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RECYCLING OF WASTE ACRYLIC TEXTILES

D5.1: State of the art of environmental friendly finishing

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Authors	Andrea Cataldi
Reviewers	Roberto Vannucci

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EXECUTIVE SUMMARY

This deliverable has been created in the context of the WP 5 (Textile production, finishing and testing) of the H2020-funded project REACT (Grant No. 820869).

The document provides a report of state of the art of environmental friendly finishing on market and their characteristics, this research of a new kinds of finishing is performed to eliminate or reduce the use of high impact finishing such as fluorocarbons-based and formaldehyde-based resins. The state of art is the starting point to choose the best mix of resins to obtain an awning with eco-friendly chemicals and without lose its characteristics. The finishing developed could be a base for the development of a new kind of chemicals that could substitute the older ones and implement the characteristics of fabrics with an increment of sustainability.

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ABBREVIATIONS

DMF	Dimethylformamide
ECHA	European Chemicals Agency
PLA	Polylactic acid
PU	Polyurethane
REACH	Registration, Evaluation, Authorisation and restriction of Chemicals
SVHC	Substances of Very High Concern

1 INTRODUCTION

The European Directive 76/464/EC, the Dangerous Substances Directive, is the starting point for the European policy on dangerous substances, focused on the water environment sector and later extended to other sectors. This directive distinguishes between substances for which use should be reduced to zero (black list) and substances for which member states must impose limits to reduce use (grey list).

In 2006, the REACH Regulation (1907/2006/EC) marked a revolution in hazardous substances policy. Industries are obliged to place products on the market with chemicals that are safe for humans and the environment. Through authorisations (Annex XIV) and restrictions (Annex XVII), the production, use and import of hazardous substances such as products and/or chemicals in textile articles are restricted.

The impact of REACH on textile finishing processes and/or chemicals is extensive. Hazardous substances have been placed on the list of SVHC (substances of very high concern), others are under consideration for inclusion on this list and others will be included in the future. Depending on the pathway followed (restriction, authorisation), the chemical will either be restricted or banned completely, to a certain extent, or will be granted an exemption for some applications.

The general trend in the textile industry to comply with REACH directives is to use less water and less harmful chemicals in finishing processes. However, this is not a foregone conclusion as it requires the replacement of often cheap and well-known processes and products. Such a change often leads, especially at the beginning of the process/chemical change, to quality differences, process instability and similar. In the future, the use of chemicals in textile finishing for clothing will be defined by various actors such as ECHA/REACH, environmental organisations, and brands.

Many chemicals used in textile finishing require specific attention with regard to the purchase, transport, storage, use (industrial and consumer) and end-of-waste phase of chemicals, but also of treated textiles. European legislation has been an important driver in addressing sustainable chemicals. Recently, the substitution of hazardous substances has become a difficult task for textile finishing companies. Substances such as easy-care products, fluorocarbons for water-repellent and oil-repellent properties, various flame retardants (based on halogens or phosphors), plasticisers and solvents such as DMF have been proposed, are already restricted, or are banned by REACH. This implies that many chemicals used in textile finishing require specific attention with regard to their purchase, transport, storage, use (industrial and consumer) and end-of-life phase. In order to avoid water emissions of chemicals and to reduce energy consumption, water consumption and waste production, new reusable chemicals have been developed, which can range from formulations without water or impacting solvents to bio-based or biodegradable substances. Many of these products have been developed for other sectors and implementation in the textile sector is not always obvious (e.g. flexibility, tactile feel and resistance to washing).

A goal of REACT project is to replace the current resins used to finish fabrics for awnings, umbrellas, and furnishings and which make these fabrics suitable for use, with eco-friendly alternatives. Commonly used finishes have been described in deliverable D1.3 - Report on acrylic textile waste characterisation, giving the fabric the necessary characteristics. Through the development of new, more sustainable types, a new product will be obtained with recycled acrylic fibre and more sustainable chemical compounds, which will influence the environmental impacts of the fabric the project will develop.

2 TECHNOLOGIES

In consideration of the goals established by the European community to be reached by 2030 and climate neutrality in 2050, industries are researching technologies and chemicals with a lower environmental impact in all production sectors. In the textile sector this means not only circular, recycled and naturally sourced fabrics, but also finishing products with less polluting potential and without the use of potentially hazardous substances.

Eco-sustainable technologies and formulations for textile finishing are well known in the textile industry.

Therefore, technologies and formulations for textile finishing specific to the REACT project objectives will be discussed in this deliverable.

In particular, evaluating the results obtained in D1.3 - Report on acrylic textile waste characterisation, the finishing agents to be substituted are melamine, fluorocarbon and acrylic resins, which provide the fabric with the desired properties of water and oil repellency, dimensional stability and better weatherability; for this reason, this chapter will analyse alternative processes and formulations that guarantee these properties with lower impacts.

2.1 Plasma technology

At the nanoscale, material properties can be easily manipulated using appropriate technologies. The use of nanotechnology in the surface treatment of textiles has increased significantly due to its versatility in improving functionality. The recent focus on 'green chemistry' strategies has boosted the application of environmentally friendly techniques used to improve various functional properties of textile materials without the use of chemicals or by reducing the quantities needed.

Plasma technology is used to modify the surface of textiles with minimal consumption of water and energy. Contrary to chemical textile processing, the modification is limited to the first atomic layers of the fibre surface and does not change the properties of the whole fibre. in addition, textiles processed with low-temperature plasma are dry, thus eliminating the need for drying processes. The overall process requires an extremely short treatment time and low temperatures. These advantages of plasma treatment reduce the use of chemicals and thus the generation of effluents, saving energy and limiting pollutant emissions.

Plasma is a mixture of activated ionised gases used to modify the surface and coating of textiles. Plasma processing uses gases that can be polymerizable, non-polymerizable and chemically inert such as air, oxygen (O2), nitrogen (N2), argon (Ar), helium (He), fluorine (F), tetrafluoroethylene (C2F4) and hexamethyldisiloxane.

Plasma induces different properties in textile materials through surface activation, oxidation, surface energy modification, coating, roughness alteration and development of micro/nano structures. These changes result in improved absorbency properties, better dyeability and increased fibre adhesion. Special functional properties such as UV protection, antimicrobial properties, water-repellence and flame retardancy are achieved by functionalising the surface with the help of precursor molecules containing fluorocarbolic, hydroxyl, vinyl or carboxyl groups.

Plasma is widely used to improve the hydrophilicity and hydrophobicity of certain textile materials based on polyester, polyethylene, polypropylene, and polytetrafluorethylene (PTFE), polyamide, nylon-cotton, elastane, polyimide, aramid and carbon fibres. It is also used to improve the hydrophilicity of certain natural fibres such as cotton, wool and silk. The increase in hydrophilicity is an important requirement for scouring, bleaching, dyeing, printing and finishing processes.

Plasma treatment is used to remove grease or wax from cotton, polyester, polyamide, polypropylene and wool. This improves dyeing processes such as dyeing speed, dye diffusion into the fibre, colour intensity and colour fastness to washing. Cotton fabrics pre-treated with plasma under atmospheric pressure show improved dyeability with acid dyes. Furthermore, by improving the wettability of the fibres, it improves the interaction of finishing chemicals, reducing their use.

Similar to the induction of hydrophilicity to textile materials, hydrophobicity can be achieved by introducing hydrophobic functional groups or by graft coating or copolymerisation of the fabric surface. To achieve hydrophobicity, fluorocarbons or silicones are used to carry out graft copolymerisation, avoiding the use of water or solvents to form the hydrophobic coating.

2.2 Sol-gel

Another system for functionalising textile materials is the sol-gel technique. This technology consists of applying ceramic, inorganic or hybrid coatings to textile surfaces from colloidal solutions. The sol-gel process involves preparing a colloidal dispersion from a suitable precursor, then applying it to the fabric and heat-treating it. In this way, a ceramic coating can be obtained on the fabric, which can be mixed with other organic and inorganic components. The first step consists in the formation of colloidal solutions, such dispersions being prepared from suitable precursors in water or water-miscible organic solvents, such as ethanol or propanol. Subsequently, condensation reactions occur within the solution between the precursors, these react to form the organic network, this reaction completing the sol-gel process. The condensation reactions proceed when these solutions are applied to textile substrates, the colloids condense and aggregate on the fabric, forming a wet layer containing the solvent, which is removed by evaporation. At the end of the evaporation, a ceramic film is formed on the fabric whose characteristics and mechanical properties are strongly influenced by the process parameters.

This new approach shows a number of potentials due to the versatility of the system, in which it is possible to incorporate active molecules within the coating and to impart numerous properties to the treated substrates. Considering the variety of organic molecules, the potential of sol-gel technology for the development and application of ceramic coatings to functionalise fabrics is evident. The addition of the functional organic component can be carried out by incorporation into the matrix or by grafting the functional molecule.

The choice of one type of hybrid over the other depends on the purpose of functionalisation. In the case of finishes with the objective of prolonged solidity, it is more appropriate to bind the active ingredient permanently, whereas if the active ingredient needs to be released, it is preferable to disperse the organic molecule in the matrix.

The sol-gel technology applied in the textile field has potentialities that make it very interesting for a series of uses. The application of a superficial ceramic layer to the fabric results in anti-wear properties; through the sol-gel technique it is possible to create coatings with high density and hardness; abrasion resistance is influenced by the synthesis conditions and the type of precursor, since adhesion and hardness depend on these conditions.

In recent years, the sol-gel technique has been exploited for flame retardant applications, particularly on cotton substrates. The interest in these treatments lies in the possibility of creating a layer of inert ceramic material on the surface of the fabric. In this way, the coating acts with a triple effect: the ceramic characteristics allow it to act as a thermal barrier by increasing the heat necessary for the ignition of the flame, it limits the contact between fuel and comburent and, the formation of water at high temperature creates an increase in the char content. In addition, nitrogen and phosphorus compounds can be added, which act in the gas phase or increase char formation.

Photoactive coatings can be produced by incorporating titanium nanoparticles into the sol-gel, which can also act as UV absorbers to increase the life of the materials and, by using titanium dioxide, post-absorption reactions can be exploited not only for a bactericidal effect, but also to degrade the dirt present.

2.3 Bio-based finishing

Biopolymers are derived from biological sources and are key resources as they are renewable and useful for the development of bioactive textiles. Biopolymers are derived from various sources such as agricultural raw materials and marine food resources. The main advantages of biopolymers include abundant availability, biocompatibility and in some cases biodegradability.

Bio-based polymers are obtained by extraction, synthesis from renewable monomers or microbiological synthesis. The adoption of biodegradable materials leads to a decrease in waste production and non-renewable resources. Some textiles are produced from biopolymers, especially fabrics made from natural and synthetic fibres, but for finishes the introduction of biobased/biodegradable materials is not well developed. Therefore, the development of bio-based and/or biodegradable finishing and impregnation formulations is necessary to reduce the environmental impact of such fabrics. This is still a challenge and requires the development of new formulations because the main application areas for commercially available biobased/biodegradable polymers are packaging, paper and wood coating.

Although a wide variety of biopolymers are available, they often do not meet the requirements (e.g. cost, durability and properties) for textile finishing. Bio-based binders can be divided into two groups:

- Drop-in biopolymers: biopolymers identical to existing petroleum-based polymers but made from renewable resources.
- New bio-based polymer chemicals such as PLA.

A significant amount of research is underway in the field of drop-in biopolymers towards bio-based PU, based on renewable polyester polyols, to replace and guarantee the mechanical performance of resins containing formaldehyde. Bio-based PUs are commonly used in the same applications as their petroleum-based counterparts, such as:

- Foam coatings
- Direct coatings
- Padding process
- Spraying process
- Thermoadhesives for Lamination
- Water column & Breathability performances
- Fashion & traditional finishing

Before being produced from renewable sources, PU has undergone various research and processes to make it environmentally sustainable through the development of alternative production methods, including formulating PU in such a way as to eliminate highly impactful solvents in fabrics such as DMF or using water-based formulations to reduce the total emission of carbon dioxide into the environment. These characteristics can also be carried over into bio-based PU formulations by adding the production of the formulation with a range of 30% to 70% renewable material content. These types of new formulations have shown handfeel, resilience and stiffness characteristics close to standard recipes of formaldehyde-based finishes.

2.4 Water repellency

The key to water repellency is the surface tension of the fabric, as long as it is lower than the surface tension of water, the fabric will not get wet. In the past, waxes and fish oil were used to give water repellency to fabrics, but then fabric manufacturers switched to using modified paraffin, which had better performance characteristics. The continuous search for improvements in existing technologies has led to the development of fluorocarbon compounds. These compounds, when applied to fabrics, drastically lower the surface tension of the fibre, forming a barrier capable of repelling water, chemicals and even oil. For this reason, fluorocarbon-based water-repellent finishes are widely used in technical textiles. Over the last decade, it has been found that these compounds, in particular PFOS and PFOA, present environmental and human health problems (Persistent, Bioaccumulative and Toxic), hence the decision to restrict their use. The immediate solution was to reduce the chain size of fluorocarbons from C8 to C6, but this resulted in a loss of efficiency on finishing properties but using less persistent and bioaccumulative compounds. The focus on the PBT effects of fluorocarbon compounds has led manufacturers to find alternative sources for the production of fluorine-free water-repellent finishes. This search for fluorine-free water repellents has led researchers to rediscover compounds used before fluorinated compounds, exploiting the development of hydrophobic polymers. Products based on alkyl ethyl acrylate copolymers are a fluorine-free alternative that provides excellent performance in terms of water repellency. Treating fabrics with this compound gives a transparent, durable water repellent finish and a soft handfeel touch, without altering the original aspect. The main characteristics of this finish are that it can be used on any type of fibre, giving it high resistance to rain and humidity stains. Furthermore, the finishing is in water emulsion, making the compound non-flammable and avoiding the use of solvents with an impact on the environment, APEO-free and compatible with different types of auxiliaries. The treatment is resistant to both domestic and dry cleaning.

The water-repellent capacity of a fabric can be also achieved through nanotreatments that reduce the use of hazardous and impactful chemicals and lower the carbon dioxide emission of the fabric manufacturing process. Water-repellent properties can be introduced in some fabrics, especially on cotton, through the formation of hydrocarbon-based nanowhiskers. These nanowhiskers, if properly engineered and three orders of magnitude smaller than the fibre, create a surface tension between the droplet and the fabric with a similarity to the lotus effect, allowing water droplets to remain on the surface of the fabric. Lotus-like superhydrophobicity can be introduced into a fabric by producing a surface roughness in the fabric without affecting the softness or mechanical properties.