Collagen and Leather

REVIEW

Recent advances concerning polyurethane in leather applications: an overview of conventional and greener solutions

Jize Liu†, Federica Recupido†, Giuseppe Cesare Lama, Maria Oliviero, Letizia Verdolotti* and Marino Lavorgna

Abstract

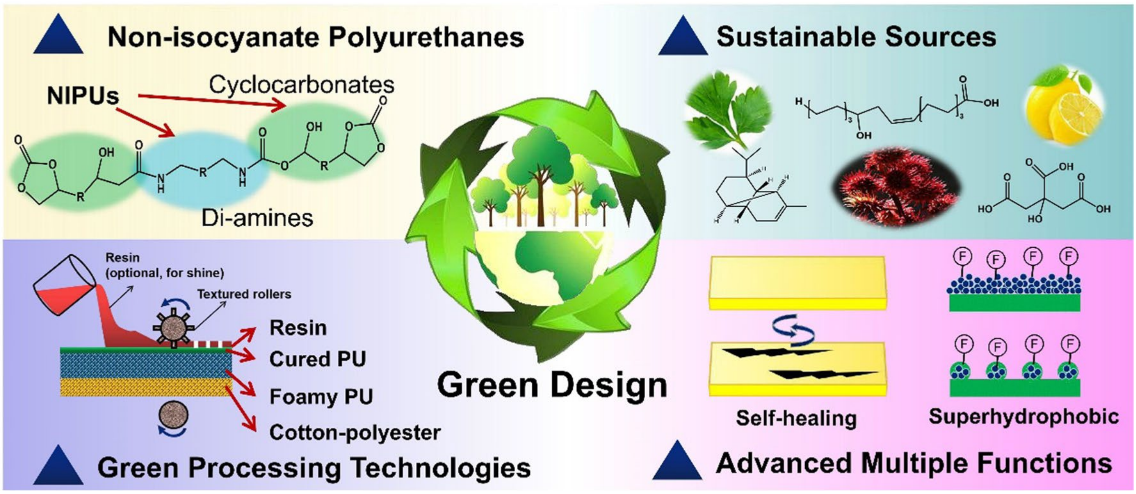
Leather is one of the most popular products across globe and holds a significant place in the economy, while the pollution, associated to traditional leather industry, is far away on the "green chemistry" principles. In this sense, polyurethanes, which exhibit tunable chemical structures by selecting suitable precursors, can fit specific requirements, and the developments of green strategies make them important candidates for leather industry. This mini review briefly outlines the recent development of conventional (petrol-based) and sustainable polyurethanes in the leather industry, including their design and properties, in applications such as synthetic leather and surface-finishing (coatings/binders). Finally, outlooks of the future tendency, including more environmental-friendly strategies, bio-sourced/recycled materials and development of high-value multifunctional leather materials, are also here proposed.

Keywords Conventional leather, Artificial leather, polyurethane-synthetic leather, polyurethane-based binders, polyurethane-based-materials, Polyurethane-based-coatings

†Jize Liu and Federica Recupido have contributed equally to this work

*Correspondence:
Letizia Verdolotti
Letizia.verdolotti@cnr.it
Full list of author information is available at the end of the article

Graphical Abstract



1 Introduction

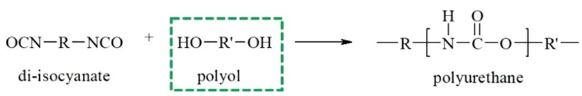
Leather is a strong, flexible and durable material obtained from tanning or chemical treatment, of animal skins and hides. The conventional tanning process consists in a chrome-based treatment and several postprocessing treatments, meant to confer peculiar characteristics to the obtained leather. The most common leathers come from cattle, sheep, goats, equine animals, buffalo, pigs and hogs. The leather is then essentially a by-product of the slaughter of the meat industry [1]. Leather can be used in a variety of sectors ranging from furniture (i.e., upholstery, chairs, armchairs) to clothing, automobiles and many other areas. It has been estimated that, the worldwide production of leather is approximately around 53.3 billion square meters and about 6.5 million tons of wet salted hides and skins are processed worldwide annually. Subsequently, 3.5 million tons of various chemicals are used in leather processing, producing a huge amount of either solid wastes or liquid effluents, among raw hide/skin trimmings, chrome shavings, buffing dust, chrome trimmings, leather strips and cuttings as well as lime and chrome sludge, making the leather manufacturing non sustainable process [2]. Therefore, literature has widely focused remarkable attention in finding new greener production strategies [3].

In this respect, the demand for high quality synthetic leather (also known as *Vegan Leather* or "*Pleather*", leather made of plastic) has increased tremendously [4, 5].

Polyurethane elastomers (PUs) are most commonly plastics used in leather manufacturing both as a bonding agent in retanning and finishing process and for the formation of coating layer. Owing to the similarity between the characteristic group of PU and the peptide chain in collagen, the resultant leathers retanned by PUs can keep the feeling of genuine leather [4]. PUs are also desirable coating materials in finishing, exhibiting many preeminent properties, such as excellent flexibility, superior handling, and adhesive strength. It is found to be capable to hide crust leather defects or irregular appearance and confer specific functional performances (hydrophobic, degradation etc.), chemical and water resistance [6–8].

Generally, PUs are obtained by the polyaddition reaction, which occurs between OH functional groups of polyol components and NCO functional groups of isocyanate source, by forming a basic repeating unit: the urethane group (–NHCOO–) [9] (see the general reaction reported in Scheme 1). Suitable additives (i.e. catalysts, flame retardants, fillers) have to be included in PU formulation to occur and regulate the polymerization reaction and/or to impart specific functional properties to the produced material [9–13].

In leather application, PUs are mainly, based on Thermoplastic polyurethanes [14] (TPUs), which are synthesized from reaction between suitable polyols, aromatic and/or aliphatic-based isocyanates and chain extender components. They are considered as block copolymers due to the presence of both rigid (hard) and flexible (soft) molecular units, alternately arranged. These units, placed in hard domains, are responsible for improved thermomechanical properties, while the soft domains mainly control the properties of flexibility at low temperatures as well as the chemical resistance to solvents and weather



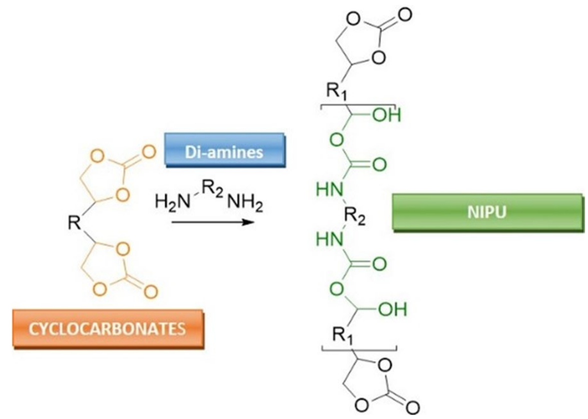
Scheme 1 Polyurethane synthesis between the isocyanate source and polyol

[15]. The chemical interactions and morphology of these domains lead to different chemical, mechanical and thermal properties. [16]. However, this class of polymers is conventionally obtained selecting petrol-based precursors [9, 10, 12, 13]. On the other hand, sustainable polymers are derived from renewable resources, which can be eventually recycled or composted after their use, displaying reduced environmental impact [17, 18]. On this account, biobased polyurethanes and in general biopolymers can be defined according to IUPAC as "*materials composed or derived in whole or in part of biological products issued from the biomass (including plant, animal, and marine or forestry materials* [19]). Consequently, theoretically, there is no limitations regarding the type and amount of sustainable components within PU formulations.

Given that the crude oil is a limited resource, researchers have developed alternative routes to produce chemical materials starting from eco-friendly and sustainable sources. In this contest, biomass-derived products as well as agricultural wastes and byproducts of industrial sectors arouse interests as sustainable sources to obtain chemicals, which could be potentially selected as raw materials to produce new generation materials [20]. Among biomass-derived sources and vegetable oils (castor oil, sunflower oil, soybean oil, rapeseed oils or linseed oils), cashew nut shell or *Arundo-donax* [20], can be selected as sustainable raw materials to extract building blocks to synthesize bio-based polyols, which can be used to produce more sustainable PUs through partially or totally, replacement of conventional polyols [21, 22].

Nonetheless, as isocyanate components have been under increasing scrutiny due to their hazardousness and toxicity, the necessity to find alternatives to isocyanate components in the polyurethane synthesis is becoming nowadays increasingly crucial. Hence, to the aforementioned bio-based PUs, another class of sustainable PUs are the Non-Isocyanate Polyurethanes (NIPUs), conventionally obtained through a reaction between polycyclic carbonate and polyfunctional amines with primary amine groups [22]. The reaction product is a poly(hydroxyurethane) e.g. urethane possessing hydroxyl groups as illustrated in Scheme 2.

However, it is noteworthy that, presently, research on this topic is still at embryonic stage. Indeed, although, NIPUs can be produced from up to 100 per cent



Scheme 2 Non Isocyanate Polyurethanes (NPIUs) synthesis

renewable raw materials, their synthesis is however characterized by low reaction rate and several side products, which, strongly affect NPIUs final properties, which are still non-comparable with those of conventional PUs [22, 23]. Therefore, currently, it is hard to achieve 100% of sustainable materials in PU formulations. In fact, NPIUs production is still a challenge and only a few papers report the synthesis of NIPU for leather application (mainly based on coating application) [23].

By summarizing, research community has demonstrated that, to make the PUs process more sustainable, two main directions can be undertaken:

- Synthesis of polyurethanes derived from "*bio-based polyols*"
- Synthesis of non-isocyanate polyurethanes, as conventional isocyanate presents extremely reactive functional groups and it is also toxic.[9, 10].

In both cases, the utilization of bio-based materials in PU composites has not been adequately studied, owing to the limitations of bio-based raw materials associated to the achievement of either performance comparable to those of conventional PUs or of high levels of sustainability. Such aspects represent the core issue of this area.

In this respect, the sustainability in the leather industry should concern the entire supply/value chain, including the choice of the raw material sources, leather process production (i.e. the skinning from the animal, the polymer-based leather transformation), the leather processing (i.e. tanning, coating, sealants and so forth) up to the delivery of the finished leather.

Nevertheless, starting from these inputs, the aim of the review is to explore the applications of sustainable PUs in leather industry. In details, this review critically analyzes the scientific literature concerning the use of PUs in leather industry as: *#Synthetic Leather PU-based*, and PUs applied in surface finishing i.e. *#Coatings PU-based* and *PU-based binders,* providing outcomes intended to motivate the increase of sustainable industry. For each section, recent findings related to the use of renewable materials in synthesis of PUs are elucidated.

2 Recent advances in leather industry

2.1 PUs-based synthetic leather from oil and sustainable sources: synthesis and properties

The development of green and sustainable materials and technologies has been turning into one of the most important trends in the leather industry around the world. [24–27]. Synthetic leather has gained remarkable attention as alternative to conventional leather due to its relatively low cost and in response of the awareness about animal protection [18]. How to make their characteristics such as flexibility, puncturing, tensile strength, resistance to abrasion, permeability to water and air, thermal stability, chemical resistance, hydrophobicity and shape stability [28] superior than those of genuine leather materials, especially based on sustainable raw materials, is the main aspect of this field. By developing green materials and advanced processing technologies, the corresponding performances make them suitable candidates in several applications such as shoes manufacturing, garments, bags [29, 30] as well as automotive [31], furniture and aircraft sectors [32].

2.1.1 The fabrication of PU-based synthetic leathers

Typically, synthetic leathers are based on PUs and composite matrix–fibril materials, consisting in artificial fibers, have been recently recognized by the scientific literature due to their high mechanical properties with respect to the pristine ones [32, 33] They basically consist in a three-dimensional (3D) reticulated network of polyamide fibers within a polyurethane matrix, suitably designated to simulate the collages bundles of the natural leathers [34]. In other words, PU-based synthetic leather represents the PU resin placed at the interface with a base fabric comprising non-woven fabrics or a network of artificial fibers.

Gurera and Brushan reported the main process steps to produce the whole synthetic leathers (depiction is reported in Fig. 1) based on PUs. [4] First, a PU solution (55 wt.% of the total mass) opportunely added with plasticizers (40 wt.% stabilizers (1 wt.%) and suitable solid fillers [4] (5 wt.%, such as milled cowhair, $CaCO_3$ and lignin and nanoclays) [27, 34] are deposited on a paper layer and pressed between heated rollers, in order to create a uniform film. Subsequently, the polymer solution, mixed with a riser, is laid on the previous layer. Then, the so-obtained material passed through an oven, forming another thick, foamy layer. The third step includes the simultaneous addition of a polyester layer and peeling off the paper layer, while the structure is cured in an oven. The fourth step is laying a resin layer and the setup being

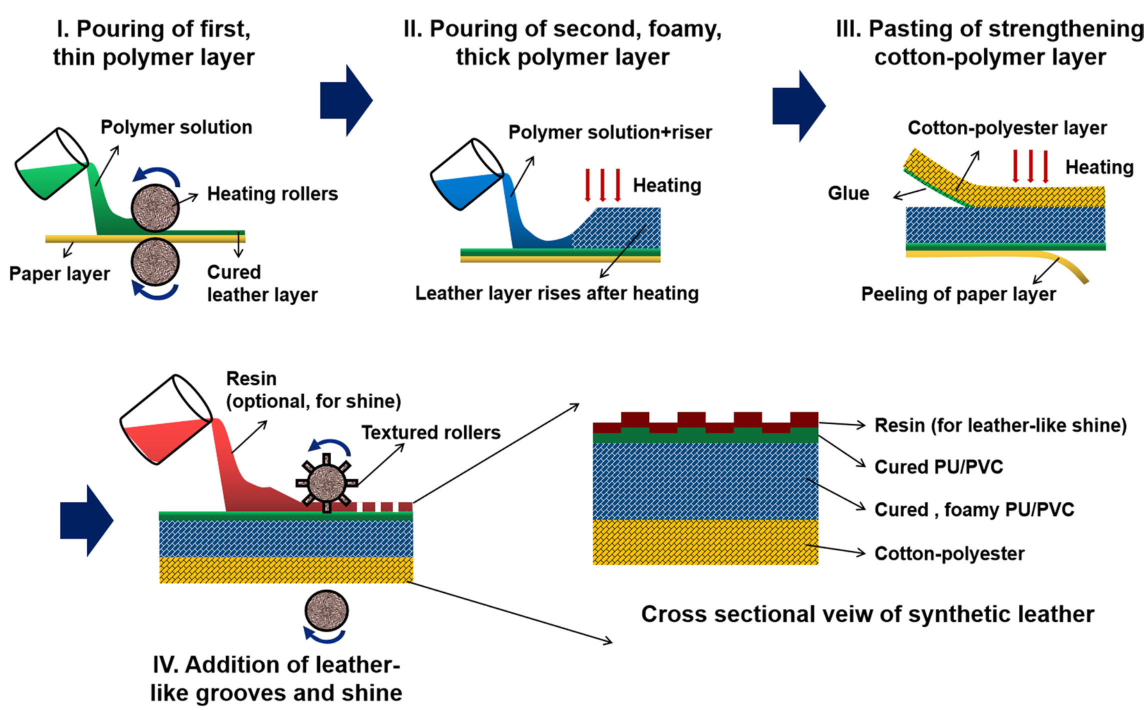


Fig. 1 Schematic representation of synthetic leather process

passed through textured rollers [4]. Several additives can be used in the process such as: non-ionic surfactants, Butyl Benzyl Phthalate (BBP) and Tri-ethyl phosphate (TEP) as well as proper fillers having different functionalities i.e. surface modifiers, coloring dye as well as riser and releasing agents.

Usually synthetic layer appears like grooved surface able to simulate leather texture, conferring some peculiar properties such as elasticity, softness and moisture permeability. Usually, the bare synthetic leather displays poorly attractive properties, in fact limiting their application in leather field. Therefore, fillers of different chemical nature and size (e.g. on nano or microscales) can be dispersed within polyurethane matrix, permitting to attain significant performances to the obtained PU leathers. On this account, graphene has been demonstrated to be a functional filler, able to efficiently improve overall properties of PUs-based composites, such as electrical conductivity, flame retardancy, UV protection and enhanced mechanical and thermal properties [35] making its PU-composite materials potentially suitable for different applications i.e., automotive and aerospace among the others. Graphene intercalation and dispersion within PUs permits to accomplish higher thermal and mechanical performances, therefore, the final leather materials present higher tear resistance, surface adhesiveness and abrasion resistance properties [36]. However, as reviewed by Zhu et al. [35], this topic has not been completely investigated in leather application, as a few results barely demonstrated an improvement of thermal and mechanical properties compared with unreinforced materials, without taking into account the multifunctionality as well as the eco-friendliness in high-performance leather finishing, which also include the use of modified graphene (i.e. graphene oxide or reduced graphene oxide), to obtain efficient antibacterial and self-clean synthetic leather products, potentially applicable as functional PU materials. Apart from graphene and its modified compounds, composite PU leathers have been usually obtained by adding $CaCO_3$ or lignin within the polymeric matrices, however some drawbacks can be here pointed out. In the first case, $CaCO_3$ (inorganic filler) possesses poor compatibility with PU and may trigger off problems such as aggregation and precipitation [32]. Alternatively, lignin improves the moisture adsorption as well as elasticity of the synthetic leathers. However, its steric hindrance firmly limits the access of its hydroxyl groups leading self-aggregation and corresponding to lower performance of the obtained PUs [37]. Additionally, the use of lignin might be associated to odor problems due to Sulphur content. However, desulfurization routes are not always feasible solutions from economical point of view. Interestingly, recycled cow hair powders (natural fibers containing keratin) have been selected to reinforce PU leathers [38]. However, some preliminary alkali sulfide processes are often required to avoid unpleasant smells in the final products. Recently, Liu et al. [32] investigates functionalization of buffering dust (BD) coming from natural proteins (having similar structure of collagen) by means of Amine-Terminated Hyperbranched polymer (A-HP), aiming to obtain reactive filler (denoted as HPBD) in PU. The authors examined the effect of HPBD concentrations on the microporous characteristics of the obtained PUs. In particular, it was found that, as the filler concentration increased, the microporosity of the obtained PU reduced (corresponding to higher number of pores), converting to excellent moisture permeability. However, the authors examined the mechanical properties of the produced composite PUs, by comparing them with those of lignin and $CaCO_3$ based PU-composites.

2.1.2 Utilization of sustainable PU materials for high-performance synthetic leather materials

Synthetic leathers can be classified as fossil derived-materials [39]. Nevertheless, like other plastics, conventional PUs are also made from fossil-based components. On this account, Nicholson et al. reported that the United States (U.S.) annual greenhouse gases emissions from polyurethane production is estimated to be 7.8 million metric tons [40]. Only a very limited literature research has focused on sustainable synthetic leathers, coming from natural resources. Vegan, animal free-based-synthetic leather materials can be obtained from biotechnological processes where fungi, yeasts and bacterial strains can be opportunely selected to obtain fibrous networks, aiming to imitate the fibrous structure similar to animal skin as single materials or as supports for a coating layer. [41] For example, *Acetobacter xylinum* strain empowers to synthesize micro cellulosic network consisting of different macromolecules such as chitin, cellulose, and proteoglycans [40, 41]. On the other hand, fiber-like structures can be also replaced by sustainable fibers coming from pineapple leaves or wood-based fibers [42]. PUs synthetic leathers can be also made partially sustainable by selecting natural filling agents, coming from agricultural wastes such as grains, apple pomace and milled cactus leaves, within the polyurethane matrix. In particular, Meyer et al. compared the technical performances of already-available commercial vegan PU leathers, having different filling agents in PU matrices i.e. polysaccharides/talcum reinforced, cellulose-based material, natural fibers-based materials (based on grains, apple pomace, milled cactus leaves and wood fibers), with (not renewable) synthetic leathers made of petrol-based PUs. The different origin of the examined synthetic leathers effectively affects the final leather structure as well as fiber arrangement and dispersion within PU matrices, inducing a variety of functional features to the leather materials. More specifically, tensile strength, water vapor permeability, water adsorption and thickness of the examined leathers were evaluated [39]. It was found that, the mechanical performances of the investigated materials were lower with respect to those of the conventional (non-biobased) synthetic leathers, especially in terms of tensile strength and tear resistance. However, the authors stated that, some of the examined vegan leathers possess natural fibers having enhanced vapor adsorption, due their high hydrophilicity, which leads to better comfort characteristics, making them suitable to be applicable in clothing sector. Indeed, it should be pointed out that, for clothing application, water permeability is a key factor as the water transport from the material bulk to surface dictates leather comfort. Yet, the authors suggested that further investigation is needed in this field, taking into also account a life cycle assessment of the vegan leathers production processes, certifying their environmental profiles. Apart from this, synthetic PU leathers might be properly designed by replacing oil-based precursors such as polyols and isocyanates. In these sense, as already mentioned in the introduction section, a lot has been done employing sustainable polyol precursors coming from natural sources, such as succinic acid [39, 43] azelaic acid [20, 39] as well as 1,3 butandiol acid [44] as well as sebaic acid or itanoic acid [39], although, still few information is reported concerning their environmental profiles (Life Cycle Assessment, LCA, [45]).

Friebels and Sydow [39] designated a new kind of sustainable PU leather material for automotive interior design, and more specifically in fabrication of dashboard or steering wheels [39]. In details, the authors employed bio-sustainable building blocks i.e. 1, 3 Propanediol (1,3 PDO), obtained through biotechnological process based on conversion of glycerol, and 1,6 Hexadiol (HDO) as polyol blends for polyurethane formation, where different percentages were selected from 0 up to 100 wt.% HDO in the polyol blend. The authors utilized also itanoic acid (at different concentrations) to produce highly cross-linked density polyurethanes and as filling agent for PU leather, wood wastes were also applied. It was shown that, the obtained PUs leathers achieved a bio-sourced proportion of >85 wt.% along with marked mechanical properties and chemical resistance features. In details, the elongation at break increased to 175% with respect to the conventional synthetic leather materials, while the bio-source leather seemed to be resistant to water and common household chemicals (i.e. ethanol). Additionally, for applications where flexible characteristics are not highly required (like in case of dashboard), UV curing of the PU leathers was also assessed, demonstrating their resistance towards sunscreens and UV degradation.

In summary, the development of new kinds of biosourced sustainable polyurethanes and solvent-free processing strategies for leather applications represent one of the most important trends of synthetic leather, while high-performances and multifunctional PUs for leather products is also highly attractive, since such advanced products better meet the requirements from market and consumers [46].

2.2 Finishing surfaces: PU-based coatings/binders from fossil and sustainable sources for leather application, synthesis and properties

During post-tanning operations, a suitable treatment, known as leather finishing process, is a necessary and highly effective strategy to inhibit a variety of negative processes such as microbe proliferation, water absorption, discoloration and at same time, to improve specific performances i.e. abrasion resistance, strength and extensibility, flame retardancy and/or antistatic properties [44]. Coatings and binders for surface finishing leathers can be divided into two macro-categories: natural ones, traditionally protein-based [47], which have some disadvantages in terms of stiffness and a certain susceptibility to water; and synthetic ones i.e. polymeric coatings based on acrylic, butadiene and/or polyurethane, which are usually employed with the aid of solvents [48–50].

In particular, thanks to a peculiar microstructure of soft and hard domains, PU coatings exhibit strong chemical resistance, adhesive force, excellent elasticity, and high strength, etc., making them the ideal polymer coating for leather. Generally, two different types of PUs for surface finishing as coatings/binders, are distinguished for leather application: (1) solvent-based PUs (aromatic or aliphatic), in which polyurethane is dispersed in organic solvent (however these systems have been restricted due to their toxicity and environmental issues) and (2) Waterborne PUs (WPUs), in which the PU is dispersed in aqueous solution (around 80wt.%). This latter, compared to solvent-based ones, are eco-friendlier; however, they present some drawbacks such as poor grafting properties and relatively higher cost. In addition, the presence of water allows to remove any unreacted isocyanate within the system. Nowadays, WPUs have been widely used in leather industry, due to their low VOCs (volatile organic compounds) content, non-flammability and not polluting for the surrounding air, since any solvent, except for water, evaporate once the coating/binder is applied [50]. Likewise, the presence of hydroxyl groups guarantees the stability of the WPU dispersion as reviewed by Salzano de Luna [51].

2.2.1 Finishing surfaces: PU-based coatings/binders from fossil sources

Endowing the coating materials with desired antimicrobial ability can efficiently prevent the microbial proliferation and formation of microbial consortia known as biofilms [52, 53], which have been the object of study during last decades [54, 55]. In this regard, antimicrobial PU coatings can be divided in three main categories: (i) microbicidal coatings that can inactivate microbes on contact and cause microbes' death. (ii) microrepelling coatings that can repel the adhesion of microbes, (iii) dual-functional coatings with microbicidal and microrepelling activities that can not only prevent the adhesion of microbes, but also kill the microbes adhered on the surface [56]. Metal active components have been used as fillers in composite PUs coatings, to impart antimicrobial features according to three distinct mechanisms: (1) formation of Reactive Oxygen Species (ROS), (2) metal releasing and cell membrane disruption and (3) interruption of DNA replication [57].

WPU-coatings filled with metal or other antimicrobial agents (such as chitosan, ammonium quaternary products or photocatalytic) have been broadly investigated in the recent years.

Zhang et al. [57] proposed an antibacterial coating composed by silver nanoparticles and WPU. More specifically, coatings were prepared by facile dispersion of silver nanoparticles, previously obtained by chemical reduction of silver ions. It was found that, the adhesion of the obtained coating materials reach grade 4, while the antibacterial testing showed bacterial reduction of 99.99% for *Escherichia coli* and 87.5% for *Staphylococcus aureus*, respectively. Therefore, filler dispersion is an important factor for the achievement of antimicrobial features of the obtained nanocomposites. In this sense, stabilizers and in situ polymerization of monomers in dispersed nanoparticles solution could be two promising strategies to enhance the dispersion of nanoparticles as reported elsewhere [47, 58, 59].

On this account, Liu et al. prepared Gallic Acid-Stabilized Silver Nanoparticles (GA@AgNPs) composite waterborne coatings, where dispersion occurred in situ. The authors revealed that, the obtained PU coatings exhibited good antimicrobial features (reduction of cell number equal or higher than 2 $\log_{10}$) against *E. coli* and S. *aureus* due to very good filler dispersion (Fig. 4b and c) [59].

Apart from conventional metal antimicrobial agents, photocatalytic antibacterial Carbon (CQD) and MoS_2 quantum dots were also employed to fabricate composite antimicrobial WPU as illustrated in the work of Ma et al. [59]. Specifically, the authors selected different loadings of carbon and MoS_2 quantum dots achieving excellent antibacterial activities of 99.98%, 95.35%, and 99.99% against *E. coli*, *S. aureus*, and *Aspergillus niger*, respectively, which are able to completely inactivate the residual bacterial cells [58]. Compared with the case of coated leather where only a few bacterial cells grew on the surfaces, the uncoated leather showed a remarkable number of *E. coli*, *S. aureus*, and *Aspergillus niger* cells which were able to proliferate and formed biofilms on the surfaces. This outcome can be associated to the significant hydrophobicity of the selected systems, which, might importantly impede bacterial adhesion. By compositing with functional nanoparticles or nanostructures, researchers worldwide have achieved a series of high-performance antibacterial coatings based on WPU materials for leather applications, which greatly benefit the commercial value of advanced materials.

Beside the most widely studied antibacterial coatings, different kinds of functional PU coatings with self-healing, waterproof and abrasion-resistant ability have also attracted attention, which opens new opportunities of high-value leather products in future intelligent trends. Su et al. [60] prepared a fluorinated PU containing short branched fluorocarbon chains, where fluorine-containing chain segments were enriched on the coating surface, resulting in excellent overall performances such as good hydrophobicity, high wear resistance, photodegradation performances, solvent-resistant and antifouling.Since the damage of leather coatings in daily use decreases their aesthetic effect and practicability, Liang and co-partners proposed a self-healing WPU leather coating with disulfide bond (schematization is shown in Fig. 2), which can be fully repaired at 60 °C for 12 h (noticeable from the SEM images reported in Fig. 2). [60]. Liu et al. fabricated a WPU leather coating with desired room temperature self-healing properties (self-healing efficiency of 93.6%) and wear-resistance based on the designed dynamic reversible covalent bonds [59].

Liang and co-partners reported a hydroxyalkyl-terminated polysiloxane modified PU coating. The author stated that, the obtained coating can endure more than 500 abrasions without obvious surface damage and 10 MPa, 150 °C hot-pressing condition without changing the gloss [60].

Leather coating actually consists in polymeric binders, playing a central role in conferring characteristics to the final material as they are components of the aqueous finishing preparation [61]. Besides acrylics and butadiene, PU and more specifically WPUs have gained attention as potential binders/sealants agents in leather finishing process. In particular, PU-based sealants offer several properties such as excellent bonding strength and tight seals [62]. Contrary to conventional PUs. WPUs are more are environmentally friendly, easy to handle and non-toxic

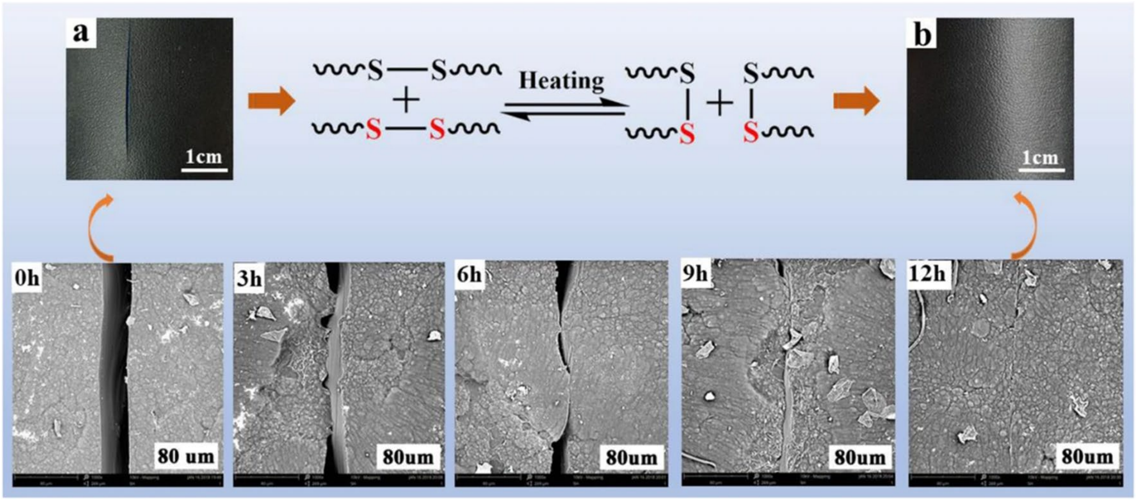


Fig. 2 Self-healing process of leather coating: **a** damaged leather coating; **b** leather coating after be repaired at 60 °C for 12 h. SEM images show the self-healing process in time. Copyright 2020, The Author(s), under the terms of the Creative Commons CC BY license [60]

compared to conventional polyurethanes [63]. Therefore, the main use of binders in the artificial leather industry consists in the formation of a compact film, enabling to bind the selected pigments with leather. Typically, WPU-based binders are divided in three subgroups: cationic, anionic and non-ionic. Among these, cationic WPU (c-WPU) have gained important attention due to their good adhesion leather, which is typically an anionic substrate [64].

Sundar et al. [48] used PUs with Vinyl Pyridine (VPy) units, in order to obtain a block copolymer water dispersion to be used as binder. The diluted pyridine cationomers, whose presence endowed with ionic centers of the hydrophobic PUs backbone, were used as binder in base coat for leather finishing water. The authors found that PU–PVPy dispersion were suitable as base coat by tailoring the PU/PVPy weight ratio. Other than consuming a lesser quantity of pigment, such dispersion provided an increased tensile strength as the increase of PVPy blocks, compared to commercial dispersion, due to the presence of the cationic charge of the polymer backbone [48].

Ryu et al. [65]. examined emulsions of emulsifier-/solvent-free waterborne polyurethane-acrylic hybrids. [65]. The effect of the amount of Glycidyl Methacrylate/Acrylonitrile (GMA/AN) ratio on final characteristics of the hybrid emulsion samples such as the shelf stability, the mean particle size and viscosity was examined. On the other hand, under different conditions, mechanical, dynamic-mechanical, and thermal properties of hybrid film samples, as well as the failure mode and adhesive strength of binder materials were evaluated. As a result, it was found that different ratios of WPU/Acrylic Hybrid (AH) and GMA/AN corresponded to a different emulsion stability as binder materials. In particular, WPU/AC-GMA0/AN20 and WPU/AC-GMA5/AN15 dispersions were able to keep stable after 6 months. However, as main outcome, the shelf stability of WPU/AC emulsions was dependent on the polarity of acrylic monomers and the GMA/AN weight ratio, which, significantly influenced the adhesive strength, mechanical/thermal properties as well as the water resistance.

Apart being used as monomer hybrid emulsions, WPU-based binders have been selected in presence of solid fillers to obtain composite WPUs and in particular, silica nanoparticles (SiO_2). Elsayed and co-workers focused their attention on the possibility to improve the water vapor permeability of the finished leather [66]. To this end, they prepared different dispersions selecting different concentration of silica nanoparticles (1–5 wt. %), introduced via sol–gel process. The water vapor permeability was hence evaluated. As an outcome, the presence of different amount of silica nanoparticles led to different variations in the interspaces of PU leather coating matrix, thus improving the water vapor permeability of the finished material. The authors also revealed that WPU binder opportunely modified with SiO_2 nanoparticles led to an improvement of mechanical properties of finished leather in terms of tensile strength, tear strength and elongation at break, attaining advanced performances as silica nanoparticles concentration increased, until a limit concentration (3%) was reached. Also, the thermal stability of the silica-coated PU leather resulted improved with respect to that of the untreated PUs. On the other hand, at higher concentrations (up to 5%) no important effect of composite PU leather thermal stability was noticed [66].

Beside improving mechanical properties, thermal stability or water permeation, other functional performances and features are requested to WPU binders in artificial leather manufacturing. Kamaruzzaman et al. [67] synthesized WPU-based binder used as shield for seawater corrosion and contamination. Specifically, food-wastes such as Egg-shells (EG) along with TiO_2 nanoparticles, was used to reduce the interaction of simulated seawater on the underlying substrate. A variable amount of EG content, as pigment in WPU, was used. It was found that the content of 20 wt.% of EG was ideal for the established aim, presenting a corrosion inhibition efficiency of about 99%, and a good impedance. More specifically a compact surface was observed, although specimens were placed in a harsh environment for a long period [67]. Such application can also be considered valuable in synthetic leather industry.

Liquid-repellant surfaces are also highly attractive in improving the quality and service life of leather products, which may include a series of excellent performances such as self-cleaning, anti-smudge, antifouling, and low-adhesion characteristics. Therefore, super hydrophobicity has been considered as a crucial characteristic of the WPU binders. In particular, among the four techniques considered in literature to impart hydrophobicity to a surface, namely Layer-by-layer, Nanoparticle-encapsulation, Liquid-impregnation and Nanoparticle/binder, this latter is mainly considered as technique to assess the super hydrophobicity of WPUs [68]. More specifically, this technique combines nanoparticles with high hardness (usually hydrophobic SiO_2 nanoparticles) and a durable polymer as a binder to create a layer having hierarchical conformation as well as re-entrant roughness (Fig. 3).

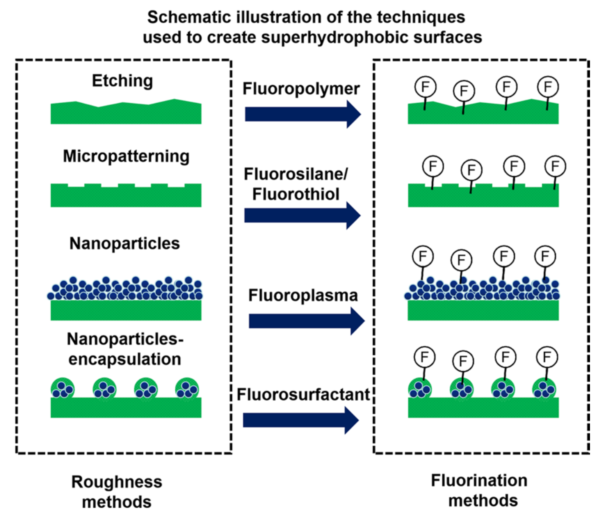


Fig. 3 Schematic illustration of the techniques used to create superhydrophobic surfaces

Another important feature of the WPU-based binders is the electrical conductivity [69]. The introduction of functional nanomaterials such as graphene, as previously reported, is able to endow the leather products with excellent electrical, mechanical properties, and also good thermal conductivity and heat dissipation. Also, in this case, it can be used in leather products design to achieve heat-management and damage detection. Wang and co-corkers developed a Gel Polymer Electrolyte (GPE) by using Potassium Polyacrylate (PAAK) dispersed in WPU [69]. Typically, PAAK exhibits a high ionic conductivity, due to its high segmental motion and a negatively charged carboxyl groups on the side chains, which attributes a cationic conductivity to the final materials. In details, the authors synthetized a ACP/WPU-PAAK-K/ACP layer in presence of an activated carbon paper, revealing a unique binder function, capable to improve the contact between electrode and electrolyte. The authors also studied the same effect in presence of Carbon Nano-Tubes (CNT), observing that, the WPU/PAAK binder significantly enhanced the area specific capacitance of the activated carbon/CNT composites, due to the formation of ionic tunnels/networks [70]. If applied to artificial leather manufacturing, this can be extremely helpful to create conductive clothes.

2.2.2 Finishing surfaces: PU-based coatings/binders from sustainable sources

The thrust toward sustainable PU coatings for leather application is continuing to attract researchers around world, to exploit new kinds of renewable resources and to develop more advanced multifunction design. However, the main challenges are how to select, modify and process these bio-sourced materials to endow the PUs with desired multifunctions. In this sense, also solvent-based PU coatings obtained from sustainable precursors have been indicated as potential candidates in greener leather industry. As also reported in the introduction section, such materials can be obtained by employing either sustainable polyols (reacting with conventional isocyanates) or by considering free isocyanate Polyurethanes (NIPUs).

Mahajan and co-partner [71] indicated a bio-sourced polyol from eugenol and linseed oil based-self-healing polyurethane coating composite by cardanol-based microcapsules having self-healing properties. In details, the authors designed a fully sustainable material, formulated by using a resin healing-agents and non-edible and abundant natural sources. In particular, the authors investigated the effect of different percentages of microcapsules in PU formulation. The selected formulations were applied on metal surface to validate their anticorrosion effectiveness. It was found that, the promising self-healing and anticorrosion characteristics were attained especially at higher microcapsules loadings [71].

In other recent work, vegetable oils such as cardanol based, have been widely investigated as they can impart multifunctional properties to the obtained PU coatings [72–74]. Somisetti et al. formulated a bio-based polyol from undecylenic acid, a byproduct of cardanol through three-steps-procedure: methylation, thiol-ene addition, and amidation. The resulting polyol, containing sulphur and nitrogen groups, was employed as polyol to formulate PU coatings [73]. Interestingly, it was found that, the obtained coatings presented excellent mechanical properties as well as good anticorrosion characteristics (corrosion rates in the range of 10^{-7} mm/year) due to the synergistic effect of Sulphur and nitrogen and conclusively, good antimicrobial performances against Gram negative and Gram-positive bacterial strains. In this latter case, the good antimicrobial features might be ascribed to some effect of nitrogen, which can be converted in quaternary ammonium compounds, acting as a powerful biocide. Apart from conventional vegetable or biomass-derived polyols, terpene-based polyols (from turpentine), representing a wide class of biosynthetic building blocks [20], have been employed as they can crosslink with polyisocyanates, by producing PU coatings having excellent impact strength, flexibility and water resistance. In addition, residues of *Eucalyptus* tar, a complex mixture containing mainly phenols i.e. guaiacyl and syringyl derivatives, being an abundant source of –OH groups, have been also indicated as possible building blocks for PU precursors. More specifically, both heavy oil and biopitch were obtained by distillation of *Eucalyptus* tar and along with castor oil used to produce renewable polyol [20, 75], to be selected for more sustainable coatings.

In the recent years a series of bio-sourced materials have been introduced into the design of WPU coatings such as castor oil, succinic, tannic acid, lignin and isosorbide, CSNL or linseed oils, to make the obtained materials more sustainable [20]. On this account, Ahmadi and partner prepared rGO nanoparticles-composite PU coatings, where the PU precursors were boronate-hyperbranched sunflower oil-based [76]. In details, the authors proposed a hybrid coating by dispersing rGO (previously functionalized through an aliphatic diol, FRGO, to enhance GO sheets in urethane reaction). The obtained coatings exhibited an enhanced corrosion protection and a desired antimicrobial surface activity with permanent contact killing properties as well as thermal stability and mechanical properties. Another approach to attain advanced sustainable PU coatings consists in introducing bio-sourced molecules as functional antibacterial contents. Zafar et al. [77] and Bramhecha and Sheikh proposed [78] bio-sourced materials such citric acid as critical structure to fabricate sustainable antibacterial WPU coatings showing inherent antibacterial properties (84–99% against *E. coli* bacteria). Huang et al. reported an effective and long-term durable antibacterial surface based on bio-based active-killing essential carvacrol oil, no fouling carboxybetaine zwitterionic moieties and highly bio-based polyurethane (possessed a bio-carbon content of over 65%) [78]. By the combination of "*kill and defend*" synergistic antibacterial function (extended release of the bounded carvacrol and prevent bacterial attachment), 98.9 and 98.7% of *E. coli* and *S. aureus* were eliminated from the coating surfaces even after 5 cycles of test, demonstrating an outstanding long-term antibacterial ability [75]. Inspired by the nature, utilization of bio-sourced materials provided insights for future development of greener antibacterial WPU coatings for leather applications. On the other hand, other sustainable components such as greener materials including zein, sodium alginate, artemisia argyi essence were also employed in waterborne PU formulations as reported by [79, 80], to fabricate microcapsules for controlled releasing coating, providing a feasible way to prepare functional and sustainable with self-healing coatings. Beside antimicrobial and self-healing properties, advanced functional properties of PU coatings were elucidated. In this regard, Xiang et al. [81] reported a more sustainable and invisible anti-counterfeiting ink, composed of WPU and water-dispersible lanthanide-doped Up-Conversion Nanoparticles (UCNPs) (Fig. 4). Coatings were easily prepared by dispersion UCNPs nanoparticles in water-based polyurethane. As a main outcome, the so-obtained coatings exhibited high photostability, non-toxicity as well as low VOC emissions and strong adhesion strength. More specifically, the obtained patterns are invisible under normal light conditions. Upon irradiation at 808 nm, the invisible patterns could be observed by naked eyes due to the visible light emitted by 808 nm excited UCNPs (as shown in Fig. 5), which opens a new pathway to design stable anti-counterfeiting function of leather materials [81].

Recent findings also reported the use of sustainable NPIUs coatings [23]. Choong et al. developed three different types of bio-/CO_2-derived non isocyanate polyurethane coatings with recyclable and healable ability under heat (thermo-healing), moisture (moisture-healing), and dry conditions at room temperature (self-healing), which mainly achieved by the presence of bio-sourced hydroxyl functionalities structure [82]. Liu et al. reported different NPIUs through the reactions of cyclic carbonate-functionalized polysiloxanes with diamines (Fig. 5) [83]. Polysiloxanes imparts several characteristics such as thermal and oxidative stability as well as flexibility and excellent hydrophobicity [63] to the obtained NPIU materials.

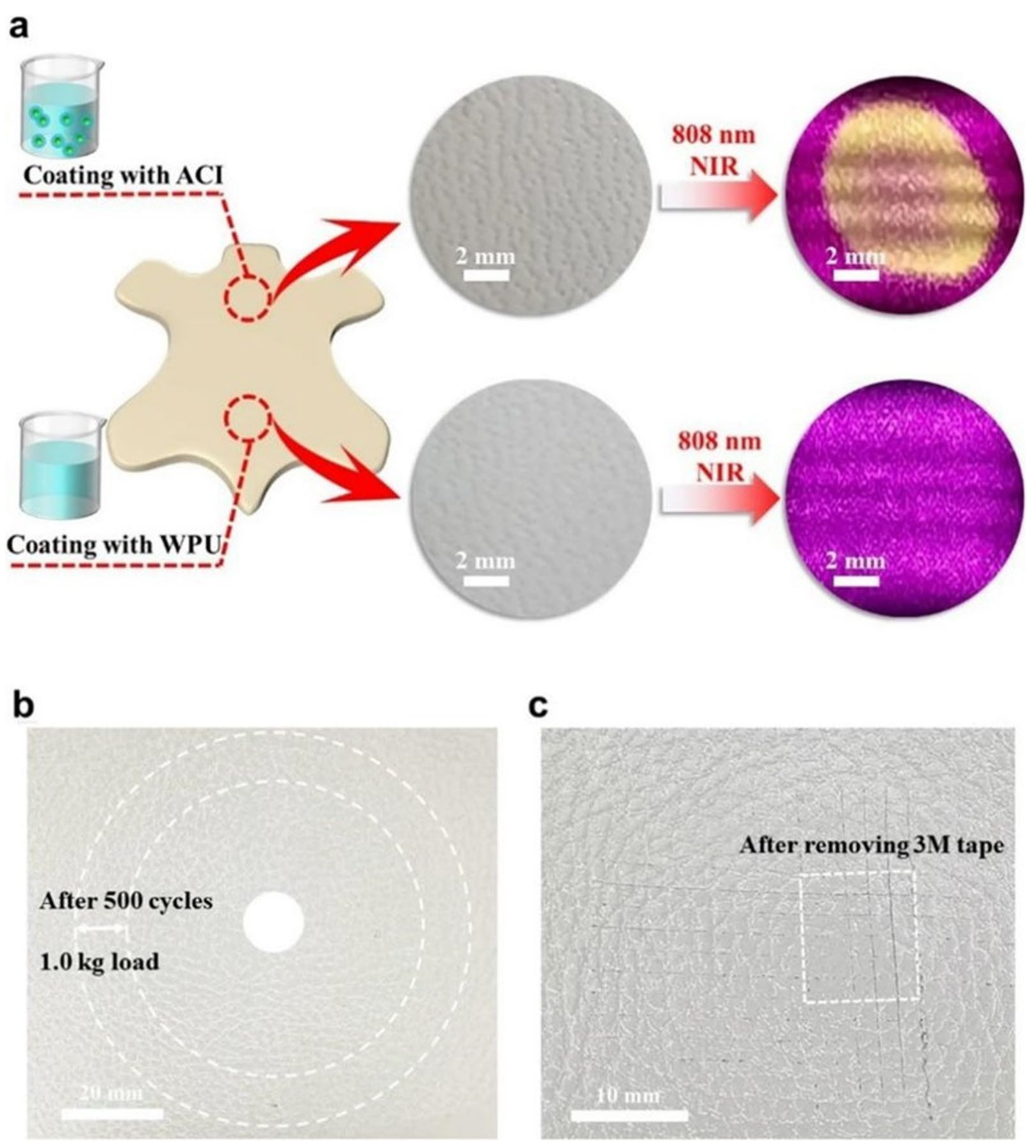


Fig. 4 **a** Naked eye observations of patterns under 808 nm NIR laser excitation of invisible anti-counterfeiting leather products. The digital images show ACLs after the abrasion test (**b**) and adhesive peel strength test (**c**) on the leather products. Scale bars = 20 mm (**a**) and 10 mm (**b**). Copyright 2021, The Author(s), under the terms of the Creative Commons CC BY license [81]

Masouremeh et al. [63] investigated NPIUs based on lignin and tannin components. In details, tannin extracted from Sumac leaves (*Rhus coriaria L.)* were employed as building blocks to prepare NPIUs, through a reaction with dimethyl carbonates and subsequently by reaction with diamines. The obtained NPIUs showed good thermal stability (mainly associated to the phenolic residues of tannin) and excellent mechanical properties [63]. Conclusively, several efforts have been made to fabricate more sustainable PU coatings either employing greener precursors such as polyols or by fabricating non-isocyanate NPIUs. In this latter case, only a few promising results have been reported and further investigations will need on this research line.

Regarding the sustainable binders in synthetic leather industry, mainly WPU based, few of those are bio-based polyurethane, because the utilization of bio-based materials in PU composites have not been adequately studied owing to the limited selection. How to develop new kind of high-performance bio-sourced materials and advanced modifying approaches to achieve excellent overall performances is the core issue. Saalah et al. [84] synthesized a renewable polyol based on jatropha oil (a non-edible renewable oil/gum, utilized in adhesives, with

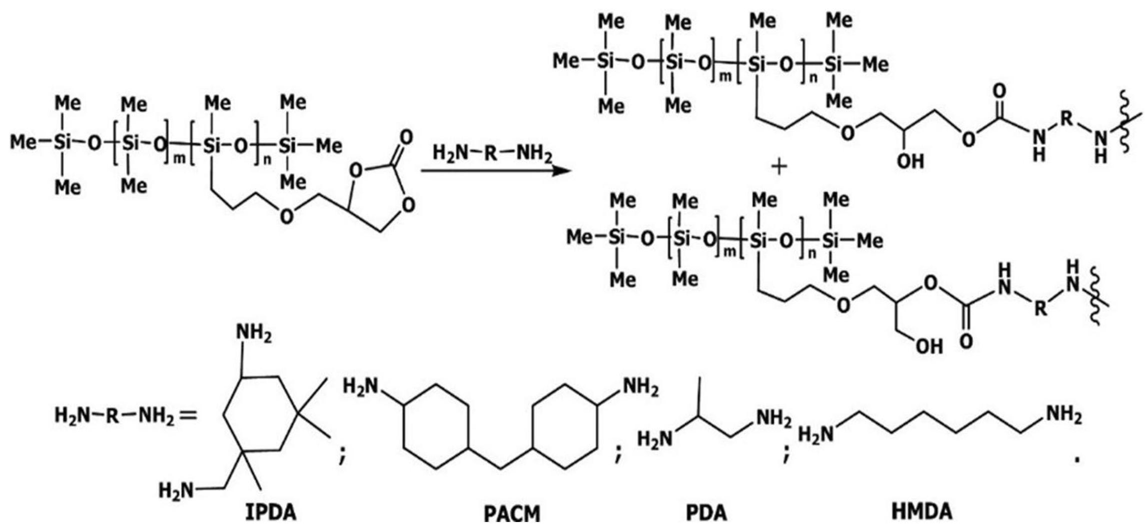


Fig. 5 Synthetic routes of the NIPU coatings.based on cyclic Polysiloxanes [63]. Copyright 2017, The Author(s), under the terms of the Creative Commons CC BY license

good adhesion and mechanical properties) by means of polymerization of the oil with isophorone diisocyanate and dimethylol propionic acid. The obtained product is widely used as a binder for wood and decorative coatings, as in artificial leather. In conclusion, also for this case, the development of new kinds of bio-sourced sustainable polyurethanes for leather binder applications is highly attractive, either due to recent major environmental issue or due to the increasing research topics related to the development of sustainable materials.

3 Conclusions

Since leather industry has faced many environmental problems, the necessity to find greener solutions represents a crucial aspect and the development of more sustainable materials and production technologies become one of the most important trends in the whole area around the world. In this minireview, recent advances concerning the use of polyurethanes (PUs)-based leathers, especially obtained from more sustainable solutions, were discussed. PUs (and more specifically thermoplastic PUs) are one of the most versatile classes of polymers owing to their adjustable chemical structures, which can fit specific requirements by the appropriate selection of precursors and fillers. According to the type and amount of precursors and additives, PUs, mainly in the form of composite PU leathers can attain several characteristics such as flexibility, puncturing, tensile strength, resistance to abrasion, permeability to water and air, thermal stability as well as chemical resistance and hydrophobicity, making them suitable for applications such as furniture, bags, aircraft, garments and automotive. Specifically, three macro areas of leather industry were examined i.e. PU synthetic leather PU leather coatings and PU-sealants/adhesives. In each section, a detailed description of the raw materials, process technologies and the resultant performances of the PUs-based materials were here analyzed. Additionally, the current status of the use of sustainable PU materials was hence presented and resumed as it follows.

Greener PUs can be obtained (i) by adding natural components/fillers to synthetic PU leathers (mainly water-borne based); (ii) selecting solvent-based PUs, where the two precursors are obtained from natural sources. In particular, precursors obtained from vegetable oils (such as linseed oil, castor oil or terpene-based oils) or biomass-derived building blocks (among the other, cardanol-based oil), can be selected along with conventional isocyanate components to properly design PU leather materials. (iii) By taking into account new “isocyanate free” routes, leading to a new class of PU materials known as NPIUs.

Conclusively, a number of reported works have developed new kinds of sustainable sourced PUs composites, solvent-free green processing technologies and advanced multiple functions. Such advances in PUs leather application has been demonstrated efficient in high-performance synthetic leather products, while the utilization of more sustainable raw materials opens up new opportunities in green technology of leather processing. Corresponding researches are expected to significantly improve the overall properties of leather materials towards future green and intelligent applications.

4 Future perspectives

How to provide sustainable solutions in leather industry by reducing pollution is highly required. Exploring the applications of advanced sustainable PUs in leather products signifies one of the most effective answers, that drives towards sustainable approaches. To achieve the important goals, future perspectives in this field might go to the following directions:

- Development of new kinds of bio-sourced sustainable materials, able to partially replace the conventional PU precursors, as well as of non-isocyanate polyurethanes and/or solvent-free and low pollution processing strategies.
- The selection of PUs leather materials, based on sustainable strategies, apart from being highly attractive solutions in greener industry, must be in compliance with the requirements from market and consumers.

Abbreviations

PUs	Polyurethanes
TPU	Thermoplastic polyurethane
IUPAC	International Union of Pure and Applied Chemistry
NPIU	Non isocyanate polyurethane
CNSL	Cashew nut shell
SEM	Scanning electron microscopy
3D	Three-dimensional
$CaCO_3$	Calcium carbonate
BBP	Butyl Benzyl Phthalate
TEP	Tri-ethyl phosphate
WPU	Water borne polyurethane
GO	Graphene oxide
BD	Buffering dust
HPBD	Hyperbranched polymer buffering dust
UV	Ultraviolet
LCA	Life cycle assessment
PDO	Propanediol
HDO	Hexadiol
VOCs	Volatile organic compounds
ROS	Reactive Oxygen Species
DNA	Deoxyribonucleic acid
GA@AgNPs	Gallic acid-functionalized silver nanoparticles
E.coli	*Escherichia coli*
S. aureus	*Staphylococcus aureus*
CQD	Carbon quantum dots
MoS_2	Molybdenum disulfide
rGO	Reduced graphene oxide
FRGO	Functionalized reduced graphene oxide
UCNPs	Up-conversion nanoparticles
CO_2	Carbon oxide
VPy	Vinyl Pyridine
GMA/AN	Glycidyl methacrylate/acrylonitrile
SiO_2NP	Silica nanoparticles
EG	Eggshells
TiO_2	Titanium oxide
GPE	Gel polymer electrolyte
PAKK	Potassium polyacrylate
CNT	Carbon nano tubes

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Author details

[1]Institute for Polymers, Composites and Biomaterials (IPCB-CNR), Piazzale Enrico Fermi 1, 80055 Portici (Naples), Italy.

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