboelectric devices by joining pieces (Cui et al., 2015), producing special yarns (Yu et al., 2017), or by screen-printing as approach (Cao et al., 2018).

Want to learn more about this topic?

In the research paper *An investigation of a wash-durable solar energy harvesting textile* (Satharasinghe, Hughes-Riley & Dias, 2020), you will find a photovoltaic fabric woven using electronic yarns with embedded miniature solar cells to create a solar energy harvesting device.

In the research papers:

- *Effect of drawing on the molecular orientation and polymorphism of melt-spun polyvinylidene fluoride fibers: Toward the development of piezoelectric force sensors* (Magniez, Krajewski, Neuenhofer & Helmer, 2013)
- *Poling and characterization of piezoelectric polymer fibers for use in textile sensors* (Nilsson, Lund, Jonasson, Johansson & Hagström, 2013)
- *Nanofiber mat-based highly compact piezoelectric-triboelectric hybrid nanogenerators* (Ünsal, & Bedeloglu, 2023)
- *Electrical power generator from randomly oriented electrospun poly(vinylidene fluoride) nanofibre membranes* (Fang, Wang & Lin, 2011)
- *Direct-Write Piezoelectric Polymeric Nanogenerator with High Energy Conversion Efficiency* (Chang, Tran, Wang, Fuh & Lin, 2010)

you will find information about the development and behaviour of piezoelectric energy harvesting textiles.

In the research papers *Wearable Triboelectric Generator for Powering the Portable Electronic Devices* (Cui et al., 2015), *Core–Shell-Yarn-Based Triboelectric Nanogenerator Textiles as Power Cloths* (Yu et al., 2017), and *Screen-Printed Washable Electronic Textiles as Self-Powered Touch/Gesture Tribo-Sensors for Intelligent Human–Machine Interaction* (Cao et al., 2018) you will find information about triboelectric energy harvesting textile devices created by joining fabric pieces, producing special yarns or screen-printing, respectively.

Summary

In this lesson you have reviewed: (1) the raw materials to generate colour response actuators in textiles, focussing on those thermal- and light- induced; (2) the phase change materials useful to provide thermal-regulation in smart textiles; (3) the shape memory alloys and polymers working principles that can lead to the production of actuators for smart textile solutions; and (4) the raw materials related to energy harvesting, more specifically the polymeric piezoelectrics for generation of sensors and the triboelectric principles to create generators.

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Partnership

Project coordinator
TUIASI - Universitatea Tehnica Gheorghe Asachi din Iasi
www.tuiasi.ro

AEI Tèxtils - Agrupació d'Empreses Innovadores Tèxtils
www.textils.cat

CIAPE – Centro pre l'Apprendimento Permanente
www.ciape.it

CRE.THI.DEV - Creative Thinking Development
www.crethidev.gr

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