Chapter

Innovation of Textiles through Natural By-Products and Wastes

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Abstract

Nowadays, the competitiveness of the textile industry and the consumers' interest have been increasing the demand for innovative and functional textiles. Allied to this, sustainable developments are playing an increasingly important role in the textile industry. Such concerns led to a new development strategy based on the valorization of bio-based wastes and by-products of different industries, inserting this in the circular economy paradigm. These bio-based wastes and by-products come from several industries, as the agri-food industry. These resources present an enormous potential for valorization in the textile finish due to their intrinsic properties (antimicrobial, prebiotic, antioxidant activity, among others). This chapter will review the latest innovation and textile product development through different by-products and wastes, their main properties and characteristics and the advantages that they offer to the textile industry.

Keywords: innovative textiles, functional textiles, waste valorization, sustainability, circular economy, protein fraction, agro-industrial wastes, vegan leather, leather waste, alternative leather

1. Introduction

In the textile industry, the utilization of low environmental impact technologies that are based on sustainable raw materials presents a novel possible way for the development of functional textiles on a large scale. By-products and wastes from different sources and industries such as proteins, vegetable, agroforestry, furniture, food, footwear and automotive industries are often used as biomass or sent to landfills. However, due to the interest in by-products as a substituent for the commercially aggressive chemicals used in the textile industry, research on the valorization of these materials has remarkably increased. In this sense, several studies were carried out to enhance the performance attributes of textile goods through finishing, coating and dipping technologies with by-products and residues, thus creating an opportunity for the establishment of partnerships and circular economy business models.

2. Natural by-product and waste compositions and properties

2.1 Whey protein

The dairy industry is characterized by a broad group of food products, such as milk, milk powder, butter, yoghurts, cream and cheese, but it is also a big source of solid and liquid by-products, but among those, whey is the one produced at the highest volumes in cheese industry. The world production of by-products in dairy industry is around 4–11 million tonnes per year, but Europe is the worldwide leader in cheese production and consequently the largest whey producer [1, 2]. This has a big environmental impact if they are disposed as wastes, so strategies to reuse these by-products are important, and there is a community pressure in this sense. Traditionally, some years ago, whey is used to be disposed of, but with environmental concerns and legislation to be implemented, the reuse appears with a prominent role [2]. Whey is considered one of the major pollutant by-products because of its high biological and chemical oxygen demands [2]. Whey is composed of 85–90% water, 10–15% lactose (carbohydrates), soluble vitamins, minerals (e.g. calcium, phosphorus, sodium and so on) and proteins (e.g. β-lactoglobulin, α-lactalbumin, bovine serum albumin (BSA), immunoglobulins and others) [1, 2]. Lactose is the main component, being responsible for most of the biological and chemical oxygen demands [2]. However, lactose and other nutrients essential for microbial growth confer whey a potential to produce several bioproducts. Whey proteins award health benefits such as high nutritional value, easy digestion and assimilation, which are interesting for the food industry too. It can be used for biotransformation feeds, bioproteins, prebiotics, and bioactive peptides after fermentation or enzymatic hydrolysis. On the other hand, the reduced-lactose whey, demineralized whey, and whey protein concentrates or isolates are used for food, cosmetic and pharmaceutical industries, especially for thier emulsifying, thickening, gelling, foaming and water-binding properties. More specific, these proteins of natural origin and with emulsifying capacity are used in the formulation of creams and shampoos as substitutes for synthetic surfactants. The whey protein hydrolysate also has this type of application for hair products. Another property of whey protein consists of gel formation, being used to produce protective films and coatings. These proteins, as they have low permeability to water vapour, are used in paper coating, providing good appearance and printability. β-Lactoglobulin and α-lactalbumin can be used as moisturizing and antiwrinkle agents. Lactoferrin is a good iron chelator, preventing the formation of free radicals. In the 1990s, whey protein, in the form of iron proteinate, was also used as an antianemic preparation [3]. Moreover, this by-product can be reused not only for its technological properties but also for its biological properties in terms of the body's benefits.

Due to its biological and chemical properties, whey has several applications, depending on the biotechnological method applied to reuse this by-product. It can be used to obtain chemical products to produce functional formulations and for food, fuel health, pharmaceuticals, biomaterials and others.

Whey has been used in the food industry to produce functional food and drinks as an innovative product with health benefits. For example, whey can be used in dairy beverages: unfermented or fermented, probiotic, refreshing soft, alcoholic, diet and high protein sport [2]. Whey is also one of the main sources of the bioactive peptides that can be used as nutritional supplements because of its structure, rapid absorption and biological properties (antihypertensive activities and antioxidant properties). On the other hand, whey protein has been explored in the food industry in edible film or coating development for food preservation, for its biochemical properties, such as its edible nature and intrinsic biodegradability, suitable mechanical barrier, flexibility and the capacity to incorporate functional compounds [4].

The improvement of knowledge has also allowed the development of biomaterials from whey, for example, to produce biodegradable capsules for drug delivery. The whey protein isolates (WPI) have been used for bone regeneration to produce bioactive glasses with potential applications in bone tissue engineering.

These biomaterials have been explored for tissue engineering applications due to their chemical and biological properties, such as the ability to retain water, easy transport/entrapment of nutrients or cells, controlled biodegradability, mechanical properties and biocompatibility [5]. However, the field of action of whey is much wider and applied to other industries as an eco-friendly alternative to conventional chemicals.

2.2 Agro-industrial wastes

Agro-industrial wastes include several different wastes from the food and agriculture industries. The amount of wastes from the food and forestry-based industries produced in the European Union (EU) is estimated to be in the order of 900 million tonnes per year. However, a large part of these wastes are considered low-value input materials instead of wastes, like sawdust that can be used to make products such as fibreboard or leaves and stalks of plants that can have other agricultural uses such as animal bedding [6]. If these wastes are released to the environment without a proper disposal procedure, they may worsen the environmental pollution and cause harmful effects on human and animal health. **Table 1** shows the estimated sustainable availability of agro-industrial wastes.

Recently, these wastes have been the focus of much attention due to their huge potential for exploration, not only for their wide availability and diversity but also for their intrinsic properties and functionalities, which make them an increasingly

Wastes	Current availability (Mtonnes/year)	2030 availability (Mtonnes/year)
Paper industry	17.5	12.3
Wood industry	8	5.6
Food and garden industries	37.6	26.3
Crop wastes	122	139
Forestry wastes	40	40

Table 1.
Agro-industrial wastes and wastes produced in the EU [6].

attractive feedstock for chemical, material and biofuel production [7]. Conscious consumption allied with ethical and sustainable values is increasing the consumers' concern in the moment of purchase: "What is the nature of the raw material?"; "What is the life cycle of the product?". This tendency has made the producers look for alternative raw material sources [8].

It was found that the typology of vegetable wastes most produced varies from year to year, with the most abundant being materials unsuitable for consumption or processing, biodegradable wastes and vegetable textile wastes [9]. The most promising vegetable and agroforestry wastes for textile application are, for example, sawdust, coffee grounds, pine bark, eucalyptus bark and others. Sawdust and composites of sawdust (in powder and in pieces) are very abundant wastes as a result of the wood processing industry such as furniture industry. Coffee grounds are highly abundant because the cultural habit of people is drinking a lot of coffee. Pine bark is a highly abundant waste that is very easy to adapt for textile coating applications, which can result in a brown powder that gives rise to coatings with a dark colour and a very attractive shade. Olive stones are also abundant, resulting from the production of olive oil or from the ginning of the olives. Almond or nutshell wastes can create coatings with very attractive colours and visual effects. Rice husk, due to its low nutritional value, is not a viable resource as food for animals, and the burning or landfill deposition of this type of waste has important environmental impacts, as it has a slow biological degradation (high silica content). Eucalyptus bark is also abundant, resulting from the paper and wood processing industries [7].

2.3 Leather wastes

The transformation of animal skins into leather allows for the recycling of what would be an organic waste from the food industry into added-value products. In this context, the animal skin is considered a by-product, as it is not reintroduced in the same productive cycle and its reuse contributes to a more sustainable and a circular economy.

There are several applications for leather, and the manufacture of leather upholstery for furniture, airplanes and automobiles has been one of the main markets in the last two decades. Although leather waste recycling has been the subject of hundreds of studies, landfilling remains the most frequent option, wasting all resources contained in leather. Also, due to environmental restrictions, the study and development of sustainable alternatives for the recovery of this waste for the manufacture of new, more sustainable materials are urgent [10].

The valorization of leather wastes such as leather shavings aims to the reduction of the presence and usage of Cr (VI), oil, hydrocarbon, and solvent absorber; adsorbent of chlorides, fats, tannins, surfactants, and dyes, used in the tanning process. Leather powder has already been applied as an oil and crude absorber, while carding powder has been used as an adsorbent for textile dyes (more anionic than cationic) [10].

This type of waste can be physically processed by crushing and grinding methods. For certain uses, its mixture with resins and catalysts for subsequent pressing between metal moulds with various configurations and sizes can produce multilayer or composite structures. Final products are obtained with a very good appearance, without the need for any additional finishing, with good sound insulation and even good thermal insulation [11]. Applications in furniture, floors and footwear components are some of the examples. Through these processes leather wastes have been used in leather-like materials and construction materials, as additives for thermoplastic composites and as filler materials for reinforcing rubbers [10].

Leather waste can also be processed chemically (alkaline or acid hydrolysis) or enzymatically, in order to obtain collagen (by-product) for application in added-value products. Collagen consists of a fibrous, insoluble and inert protein, which after alkaline/acid/enzymatic hydrolysis is divided into gelatine and hydrolysed (soluble) collagen, by breaking the chromium-collagen bond established during the tanning phase and breaking non-covalent bonds in the protein's structure that lead to its swelling and solubilization [12, 13].

The chemical processing of leather wastes also results in Cr (VI), which can be reintroduced upstream into the leather tanning process. Another type of chemical processing reported for the recovery of Cr (VI) involves the incineration of tanned chips and blue chips and later transformation of the ashes by converting chromium (III) oxide into sodium chromate [Cr (VI)] [14, 15].

Given that the present method of recovering collagen from leather wastes is free of complex installations and equipment, its implementation in the productive cycle of companies is economically attractive [14].

3. Functional properties of natural by-products and wastes

3.1 Whey protein

Whey exhibits many unique functional properties such as antibacterial and antioxidant activity and odour and water vapour absorber, among others. Therefore, whey has become an attractive product for its versatile applications in different fields, including textile industry. Many of these applications are also reported in the development of new functional products in the food and pharmaceutical fields, due to the properties (such as antimicrobials, antioxidants, and anticancer drugs) and structures of whey protein and its fractions. **Table 2** shows some examples of applying these fractions to obtain the functionalities described.

Another application for whey or milk fractions is related to the production of microcapsules. In fact, globular proteins had been used as a vehicle for the micro-/nanoencapsulation of bioactive compounds. Milk proteins, namely, whey protein, have been used for the microencapsulation of aromas. Using serum protein isolate and gum arabic, it is possible to encapsulate β-carotene. The same gum arabic had already been shown to be effective in promoting self-aggregation, and consequent capsule formation, of β-lactoglobulin [28–30]. Another aspect is the microencapsulation of β-lactoglobulin with another polysaccharide, chitosan, and this has a

Functionality	Description	Ref.
Antioxidant	Several studies show that whey has antioxidant properties. It is maximized with an enzymatic treatment of whey, milk or cheese and with the hydrolysate's valorization (microbial proteases, β-lactoglobulin and α-lactalbumin). This evaluation was done with ABTS or ORAC-FL method	[16–19]
Deodorant property	Milk and whey proteins are effective in the absorption of odours, given their composition in proteins and lipids. Lactose is described by its ability to retain odours, absorbing them on its surface as the crystals form	[20, 21]
Antimicrobial	Two of the whey fractions, lactoferrin and lactoperoxidase, present an antimicrobial activity. Lactoferrin has several antimicrobial peptides that are released after hydrolysis by proteases. Lactoperoxidase has a high antimicrobial capacity through catalytic and chemical processes	[22–27]

Table 2.
Whey, protein fraction and dairy by-product functionalities.

stabilizing effect on serum proteins, protecting them from denaturation at temperatures up to 90°C. Due to its structure, β-lactoglobulin can also form complexes with vitamins and nutraceuticals, such as folic acid. β-Lactoglobulin/folic acid complexes exhibit particle sizes below 10 nm and exhibit stability over a wide range of pH values [31–33].

3.2 Agro-industrial wastes

The passage of traditional industrial processes to more sustainable patterns and a circular economy model are mandatory given the limited resources and adverse environmental effects that are noticeable today. In this sense, the establishment of bio-based economies and industrial processes, such as the textile industry, will contribute directly to substitute emission-intensive and non-renewable resources with renewable resources, as well as create innovative and functional added-value solutions [9]. Some wastes or natural additives can provide a wide range of functional properties to textiles, opening an opportunity for the development of new and innovative textile solutions. Some potential functionalities of some vegetable and agroforestry wastes and by-products are presented in **Table 3**.

3.3 Leather wastes

The manufacture of leather upholstery for furniture, airplanes and automobiles has been one of the main markets in the last two decades. Currently, in Europe, 14% of all new cars have leather coverings, and an additional 4% are made in combinations of leather, textiles, composite materials and imitation leather. The world's leading car manufacturers have focused on looking for renewable materials, recycling materials in manufacturing processes and using less toxic materials to improve car recyclability [43]. In the European footwear industry, the production of about $1–2 \times 10^5$ tonnes of leather waste per year is estimated, with the annual cost associated with its management between 4 and 10×10^6 € [44]. In the manufacture of footwear, more than 70% of the leather used is leather tanned with chromium [10].

Despite the many methodologies and systems studied and implemented in the last decades, which allowed the minimization of waste production during the manufacture of leather and its processing by user industries, such as the automotive and footwear industries, these production processes inevitably generate waste leather which can be disposed or valorized as it is or by chemical conversion into other added-value products (collagen) [10].

Native collagen and its derivatives are widely applied in the food, agrarian (fertilizer), cosmetic and biomedical industries, as well as in the textile industry, due

Waste/by-product	Source	Functionalities	Ref.
Coffee grounds	Coffee production process	Anti-odour, antimicrobial, aromatic; UV radiation protection	[34, 35]
Rice husks	Rice processing	Thermal insulation potential	[36]
Eucalyptus bark	Wood processing industry	Antimicrobial, aromatic	[37, 38]
Pine bark	To feed	Antioxidant, antimicrobial, aromatic	[39, 40]
Pine sawdust, composite sawdust, powder and pieces	Wood processing industry	Absorbent, mechanical and structural properties	[41, 42]

Table 3.
Vegetable and agroforestry wastes and by-products and functionalities.

Functionality	Description	Ref.
Gelling and dilating	Aggregation of molecules at 30°C to form hydrolysed collagen gels and gelatine; swelling in the presence of water	[45–47]
Foaming	The presence of hydrophobic and hydrophilic amino acids provides excellent foaming properties, even in the absence of gelling	
Antimicrobial	Hydrophobic amino acids penetrate the peptide chains that make up bacterial membranes, acting as a natural fungicide and bactericide	
Antioxidant/anti-ageing	Inhibition of lipid peroxidation, elimination of free radicals and acting as transition metal ion chelating agents, protecting cells from damage caused by oxidation and helping to improve skin firmness	

Table 4.
Different functionalities of collagen and its derivatives and respective area of application.

to their biodegradability, biocompatibility, etc. [15]. In addition, collagen and its derivatives have also another set of properties that enhance their potential, not only for the direct functionalization of textile substrates but also for the development of the coating formulations (**Table 4**) [15, 45, 46].

4. Functional applications of natural by-products and wastes in the textile industry

The consumer demand for more environmentally responsible products with better sustainability credentials is increasingly growing, in addition to progressively more restrictive legislation regarding the environmental impact of industrial activity. Additionally, other increasingly important factors are the search for textile products with differentiated technical and functional properties and with better sustainability credentials, without compromising the appearance, touch, and comfort of the article.

These facts have led companies in the textile and clothing sector to gradually invest in an investigation strategy that leads to the adoption of sustainable policies and reduction of environmental impacts, based on the valorization of wastes and by-products of industries that are geographically close. In this scenario, the reuse of these natural by-products and wastes as a bio-resource in the demanding textile sector presents itself as an alternative.

4.1 Textile fibres with whey protein

The use of milk proteins for fibre production and application in textile industry remotes back to the beginning of the twentieth century. The conventional fibre production method consists in dissolving 20–25% milk proteins, including whey protein and its fractions, in a 2% NaOH solution to obtain a solution of adequate viscosity for fibre production by wet spinning extrusion (10–30% solid material) [48, 49]. In this process, the protein solution is pumped through a spinneret into an acid bath with a pH below the isoelectric point of the protein (4.5–4.6) to cause its coagulation [48, 50, 51]. The coagulate is afterwards stretched and drawn to increase polymer chain orientation and tensile strength of the fibre. Coagulation baths, containing aluminium salts of formaldehyde, may further increase the fibre stretching and enhance its physical properties [48, 51].

There are already several studies and patents on the production of fibres from whey proteins aiming to obtain fibres with improved mechanical properties and to use of more ecological productive processes. Kamada et al. produced fibres from β-lactoglobulin nanofibrils in the presence of alcohols, low pH and elevated temperature (hydrolysis of the protein in low molecular weight peptides for the formation of nanofibrils) [52]. Sullivan et al. produced nanofibres, by electrospinning, from WPI solutions (75%) and polyethylene oxide (PEO) (4%) and solutions of β-lactoglobulin (75%) and PEO (10%) in water [53]. Drosou et al. [54] studied the possibility to make whey protein fibres by electrospinning. However, electrospinning of nanofibres from proteins has proven to be quite challenging due to their globular nature, in most cases, the low viscosity of their aqueous solutions and potential lack of intermolecular entanglements [54]. To overcome these challenges, blends of proteins and other bio-based materials have been used. Drosou also tested some WPI/pullulan blends and was able to obtain continuous and uniform fibres [54]. The presence of the pullulan increased the viscosity of the solution, having a big impact in the process parameters. Zhong et al. adopted a similar strategy to obtain also whey protein nanofibres through electrospinning [55]. In this case the authors blended the whey protein with PEO and were not able to produce pure protein fibres. The ability of the whey protein solutions to produce fibres changed over time after dissolution [55]. Oktar et al. produced fibres from WPC blended with poly-ε-caprolactone (80 kDa) [56]. The obtained fibres showed improved mechanical properties to higher WPC concentrations (3–8% w/v). Kutzli et al. produced whey protein fibres by electrospinning, blending the proteins with enzymatically treated starch (maltodextrin) [57]. Using two different maltodextrins, with different molecular weights, the authors found that the spinnability of the solution is heavily dependent on the average size of the maltodextrin. Aman Mohammadi et al. obtained whey protein fibres by electrospinning, mixing WPI and guar gum [58].

As already mentioned, fibres resulting from these processes usually fail to have the mechanical properties for weaving and textile production. For this reason, whey protein fibres are often mixed with other fibres with appropriate mechanical properties (mostly cotton, silk and wool, with tensile strengths) [59].

The valorization of by-products of the dairy industry by wet spinning generates corrosive effluents rich in metal salts. This type of effluent requires appropriate conditioning and downstream steps of neutralization and precipitation of metals, which may entail large costs for its treatment and disposal (in order to avoid acidification of soils and water resources, increase of the dissolved salt content and the appearance of health problems in animals and humans resulting from untreated discards in water bodies used to supply populations) [60].

4.2 Textile finishing with whey protein

Whey proteins have also been studied for their applicability as coatings and additives in the textile industry. Pisitsak et al. (2015) studied the dyeability increase of cotton for a tannin-rich dye extracted from *Xylocarpus granatum* bark. Cotton fabrics were pretreated with WPI by a padding technique. The improvement in the dye absorption after protein pretreatment is ascribed to the insoluble complex formation between the tannin and the proteins present in the fabric, stabilized through hydrogen bonding and hydrophobic interactions, which makes it easy to be coloured. Besides that, both protein treatment and dyeing improved the ultraviolet (UV) shielding efficiency of the cotton fabrics [61].

Proteins are not the only milk component able to facilitate the dyeing process. Dyes are generally applied in an aqueous solution, and some of them require chemical auxiliaries to improve their water solubility and to improve the dyeing process. Bianchini et al. [62] reported a study to naturalize two synthetic azadyes through their linkage with lactose to induce their water solubility. In this study, a chromophore was transformed into a hydrosoluble species through glycol conjugation with a sugar, and a preliminary tinctorial test was carried out with polyester, cotton, acetate, wool and acrylic fabrics. Results showed several benefits since the modification of the dyes with lactose, as this improved their water solubility, allowing the elimination of surfactants and mordants, making the dyeing process easier and avoiding high temperatures and high pressures. Besides that, the new hydrosoluble dyes showed a better affinity towards different fabrics (synthetic, natural, artificial), improving efficacy and reducing waste [62].

These developments brought benefits not only in terms of textile valorization but also in terms of the use and recovery of wastes and by-products. The utilization of carbohydrates largely and cheaply available, such as D-glucose, D-galactose and lactose, normally discarded in huge quantities in the environment, with no negligible impact, brings new possibilities for efficient and more selective waste treatment by using, for instance, live micro-organisms to attack the sugar moiety and consequently the covalently bonded chromophore, or the use of enzymes able to destroy dyes [62].

In the past years, novel and innovative solutions for flame retardant systems, for replacing the traditional additives, have been explored. In particular, the availability of a formaldehyde-free flame retardant system based on natural macromolecules such as proteins could be extremely interesting for a possible industrial application [63]. Considering the environmental concern, more ecological and effective solutions have been studied, in the field of flame retardancy, since the solutions mostly used are based on halogenates or phosphorus, being persistent and bioaccumulating in the soil and even carcinogenic and/or toxic for animals and humans. In this sense, biomacromolecules have aroused interest as a green solution in this field, particularly whey proteins and caseins. In addition to being biological additives, they can have added value, as they can be considered by-products or even wastes from the agro-food industry and their recoveries and subsequent use as flame retardants may comply with the current needs of valorization of agro-food crops, avoiding their landfill confinement [57, 58].

Therefore, different novel strategies have been designed in order to enable the use of green flame retardant systems. Due to the ability of whey proteins to act as water vapour absorbers and as oxygen barriers, textiles treated with this by-product have been exploited in order to increase their thermal stability and flame retardancy [63]. For this, folded and unfolded whey protein isolates were deposited on cotton fabrics. Through thermogravimetric analysis it was observed that whey protein coatings significantly affected the thermal degradation of cotton in an inert and oxidative atmosphere. Specifically, the application of whey protein coating contributed to the delay of the thermal degradation of the textile, also resulting in a smaller total mass loss. Besides that, the treated fabrics have shown a decrease of burning rate and an increase of total burning time, determined by the flammability tests in horizontal configuration [63].

The antibacterial properties of some of the whey components have also been studied. Through the cross-linking between microbial transglutaminase (mTGase) and lactoferrin, the antibacterial properties of wool were improved to *E. coli* (Gram-negative) and *S. aureus* (Gram-positive) bacteria. It was observed that the amount of lactoferrin deposited on the wool fabric was improved with the cross-linking reaction with mTGase, when compared to the control sample. The wool fabrics immobilized with lactoferrin exhibited approximately 70 and 60% inhibition for *E. coli* and *S. aureus*, respectively, showing a good antibacterial property [64].

The same was observed in a recent study developed by Srisod et al. [65]. It was described the utilization of WPI as reducing and stabilizing agent in a green synthesis of silver nanoparticles (AgNps) from silver nitrate. In addition, a natural tannin-rich extract was applied to cross-link the WPI/AgNps to cotton fabric through the formation of an insoluble binder. The cotton fabric treated showed an excellent antibacterial performance against *S. aureus*, even after 50 washing cycles, showing no toxicity to L929 cell changes to the intrinsic properties of the substrate (drapeability and tearing strength) [65].

Regarding the globular structure of whey proteins, due to their properties and structures, they have been used as a vehicle for active substances such as antimicrobials, antioxidants and drugs, among others, for the development of new functional products [66–69]. This approach is widely used in several industrial sectors, providing the possibility of a controlled release of bioactive compounds. It can easily be applied to the textile industry, with the possibility to add functionality to textiles.

The antioxidant effects of vitamin E encapsulated in BSA nanoparticles in cotton have already been studied [70]. The nanoparticles, produced by ultrasonic emulsification, have a size between 200 and 300 nm and have the capacity to encapsulate 99% of the vitamin. After impregnation onto cotton fabrics, they present an antioxidant activity and wash resistance up to ten cycles [71].

Microspheres of BSA have also been tested as encapsulation agents of an antibiotic, tetracycline, in order to obtain an antibacterial coating for cotton and polyester fabrics [72]. These capsules demonstrated not only good encapsulation capacity but also gave the textiles antimicrobial properties [72].

Nonetheless, these types of applications at an industrial level have some limitations since the cost-effectiveness ratio of these biomacromolecules may not compensate until now. In addition, the durability to the laundering was not yet achieved in an effectively sustainable and long-lasting way, since these biomacromolecules have a waterborne character and these coatings come off from the textile when subjected to washing. When adding binding agents to biomacromolecules, a balance must be sought between their green characteristics and the use of chemicals that do not eradicate the sustainability of the process. In this sense, exploitation of biologically derived chemical treatments, or at least chemicals with a low environmental impact, which could make the proposed biomacromolecules more durable than they are today, while maintaining their effective functionalities, is being carried out [73, 74].

4.3 Textile coating as a sustainable alternative to genuine leather

Genuine leather is made of animal skin, namely, bovine leather, tanned and finished with products of synthetic origin (chromium). It is used as a noble material for the manufacture of various products with applications in various industries, such as fashion, fashion accessories, footwear, decoration, automobiles, etc., and is the one that has the greatest expression in the market due to its excellent properties such as porosity, breathability, softness, comfort and fall, among others [75, 76]. Ecological leather refers to a leather tanning process that does not use metals such as chromium but in alternative recurs to substances of natural origin (vegetable, animal or mineral), such as vegetable tannins (polyphenols of plant origin) [77]. Though ecological leather has a lesser environmental impact than genuine leather, it still does not have the same properties of thermal resistance, colour fixation and versatility as the leather resulting from the treatment of tanning with chromium [75]. In addition, there are several ethical and environmental concerns involved in the use of genuine and ecological leather, such as the killing of animals and the high environmental impact resulting from their processing, which have triggered the growing interest on the part of the consumer in more sustainable alternative solutions to leather of animal origin ethically and environmentally. This generated a search for alternative solutions with the same performance of genuine leather, which catapulted textile industries towards sustainable innovation as a means of answering the markets' demands.

Vegetable leather is a sustainable product of plant origin resulting from the use of vegetable wastes or by-products. There are already some alternatives of vegetable leather on the market to replace animal leather, although they do not fully reproduce the characteristics of animal leather. Of the solutions on the market, the main examples are presented.

Latex-based leather is the name given to a fabric made up of two renewable raw materials, the latex extracted from the rubber tree (*Hevea brasiliensis*) from the Amazonian forests and cotton. The cotton is impregnated with latex, natural rubber (primary product of the smoking of latex extracted from the rubber tree). These can be used in the production of bags, wallets, clothing, footwear and other objects usually produced in leather. The commercialization of these products has become a reason for hope for the improvement of the life of rubber tappers, their permanence in the forest and the sustainable development of the Amazon, generating work and income in indigenous and traditional communities [78–80].

The company Ananas Anam has developed an innovative, natural and sustainable non-woven leather called Piñatex™, produced from pineapple leaf fibres, considered as a vegan alternative to traditional leather. From the pineapple leaf fibres, screens are obtained, which can be dyed, printed and treated to obtain different textures [81]. The material is strong, versatile (different colours, patterns, textures, thicknesses), breathable, smooth, light, flexible, sewable, resistant to water and abrasion and resistant to ignition by cigarettes [82–84].

Products based on thin sheets of cork, laminated with a textile substrate that gives it resistance, are increasingly being introduced to the market as a sustainable vegan alternative to traditional/synthetic leather. They have characteristics equivalent to leather, such as resistance, lightness, breathability, malleability, thermal insulation and impermeability, adding the properties of low density and thermal conductivity. There are several products based on cork leather (cork sheet) on the market, created and launched by designers/brands and national reference companies, such as Bleed—We bleed for nature, Pelcor, and Artelusa, and international, such as Chanel, inter Louboutin, Stella McCartney, Yves Saint Laurent, Prada, Dior, Manolo Blahnik, Dolce & Gabbana and Gucci. These products are based on fashion accessories (wallets, belts, etc.), clothing, umbrellas, footwear, sports goods, furniture, car upholstery lining, etc. [76, 85–90].

Wood-based leather is similar to cork but made from wood from fast-growing trees, such as oak bark, treated with non-toxic chemicals to make it durable, flexible and malleable. Wood leather can be as thick as genuine leather. Dolce & Gabbana is a market reference that has already used this material in a recent collection of bags and shoes [41]. The German shoe brand nat-2™ also recently launched a line of shoes in which up to 90% of the upper surface of the shoe is covered with wood, which is applied over an organic cotton, in order to become a flexible, soft material that allows to smell the wood and observe its natural texture [91]. Another solution is Wooden Textiles, created by Elisa Strozyk. These materials, which also bear some resemblance to leather, are obtained after cutting thin sheets of wood into pieces and adhering them to a textile substrate. The result is a material that smells like wood, but with some flexibility and softness. There are applications in decoration and furniture [92].

Vegea® is a biomaterial produced by the Italian company Vegea, founded by Gianpiero Tessitore and Francesco Merlino [86, 87]. This material, with a similar aspect to leather, valorizes residues from bagasse (skins and tales from grapes), and does not use water in its production [74]. This leather, also known as WineLeather, is already available in several colors, and it can be used for studying or obtaining different thicknesses, strengths, finishes, and textures. It is already applied in the production of clothing, bags and shoes, furniture, packaging, and automobile and transport accessories [93]. It is used to coat a textile substrate with a polymeric mixture, consisting of a cake residue flour and a derived polymer of oil extracted from grapes [94].

The German company nat-2™ developed a material similar to leather, obtained from coffee bean wastes [95, 96]. With this material a line of unisex sneakers was created, whose upper part contains recycled coffee, coffee beans and coffee plant, which constitutes up to 50% of the footwear surface, according the model. The coffee is applied in a layer, giving a soft touch and a coffee aroma. Two Mexican inventors, Adrian Lopez and Marte Cazarez, recently created a laminate based on nopal cactus (or figs), which resembles animal leather, that is breathable, environmentally sustainable and totally plant-based (cotton and Nopal blend), lasts at least 10 years and has the chemical and physical properties required by the fashion industries, furniture, leather goods and automobiles [97, 98]. The material is obtained by coating a cotton substrate with a mixture of dry (in the sun) and crushed cactus powder and protein extracted from the cactus, which serves as a natural binder [99].

Another leather-like material example is bonded leather or reconstituted leather. This consists of the preparation of a paste with ground leather wastes and binding agents, which is extruded, using a process similar to the production of paper [100]. This paste can be applied on a textile support, coated with a PU film and embossed to gain a leather-like texture [101]. The colour and pattern are checked by a surface treatment. The amount of leather fibres in bonded leather can vary, which is reflected in the quality of the material. This product is usually used in furniture, bookbinding and fashion accessories. Depending on the quality of the product, it can be a durable material, with flame retardancy, and does not develop a patina. The number of patents on reconstituted or recycled leather is extensive, without, however, mentioning the use of textile support for the application of the paste with leather wastes [102–124].

RecycLeather™ is a green technology company that produces recycled materials with the look and feel of leather, highly durable, resistant and light. The materials are obtained from leather waste, in particular, cut pieces from gloves. It consists of 60% leather waste, 30% latex (a natural binder) and 10% synthetic products, such as water and pigments [125].

EcoDomo also has some collections with recycled leather [126]. This is obtained by pulverized leather fibres, obtaining materials with a leather content of up to 70%. It is available for different applications, such as furniture, panels, flooring, etc. Embrace™ also has different materials, similar to leather, obtained from leather waste (43–58%), blended with cotton and polyester, and a PU topcoat [127].

Hydrolysed collagen has recently been applied in the leather manufacturing process, and in the production of flexible composite sheets, with polyvinylpyrrolidone (PVP) and cellulose derivatives, for application products in the area of footwear, clothing, etc. [128–130]. The application of collagen hydrolysates in leather production consisted of its mixture with oxazolidines before application, but the obtained results were not as good as those attained by tanning [45, 46]. The application of this by-product, without chromium separation, in the manufacture of flexible composite sheets with both PVP and cellulose allowed the obtaining of composites with improved mechanical properties (composites with PVP and cellulose) and greater thermal stability (cellulose composites) [47, 131].

Gelatex is a non-woven fabric (with nanofibres) made from gelatine derived from waste from the meat and leather industries, developed by Gelatex Technologies, a start-up from Estonia [132]. It is a material with a touch similar to leather and is breathable, durable and customizable (texture, thickness, water resistance, etc.). This material won the The Green Alley Award 2019 [133].

5. Case of study

The mobilizing project TexBoost—less Commodities more Specialties is a structuring project of the Textile Cluster: Technology and Fashion, which aims to include a set of R&D initiatives with a strong collective character and high inductor and demonstrator effect, with the central involvement of companies of the textile and clothing sector, but also of other complementary sectors of the economy [134]. TexBoost consortium, led by RIOPELE and under the technical coordination of CITEVE, involves a total of 43 entities, of which 23 are industrial companies of the entire textile industry and 15 are non-corporate entities of the research and innovation system.

The project is organized into six PPS—products, processes and services—of which it is worth highlighting the PPS5, sustainability and circular economy. This PPS5 aims the development of materials and solutions using wastes and by-products of other industries (footwear, automobile, cork, forest and milk industry) in new and innovative textile solutions.

For the first nuclear activity, vegan leather, the R&D work was focused in the development of a new generation of coated textile solutions that could be used as an alternative to natural and/or synthetic leather, using wastes and by-products of vegetable origin with new multifunctional properties combined with design and special fashion effects form the basis of this activity. The aim of this work were also to respond to one of the major trends in consumption, related to ethically and environmentally sustainable attitudes, developing products with a high potential for application in technical and functional areas, such as technofashion, eco-design, clothing, decoration, home textiles, footwear, fashion accessories, sport and protection, among others.

During the project, several agro-industrial wastes were studied, and from them, eco-friendly and Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)-compliant coating formulations were developed, and 100% cotton textile substrates were coated by knife coating (**Figure 1**).

The mechanical performance of the developed solutions was assessed through a series of normalized tests, namely, Veslic friction resistance (ISO 11640: 2012), Martindale abrasion resistance (ISO 17704:2004), Crockmeter friction resistance (ISO 20433:2012), colour fastness (ISO 105-B02) and coating peeling (ISO 11644:2009) (N/cm). The obtained results are summarized in **Table 5**. In a general way, it is possible to conclude that the developed solutions pass the performance norms and specifications.

Regarding the second nuclear activity—alternative leather solutions—the R&D activities focused on the development of a new generation of coated textile solutions by using wastes and by-products resulting from industrial operations, such as the tanning industry, natural leather cutting (for indoor automotive) and EVA (for shoe components), here highlighting the leather wastes, with new multifunctional properties combined with fashion design and special effects. The aim was also to meet one of the major trends of current consumption, which is related to ethically and environmentally sustainable behaviour, developing products with high potential for application in technical and functional areas and in rapid expansion: technofashion, eco-design, clothing, decoration, home textiles, footwear, fashion accessories, sport and protection, among others.

During the project, leather waste was studied, eco-friendly and REACH-compliant coating formulations were developed, and 100% cotton textile substrates were coated by knife coating (**Figure 2**).

Figure 1.
Vegan leather solutions based on sawdust (left) and coffee grounds (right).

Normative test	Coffee ground-based vegan leather	Sawdust-based vegan leather
Veslic[a,b]	5	5
Martindale[c]	3200 rev.: A 6400 rev.: B 51,200 rev.: B	3200 rev.: A 6400 rev.: B 12,800 rev.: B 25,600 rev.: C 51,200 rev.: C
Crockmeter[d]	5	5
Colour fastness[e]	3–4	3
Coating peeling (dry)/(N/cm)	30	31.2

[a]*Veslic friction resistance: flower side, degree of staining; dry skin/wet felt—50/100 cycles.*
[b]*Veslic friction resistance: flower side, degree of colour change; dry skin/wet felt—50/100 cycles.*
[c]*Martindale abrasion resistance: dry, abrasion degree.*
[d]*Crockmeter friction resistance: flower side, degree of staining; wet and dry—ten cycles.*
[e]*Light fastness: xenon lamp, flower side; colour fastness.*

Table 5.
Mechanical performance evaluation of the coffee ground-based vegan leather and of the sawdust vegan leather samples.

The mechanical performance of the developed solutions was assessed through a series of normalized tests, namely, Veslic friction resistance (ISO 11640: 2012), Martindale abrasion resistance (ISO 17704:2004), Crockmeter fiction resistance (ISO 20433:2012), and colour fastness (ISO 105-B02). The obtained results are summarized in **Table 6**. In a general way, it is possible to conclude that the developed solutions pass the performance norms and specifications.

Finally, the other approach of the PPS was research and development of a new generation of coated textile solutions, using wastes and by-products of the dairy industry, with new multifunctional properties combined with design and special fashion effects. Specifically, the two main goals were functionalization of textiles with milk proteins to improve UV protection and use of milk proteins to encapsulate bioactive compounds (such as antioxidants) and subsequent functionalization of textiles.

So, in the present project, 2,2-azino-bis-(3-ethylbenzothiazoline)-6-sulfonic acid (ABTS) method was used for the evaluation of antioxidant activity of a whey protein fraction impregnated in textile substrate. This spectrophotometric method assesses the stabilization capacity of the ABTS radical formed from certain compounds. In other words, it indicates the percentage of inhibition of the ABTS radical after contact with the compounds.

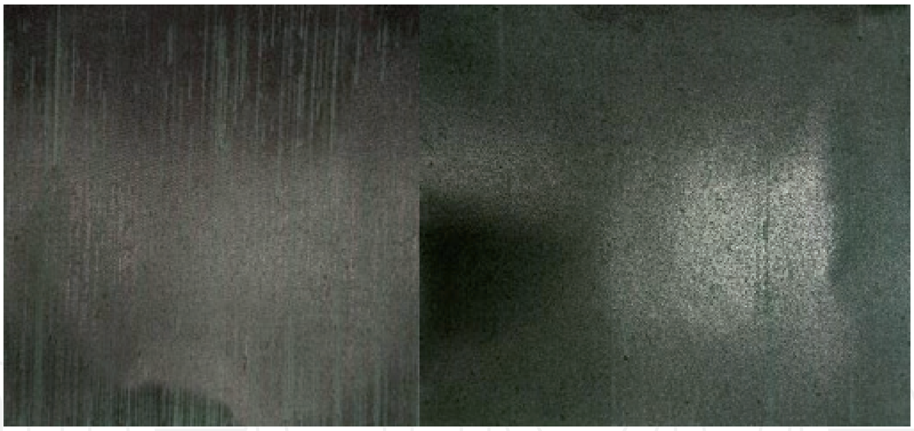

Figure 2.
Alternative leather solutions based on leather waste (left) and hydrolysed collagen (right).

Normative test	Leather waste-based alternative leather	Hydrolysed collagen-based vegan leather
Veslic[a,b]	3–5	3–5
Martindale[c]	1600 rev.: A 3200 rev.: B 12,800 rev:B 25,600 rev:C 51,200 rev:C	1600–3200 rev.: A 6400–51,200 rev.: B
Crockmeter[d]	2–5	3–5
Colour fastness[e]	3–4	4–5

[a]*Veslic friction resistance: flower side, degree of staining; dry skin/wet felt—50/100 cycles.*
[b]*Veslic friction resistance: flower side, degree of colour change; dry skin/wet felt—50/100 cycles.*
[c]*Martindale abrasion resistance: dry, abrasion degree.*
[d]*Crockmeter friction resistance: flower side, degree of staining; wet and dry—ten cycles.*
[e]*Light fastness: xenon lamp, flower side; colour fastness.*

Table 6.
Mechanical performance evaluation of the alternative leather samples.

For this, microcapsules of a milk fraction were prepared with and without an antioxidant compound. These microcapsules were used to functionalize a textile substrate and analysed by ABTS method. To the textile substrate, the relative antioxidant ability to scavenge the radical ABTS+ was compared to the textile control, without functionalization. It was possible to verify that all the protein fraction gave the substrates significantly higher ABTS inhibition percentages than the controls, with a slight increase when the antioxidant is present.

Since textiles had a high antioxidant potential, the capacity of this potential was verified in terms of protecting the colours of textiles when exposed to UV radiation. In this way, the textiles were stained with a dye and exposed for 12 hours to UV radiation. It was found that after 12 hours of exposure to UV radiation, the control showed a high degradation of the stain colour. On the other hand, the functionalization of textiles delayed the process of colour photodegradation, since after 12 hours of exposure, none of the stains had yet reached the same colour reduction.

6. Conclusions

The potential for reusing natural by-products and wastes from different sources was reviewed in this chapter, describing their most attractive properties and characteristics. The most recent innovations and developments in this area were listed and presented, showing a novel possible way for the development of technical and functional textiles. The main potential applications for the valorization of whey protein by the production of textile fibres have been described, as well as by its application as a textile finish. The different applications already tested and the main products already available on the market for sustainable alternatives to produce genuine leather were also listed. Although these types of applications at an industrial level have some limitations, as cost-effectiveness ratio, permanence of the intrinsic properties of the substrates and durability to the laundering, for example, the reuse of these natural by-products and wastes as a bio-resource in the demanding textile sector presents itself as an attractive alternative.

Acknowledgements

The mobilizing project TexBoost—less Commodities more Specialties (no 24523), in PPS 5, sustainability and circular economy, a project co-financed by COMPETE 2020—Operational Program for Competitiveness and Internationalization—and in Portugal 2020 through the European Regional Development Fund (ERDF).

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