Since January 2020 Elsevier has created a COVID-19 resource centre with free information in English and Mandarin on the novel coronavirus COVID-19. The COVID-19 resource centre is hosted on Elsevier Connect, the company's public news and information website.

Elsevier hereby grants permission to make all its COVID-19-related research that is available on the COVID-19 resource centre - including this research content - immediately available in PubMed Central and other publicly funded repositories, such as the WHO COVID database with rights for unrestricted research re-use and analyses in any form or by any means with acknowledgement of the original source. These permissions are granted for free by Elsevier for as long as the COVID-19 resource centre remains active.
Research advances in the fabrication of biosafety and functional leather: A way-forward for effective management of COVID-19 outbreak

Ramesh Renganath Rao a, b, Murali Sathish c, Jonnalagadda Raghava Rao d, *

a Leather Process Technology Department, CSIR-Central Leather Research Institute, Chennai, 600020, Tamil Nadu, India
b Department of Leather Technology (Housed at CSIR-Central Leather Research Institute), Alagappa College of Technology, Anna University, Chennai, 600020, Tamil Nadu, India
c Regional Centre for Extension and Development, CSIR-Central Leather Research Institute, Kolkata, 700046, West Bengal, India
d Inorganic and Physical Chemistry Laboratory, CSIR-Central Leather Research Institute, Chennai, 600020, Tamil Nadu, India

ARTICLE INFO
Handling editor: Prof. Jiri Jaromir Klemes

Keywords:
COVID-19
Bio-safety
Leather
Functional materials
Antimicrobial leather

ABSTRACT
With the recent events following the pandemic COVID-19, global awareness about the use of biosafety materials has been in raise. Leather industry being a major commodity-driven sector, its role in addressing the issues concerning the safe use of leather products has become inevitable for the sustainability of the industry. A significant number of researches have been conducted to fabricate bio-safe leather by incorporating different types of antimicrobial agents during leather manufacturing. Besides, the increasing diversity in the development of synthetic materials and the impact of COVID-19 outbreak on automotive industry may create more demand from customers for incorporating different functionalities in leather without losing its inherent properties. Some of the key functionalities discussed include resistance to microbial growth, self-cleaning through superhydrophobicity and photocatalysis, thermal regulation, flame retardance and scented leather. This review focusses on the fabrication of such advanced functional leather materials over the past decade with special emphasis on antimicrobial leather. Some of the key factors elaborated in the review include the state of art approaches for the preparation of functional materials, mode of incorporation of the same into the leather matrix, the mechanism behind with a perspective on the challenges involved in fabrication for real-world applications. A major outcome of this review is that even though several kinds of cutting edge researches are happening in the field of leather manufacturing, most of them were not validated for its practical applicability and sustainability of the proposed solution. This could be majorly attributed to the cost involved in fabrication of such materials, which forms a crucial factor when it comes to a mass production industry such as leather. Also, the researchers should concentrate on the toxicity of the fabricated materials which can impede the process of adopting such emerging and need of the hour technologies in the near future. Knowledge obtained from this review on fabrication of biosafety leather against bacteria, mold and fungi would help further to integrate the antiviral property into the same which is a global need. Also, fabrication of functionalized leather would open new avenues for leather manufactures to venture into the development of advanced leather products such as flexible electronics, radiation shielding and fire fighting garments etc.

1. Introduction

COVID-19, a viral infection has created a topsy-turvy effect on global research in the field of material science research and manufacturing sector (Huang et al., 2020). Nicola et al., highlighted the socio-economic implications that has been caused by this pandemic on the different aspects of the world economy (Nicola et al., 2020). Moreover, the measures taken to prevent the spread of novel corona virus has also brought an immense social and economic impact on various industrial sectors including textile, leather and footwear products. Leather and leather products have been a sought after material despite the advent of synthetic materials owing to its versatile properties that cannot be matched by the latter (Kral et al., 2014). Though animal skins were first used by people as a means to protect their body, it has transformed immensely owing to the technological and scientific advancements, making it change from an essential commodity into a niche market
Leather industry plays a prominent role in the world’s economy, with an estimated global trade value of approximately USD 100 billion per year (UNIDO, 2010). To represent the effect of COVID-19 on leather business, the scenario of Indian leather export is explained as a model system considering the fact that India is the second major producer of leather. India exports leather products valued at 5.5 to 6 billion USD annually but the impact of COVID-19 has caused a huge loss in export value of up to 1.5 billion USD. Major leather production units situated in Tamil Nadu and Kanpur has been shut due to the pandemic causing and with the continued lockdown it is predicted to turn into a major financial loss and an economic crisis. Apart from this, since leather industry employs majority of its manpower based on skilled workforce, it represents a major bread earner for the people from weaker economic and financial background. Similar situation is also observed in other major leather manufacturing countries across the world. To add to this, global awareness about the use of biosafety materials has been in raise creating a demand to fabricate bio-safe materials for day-to-day needs such as leather products (Yu et al., 2020).

Leather industry being a major commodity-driven sector, its role in addressing the issues concerning the safe use of leather products has become inevitable. To combat this situation, leather manufacturers are on the look out for various options aiming to fabricating antimicrobial leather.

Leather, a natural biopolymer is manufactured by stabilization of skin protein against the attack of microbes, acid, alkali and heat using chemical cross-linkers called as tanning agents. The leather making process is compartmentalized into four stages viz. pre-tanning, tanning, post-tanning and finishing (Thanikaivelan et al., 2005). Even though the first two stages of processing remain the same for manufacturing any kind of leather, the post-tanning process varies according to the intended use of the final material (Heidemann, 1993). Post-tanning is a prime process by which different functional properties are imparted to the tanned leather by employing polymeric fillers, dyes and lubricating agents (Heidemann, 2000). Finishing, the final step is done to protect the leather from its surrounding environment by forming a thin film on its surface and also to improve the aesthetic appeal using polymeric binders, pigments and various feel modifiers (Covington and Wise, 2020). Though the tanning process provides antibacterial resistance to the fibrous matrix, the presence of various leather making auxiliaries makes it vulnerable to microbial attack (Barigoorn, 1950). And its impact would be much pronounced while leather products are stored for a longer duration. Although considerable attempts were made to develop antimicrobial leather, revisiting of such technological interventions would help to design a process that completely ensures the bio-safety of leather products. Besides the leather’s superior characteristics like breathability and unmatched strength properties compared to that of synthetic material, nowadays consumers are demanding for special and unique properties on their products without compromising the basic nature of leather. In addition, it is forecasted that the automotive industry is set to boom again within a few years owing to the awareness created by the COVID-19 pandemic on social distancing making people shift from public to more of personal transportation. Thus it is expected that vehicles are soon to be considered as next living spaces leading to an increase in hygiene standards alongside a supplemented interactive environment. Since the leather industry caters to a major part of automotive upholsteries, it is expected to meet such standards by incorporating the novel functional materials and cater to the needs of the consumers.

In this aspect, several attempts were made to incorporate functional properties such as self-cleaning, thermoregulation, flame retardancy, fragrance release etc., as shown in Fig. 1 to leather through material science interventions for fabricating leather with more functional properties and also to extend its usage in various fields. Such developments may also lead to the use of leather for non-conventional applications viz., flexible electronic, radiation shielding etc., thus opening new avenues for the leather manufacturers to explore. In leather manufacturing, functional materials (materials that exhibit specific native properties and functions of their own (Wang and Kang, 1998) are incorporated predominantly during post-tanning and finishing process. The major challenge that is to be taken care while fabricating such functional materials is that they should act constructively with the other natural properties of leather.

Thus, there is a need for the development of a comprehensive review of functional materials based on leather matrix that can serve as a database for the researchers and guide them in the fabrication of newer advanced materials as per the needs of the industry and its customers. Accordingly, this review primarily discusses the noteworthy progress made in the field of development of different kinds of functional materials using the leather matrix as a platform, their method of incorporation, challenges faced in making such materials and its applications in the real world.

### 2. Methods

The review process was started with the identification of essential properties that may be imposed on the leather based materials owing to the COVID-19 pandemic. Also, the effect of same on the automotive industry which utilizes the leather products in its production was also considered for short listing of the functional properties that may become the need of the hour. Accordingly, the research articles giving solutions to such problems were identified from databases such as Google scholar, Web of Science and Science Direct using the keyword such as ‘Antimicrobial leather’, ‘functional leather’, ‘self cleaning leather’, ‘flame retardants’, ‘thermo regulation in leather’. The identified literatures were then grouped as per the property that is imparted to the leather by manually going through the data provided in the abstract initially. Further, it was categorized and tabulated based on the following parameters.

- Strategy adopted for arriving at the solutions for the identified problems.
- Methods for the synthesis of the functional material and the mode of integration of the same with leather chemicals. ie through physical blending or chemical functionalization.
- What is the mode of incorporation of the functional materials into leather matrix? ie either through post tanning or through finishing?
3. Innovative methods employed for development of functional leather materials

3.1. Antimicrobial leather

Even though, the process of tanning makes the leather matrix resistant towards the action of bacteria, the auxiliaries such as polyurethane, natural beeswax and casein used in finishing process are susceptible to microbial attack (Howard, 2011). To avoid this, generally the auxiliaries used in leather finishing process are formulated with biocides such as chlorinated phenols, dimethyl furmarate, OIT (2-n-octylthiazolidin-3-one), TCMTB (2-thiocyanothiothiylethio) benzothiazole), OPP (ortho-phenylphenol), PCMC (para-chlor-meta-cresol) compounds. However, the adverse effects due to the sustained release of these biocides include eye and skin irritation upon frequent exposure and physical injuries in the case of inhalation or occasional ingestion (Giménez-Arnau et al., 2009). Additionally, the migration of these toxic substances and its contact with human foot is further enhanced by the porous nature of the leather matrix. The porous matrix also absorbs more amount of sweat, oil/grease which get accumulated resulting in colonization of microbes and may cause adverse effects for people with health conditions such as diabetes (Ara et al., 2006; Jennings et al., 1999). Alternatively, antiperspirants and antifungal formulations are sprayed on the foot to control the release of sweat (Aksoy and Kaplan, 2013), however it is not advisable for regular usage. Even though, the finish film contains antimicrobial agent, storage of leather and leather products for a long time in humid conditions such as shopping mall are prone to microbial attack. This scenario was observed during COVID-19 lockdown period in a shopping mall located at Malaysia and the same is shown in Fig. 2.

With the recent outbreak of COVID-19, the customers may demand for the product used in day-to-day activities with an antimicrobial surface. As, the leather products occupies a prominent place in human life, it is important to develop leather fabric with inherent antimicrobial activity capable of providing hygiene and comfort to its user. The knowledge obtained from textile industry on development of antimicrobial fabric was explored as a way towards the development of antimicrobial leather (Ballottin et al., 2017; Silva et al., 2018). This section summarizes the various notable attempts that have been taken to manufacture antimicrobial leather. In leather manufacturing, incorporation of such functionality can be achieved through both the post tanning process and finishing process as shown in the Fig. 3.

3.1.1. Antimicrobial leather based on antibiotics incorporation

Hong and Sun (2010) coated a polyurethane (PU) formulation containing switchable photoactive antimicrobial agents such as benzophenone (BP) and rose Bengal (RB) on leather surface at a concentration ranging from 0 to 1.43% (w/w). Subsequently, S. aureus and E. coli cultures were inoculated. The activity of these compounds on microbes was studied by irradiating with UVA (~365 nm), fluorescent (400 lm) and daylight. Similar experiment was setup without use of antimicrobial agents as control. Both the photactive agents at 1.43% were capable of killing 99.99% of the microbes after an hour of irradiation with UVA/fluorescent light or 40 days of daylight irradiation. The mechanism of antimicrobial activity of BP was explained by the formation of BP radicals after irradiation with UVA light (Hong and Sun, 2007a, 2007b, 2008, 2007b). Additionally, BP being a known photosensitizer, it is capable of abstracting protons from carbamate group of polyurethane to form BP Ketyl (BPK) radicals. The formed BPK radicals attack microbes by inducing unwanted side reactions in biological processes following the classic free radical syndrome. Additionally, BPK radicals gets oxidized back to BP on exposure to oxygen leading to formation of hydrogen peroxides as by product, which further enhances the antimicrobial activity. In case of RB PU coating, RB generates singlet oxygen (reactive oxygen species) upon irradiation with UVA light that are capable of killing the microbes as shown in Fig. 4 (Chang et al., 2008; Killig et al., 2004). These coatings retained their antimicrobial activity even after 500 abrasion cycles. But, due to reddish hue of rose Bengal, its application could be restricted as leather being a product for fashion industry color plays a big role here.

Alternatively, in order to prevent the migration of biocides and its contact with human skin, an attempt was made to covalently attach the biocides with film forming material such as PU. The release of biocides from PU backbone is triggered, only when it comes into contact with certain kind of enzymes secreted by microbes. In this view, linear isocyanate terminated pre-polymer was synthesized using polycaprolactone and isophorone diisocyanate by emulsion polymerization technique (Xu et al., 2013). Subsequently, free isocyanate group of pre-polymer was covalently linked with biocide (sulfanilamide (SA)) and named PU/SA. It was noted that the microbe degrading the leather was found to secrete large amount of urease enzyme making it an ideal choice to test as key to trigger the release of conjugated biocide from the polymer (Orlita, 2004). The release of biocide (SA) was triggered by incubating the steel discs coated with PU/SA in a solution of urease enzyme and it was identified that there was sustained release of SA till 96 h after which there was degradation in PU backbone by urease enzyme which was confirmed with HPLC-MS/MS. The release kinetics of SA fitted to an empirical model proposed by H.B. Hopfenberg showed a release kinetic constant of 0.479% μm/h with a high coefficient of determination (R² = 0.91) (Hopfenberg, 1976). This proved that the release of SA was controlled by urease enzyme and could be stopped in its absence making it a urease-modulated on-off switch system (Fig. 5).

The bacteriostatic efficiency of the released SA was checked against range of microorganisms and found to have a maximum of 60% efficiency in inhibiting Pseudomonas species. The cytotoxicity studies showed that the PU/SA coating did not interfere with cell proliferation making this antimicrobial leather coating to be skin-friendly to the wearers.

Similarly, Chang et al., prepared a water soluble acryloylated ciprofloxacin and acrylic acid co-polymer for antimicrobial coating along with waterborne polyurethane (WP) emulsion (Chang et al., 2017). Briefly, ciprofloxacin was acryloylated using acryloyl chloride at

Fig. 2. Microbial growth observed on leather products at a shopping mall located in Malaysia during COVID-19 lockdown period.
7-piperazinyl secondary amine to introduce polymerisable vinyl groups in the backbone. Acryloylated ciprofloxacin exerted no influence on the 3-carboxyl and 4-keto group in ciprofloxacin, both essential for hydrogen-bonding with microbial DNA to elicit antimicrobial activity (Bryskier, 1993). Additionally, it also did not exert any influence upon the bicyclic heteroaromatic quinolone pharmacophore and π-π ring stacking, permitting flexibility in adjusting position of ciprofloxacin for optimal hydrogen-bonding configuration. Thus, the resulting acryloylated ciprofloxacin (ACPF) remained microbiologically active (Chang et al., 2015; Xue et al., 2012). Also, the washing efficiency showed sustained antimicrobial efficiency even after 10 cycles.

3.1.2. Antimicrobial leather based on metal oxide incorporation

Chen et al., impregnated nano TiO$_2$ (using tetrabutyl titanate modified with acetylacetone) into leather along with polyurethane (PU) by wet phase inversion method (Chen et al., 2010). Briefly, PU solution containing the titanium precursor was casted on a pre-wetted leather sample and soaked in an aqueous bath wherein PU solution coagulates along with hydrolyzed and condensed titanium nanoparticles to form a uniform coating on leather (PUT). SEM images showed TiO$_2$ NPs in size of 60–120 nm dispersed well in PU coating. The antibacterial efficiency of PUT films increased up to ~96% with 0.75% TiO$_2$. Highest antifungal activity was also observed in same concentration of TiO$_2$ with no fungal growth even after 28 days. The antimicrobial activity was attributed to
the photocatalytic activity of TiO$_2$. When exposed to UV light ($\lambda < 385$ nm), TiO$_2$ generates electron-hole pairs following TiO$_2$ + hv $\rightarrow$ TiO$_2$ ($h^+ + e^-$). The electrons produced can reduce oxygen to superoxide anions, while holes oxidize water to produce hydroxyl radicals. These reactive species can then effectively kill a wide spectrum of organisms such as bacteria and fungi through redox reaction (Robertson et al., 2005). Also, toxicity studies using normal human dermal fibroblasts showed that PUT films were completely non-toxic.

Similarly, Liu et al., 2014 prepared zinc oxide nanocomposite based on methyl methacrylate and butyl acrylate by emulsion polymerization technique (Liu et al., 2014). Initially, to improve the dispersion of ZnO in aqueous medium, an anionic polymer (PA30) was used prior to polymerization process. The size of the PA30 modified ZnO was about 329.8 nm with PDI of 0.119. The prepared nanocomposite is thermally stable (300 °C) and crystalline in nature. The prepared nanocomposite was spray coated on leather and checked for fungal growth using Aspergillus flavus as model microbe. The antimicrobial activity of the ZnO nanocomposite is related to its ability to generate reactive oxygen species and hydrogen peroxide ($H_2O_2$) upon irradiation (Sivakumar et al., 2010; Yi et al., 2019). The properties of the coating were on par with bare polyacrylate based coating and also inhibited the fungal growth (Fig. 6).

Further, Bao et al., studied how the effect of nanoparticle morphology plays an important role in affecting the properties of composite film (Bao et al., 2017). Different ZnO structures viz., rod, hollow fusiform and hollow columnar were synthesized by direct precipitation method using ammonia and combination of solvents. Even though there was no significant impact of morphology on antimicrobial activity, it still influenced water uptake and water vapor permeability of the film. The increase in water vapor permeability of ZnO polyacrylate films was attributed to the increase of free volume in the composite film, inherent cavities of nanoparticles and generation of interfacial pores between the ZnO and the polymeric chain which can let water vapor molecules to move freely in the film (Fama et al., 2012). But in contrary, water resistance of the ZnO (rod and columnar)/polymeric films increased due to the neutralization of negative charge of carboxyl group on the polymer and positive charge on the ZnO by coulombic forces of attraction. However, the water resistance of fusiform ZnO decreased due to the presence of more free hydroxyl group on ZnO microstructure. Additionally, coulombic forces aided better dispersion of the ZnO in polymer which further enhanced the mechanical properties of the film. As discussed earlier, ZnO exhibited good antimicrobial effect as shown in Fig. 7.

3.1.3. Antimicrobial leather based on chitosan incorporation

Chitosan (CS) is a linear polysaccharide with partly acetylated (1-4)-2-amino-2-deoxy-β-D-glucan and is used in a wide range of biomedical applications due to its non-toxicity, film forming ability and antimicrobial activity (Rinaudo, 2006; Ferrero et al., 2015). Fernandes et al., fabricated chitosan based coatings on leather by spraying, calendaring and drumming and also studied its efficacy on antimicrobial activity (Fernandes et al., 2013). Since, the chitosan is soluble in acidic condition, in drum based coating it is offered along with formic acid during fixing of post-tanning chemicals. It was hypothesized that chitosan ionically interacts with the collagen and other post-tanning auxiliaries (Torres-Giner et al., 2008). Initial pilot scale studies showed drumming based method of impregnation provided better antimicrobial activity than other methods of application. It was found that 1% chitosan in formic acid with an impregnation time of 2 h showed the most optimum antimicrobial action. Same kind of studies were also done by incorporating chitosan formate (MIC 0.25–0.50 mg/mL) into leather as re-tanning agent and showed similar resistance to fungal growth (Ocak et al., 2015).

In order to improve the solubility of chitosan in wide spectrum of pH which is necessary for leather manufacturing, Luo et al., grafted polyethylene glycol (PEG-1000) on to chitosan (CS-8000) at different degree (Substitution Degree (SD%): number of PEG groups per 100 amino groups of chitosan determined by TNBS method) such as 4% and 8% (Fig. 8). Proton-NMR spectrum with peaks at chemical shift of 3.1 and 3.6 ppm confirmed the attachment of the PEG to chitosan substrate (Luo et al., 2012). But in contrary, water resistance of the ZnO (rod and columnar)/polymeric films increased due to the neutralization of negative charge of carboxyl group on the polymer and positive charge on the ZnO by coulombic forces of attraction. However, the water resistance of fusiform ZnO decreased due to the presence of more free hydroxyl group on ZnO microstructure. Additionally, coulombic forces aided better dispersion of the ZnO in polymer which further enhanced the mechanical properties of the film. As discussed earlier, ZnO exhibited good antimicrobial effect as shown in Fig. 7.

3.1.3. Antimicrobial leather based on chitosan incorporation

Chitosan (CS) is a linear polysaccharide with partly acetylated (1-4)-2-amino-2-deoxy-β-D-glucan and is used in a wide range of biomedical applications due to its non-toxicity, film forming ability and antimicrobial activity (Rinaudo, 2006; Ferrero et al., 2015). Fernandes et al., fabricated chitosan based coatings on leather by spraying, calendaring and drumming and also studied its efficacy on antimicrobial activity (Fernandes et al., 2013). Since, the chitosan is soluble in acidic condition, in drum based coating it is offered along with formic acid during fixing of post-tanning chemicals. It was hypothesized that chitosan ionically interacts with the collagen and other post-tanning auxiliaries (Torres-Giner et al., 2008). Initial pilot scale studies showed drumming based method of impregnation provided better antimicrobial activity than other methods of application. It was found that 1% chitosan in formic acid with an impregnation time of 2 h showed the most optimum antimicrobial action. Same kind of studies were also done by incorporating chitosan formate (MIC 0.25–0.50 mg/mL) into leather as re-tanning agent and showed similar resistance to fungal growth (Ocak et al., 2015).

In order to improve the solubility of chitosan in wide spectrum of pH which is necessary for leather manufacturing, Luo et al., grafted polyethylene glycol (PEG-1000) on to chitosan (CS-8000) at different degree (Substitution Degree (SD%): number of PEG groups per 100 amino groups of chitosan determined by TNBS method) such as 4% and 8% (Fig. 8). Proton-NMR spectrum with peaks at chemical shift of 3.1 and 3.6 ppm confirmed the attachment of the PEG to chitosan substrate (Luo et al., 2012).
The MIC values were found to be 25, 3.12, and 0.78 mg/mL for CS, PEG−CS−4%, and PEG−CS−8% and the increasing antibacterial activity was attributed to better solubility of PEG-CS compared to CS. PEG-CS coated leather was prepared by immersing the leather in PEG-CS solution for 2 h with stirring and then dried. Visualization of formed coatings under SEM showed a thickness of 21.1 ± 2.2 μm, 23.6 ± 4.5 μm and 26.4 ± 4.4 μm coats for control and PEG-CS 4% and 8% respectively. Zone of inhibition (ZOI) study showed that the PEG-CS 8% had the highest antimicrobial activity and same is shown in Fig. 9. In addition, the antifouling property of PEG helps preventing the adhesion of
microorganism on the leather surface (Saldarriaga et al., 2007).

Further to improve the antimicrobial activity, PEG–CS–8% was used as a stabilizing agent in the silver nanoparticle preparation where PEG-CS solution (2 mg/mL) and silver nitrate was added dropwise into sodium borohydride solution to form (PEG–CS–AgNPs) (Liu et al., 2017). Prior to coating, the leather surface was subjected to CO₂ plasma treatment to expose more carboxylic groups of collagen to form electrostatic interaction with PEG–CS–AgNPs. The antimicrobial property of PEG–CS–AgNPs showed a very low MIC of 0.094 mg/mL. The treated leather exhibited a good ZOI and the bacterial cell membrane destruction by combined action of chitosan and AgNPs was observed when visualized under SEM as shown in Fig. 10.

3.1.4. Antimicrobial leather based on silver nanoparticles incorporation

Silver nanoparticles (AgNPs) are majorly looked upon in this avenue due to its unmatched broad spectrum antimicrobial efficacy (Eman et al., 2013) and good biocompatibility (Stanić et al., 2011). Even though the mechanism of antimicrobial activity of silver ions is well studied, its not same case when considering AgNPs. Some important modes of the antimicrobial activity of AgNPs are explained below.

Hebeish et al., proposed that the antimicrobial activity of AgNPs is due to the conversion of zerovalent Ag to Ag⁺ ion upon oxidation owing to its extreme sensitivity to oxygen (Hebeish et al., 2011). These ions can react with the negatively charged sulfur containing bacterial cell membrane and allow it to pass in and out of the system affecting the cell viability. Consequently, some important modes of the antimicrobial activity of AgNPs are explained below. Hebeish et al., proposed that the antimicrobial activity of AgNPs is due to the conversion of zerovalent Ag to Ag⁺ ion upon oxidation owing to its extreme sensitivity to oxygen (Hebeish et al., 2011). These ions can react with the negatively charged sulfur containing bacterial cell membrane and allow it to pass in and out of the system affecting the cell viability (Mijakovic et al., 2005; Lin et al., 1998; Zhang et al., 2010; Sathishkumar et al., 2009). Also, this leads to the destabilization of outer membrane and plasma membrane rupture leading to the depletion of intracellular ATP (Lok et al., 2006). Another mechanism involves the formation of R-S-S-R bonds due to the reaction between silver and the sulphydryl groups of the cell effectively blocking the cellular respiration and eventually causing cell death (Kumar et al., 2004). Kim et al. (2007) proposed the antimicrobial activity can also be attributed to the generation of free radicals that are capable of inhibiting microbial growth. Due to such a diverse mechanism, researchers have found AgNPs based antimicrobial systems as a way forward in developing multifunctional materials.

Velmurugan et al., prepared AgNPs with hydrodynamic diameter of 10–20 nm from silver nitrate using aqueous extract of E. annua as a reducing agent in a greener way (Velmurugan et al., 2014). The synthesized AgNPs showed a sharp absorption peak at 434 nm due to the surface plasmon resonance and EDAX spectrum showing a strong peak at 3 keV, indicating the presence of silver in elemental form (Lee et al., 2008). The AgNPs along with flower extract were incorporated into chrome tanned leather by ultra sonication process for 20 min. The ZOI and minimum bactericidal concentration of the treated leather against B. linens and S. epidermidis was found to be 5.0 ± 0.1 mm, 1.0 ± 0.7 mm and 30.27 ± 11.08% and 46.63 ± 11.08%.

Koizhaiganova et al., synthesized silver doped hydroxyapatite (Ag-HA) and spray coated it on leather surface at different concentrations of Ag (0–5%) along with lacquer and dried (Koizhaiganova et al., 2015). The treated sample was tested against S. aureus, B. subtilis, E. faecalis as Gram positive bacteria, E. coli, S. typhimurium, K. pneumoniae and P. aeruginosa as Gram negative bacteria and the yeast C. albicans. All microorganisms tested, except C. albicans, were found to be sensitive at concentrations more than 3% Ag. But this paper did not highlight the rationale behind the use of HA. Similarly, Sportelli et al., synthesized AgNPs in situ by photo-reduction of silver nitrate treated leather using UVC light demonstrating a new route for incorporation of antimicrobial agents into leather (Sportelli et al., 2017).

Liu et al., synthesized gallic acid stabilized silver nanoparticle (GA-AgNPs) of 8.5 nm AgNPs with GA core shell of 3.4 nm (Liu et al., 2018). The activity of GA-AgNPs on S. aureus and E. coli was found to be maximum of 99.9% at MIC of 10 μg/mL. GA-AgNPs were used as a replacement for polyacrylic acid syntans to chrome tanned leather as retanning agents at a concentration of 0.1% w/w. The hypothesized

![Image](image-url)
interaction of GA-AgNPs to leather collagen (Fig. 11a) was confirmed using XPS analysis, wherein the leather exhibited the presence of Ag 3d doublet signal at 368.3 and 374.3 eV corresponding to Ag 3d5/2 and Ag 3d3/2 binding energies with a splitting of 6.0 eV implying the formation of metallic AgNPs on the collagen fiber surface (Zhang et al., 2011). Additionally, due to the deposition of AgNPs, the roughness of collagen fibres increased which led to a hydrophobic behavior with a contact of 113° compared to 0° of pristine leather after 120 s of contact with water droplet. The release of Ag⁺ ions from re-tanned leather (silver content of 6.4 mg/g of dry leather) was studied using ICP-AES, which showed a maximum release of 0.08% of Ag⁺ ions/g of leather after being dipped in 10 mL of water for 72 h.

The same research group tried coating GA-AgNPs on leather surface at a concentration of 100 ppm by spray coating (Xia et al., 2019). The morphology of treated leather demonstrated that the natural structures of leather were not damaged or affected by the GA-AgNPs spray coating and its interaction with free Cr³⁺ available in the chrome tanned leather was studied by XPS analysis. O1s XPS spectra of pristine and GA-AgNPs coated leather showed similar peaks at 531.65 eV and 532.58 eV that are attributed to the carboxyl groups (C–O and C=O) of collagen fibers (Liang et al., 2014) and peak at 530.86 eV is attributed to the oxygen atoms in Cr–O component, indicating the coordinated complexation between Cr³⁺ and carboxyl groups on collagen fibers of the chrome tanned leather (Jan et al., 2018; Lippitz and Hübert, 2005). However, the area under these peaks were high in case of treated leather than pristine which confirms the interaction between carboxyl group of GA-AgNPs and free Cr³⁺ present in the leather matrix. The GA-AgNPs on leather surface was also observed to be very effective in killing the wide range of microbes along with release of dead cells imparting anti-adhesion behavior to the leather matrix as shown in Fig. 11b.

3.1.5. Antimicrobial leather based on natural biocide incorporation

As essential oils are known natural biocides, they were used in post tanning process as lubricant as such without any treatment. The natural biocides used in the study included oregano oil (Bielak et al, 2017, 2020; Eke Bayramoglu et al., 2006; Bayramoglu, 2007), eucalyptus oil and lavender oil (Sirvaityte et al., 2011), thyme oil (Sirvaitytė et al., 2012) and cinnamon oil (Bielak et al., 2016). These treated leather was also found to resist both bacterial and fungal growth over a period of long time. This section also includes the oil treated leathers for the fabrication of scented leather as they are also considered as natural biocides and shows good antimicrobial activity.

The important finding from the above scientific outputs were that the leather fraternity majorly focused its research on the prevention of mold and fungal growth on final leather to ensure the bio-safety of leather products. However, COVID-19 pandemic and consumer awareness on
bio-safety leather products would put-forth the researchers to seek options to incorporate antiviral activity on the same. Accordingly, this review can help researchers visualize different strategies for achieving the efficient mode of incorporation of antiviral agents and fabricate such kind of advanced materials based on leather matrix in a rapid manner.

3.2. Fragranced/scented leather

The development for leather matrix capable of sustained fragrance release has been looked upon as a value addition to leather. Such a property can add new dimensions to leather products particularly when it comes to garment and upholstery leather. Additionally, as the washing of leather needs special care, introduction of fragrance can help with managing bad odor during longer usage. Similar functionality of aroma release was reported in textile fabrics creating a unique experience for the users (Ghayempour and Mortazavi, 2015; Tzhayik et al., 2017; Shahid-ul-Islam et al., 2013). A general method of introducing aroma into fabrics was achieved by incorporating polymeric encapsulates of fragrance compounds or scented oils into the leather matrix.

Velmurugan et al., developed oil-in-water emulsion of lemongrass oil that was encapsulated into chitosan-acrylic acid (1:2) nanospheres through emulsion polymerization technique (Velmurugan et al., 2015). The oil loading (%), oil content (%), and encapsulation efficiency (%) of lemongrass oil in nanospheres were 299.39 ± 2.31%, 91.77 ± 1.16% and 32.66 ± 1.13%, respectively. The size of the nanosphere ranged from 100 to 500 nm with an average diameter of 117 ± 11 nm. FTIR spectroscopy revealed electrostatic interaction between the lemon grass oil and the nanosphere wall material. The product was applied on neutralized chrome tanned leather as a re-tanning agent at an oil concentration of 5% w/w. It was posited that the nanosphere interact with the collagenous matrix through hydrogen bonding. The same research group established a similar method of producing oil-in-water emulsions of orange and lavender oil using Triton X100 as emulsifying agent (Velmurugan et al., 2017). This was followed by encapsulation into polymeric nanoparticles by grafting acrylic acid monomer onto chitosan backbone through emulsion polymerization technique. The chitosan-acrylic acid walls act as a barrier to prevent the oxidation of oils by reducing hydroperoxide and diene formation (Shahidi et al., 2002). The perception of scent was measured qualitatively by experienced tanners and it was reported that the leather had strong perception even after several water and solvent washes. It was also found that the lavender oil infused leather had stronger perception than orange oil scented leather. The strength and organoleptic properties of scented leather were on par with the conventionally processed leather. Additionally, the scented leather was found to be resistant to fungal attack due to the inherent antimicrobial activity of scented oils and chitosan.

Alternatively, scented leather was fabricated by facile Layer By Layer (LBL) deposition method (Fig. 13). In this technique, initially leather matrix was coated with polyacrylate emulsion followed by an ethanolic solution of vanillin and further covered with silicon dioxide which

![Fig. 12. (a) Schematic illustration for the layered deposition of antimicrobial agents with subsequent crosslinking (b and c) Proposed mode of antimicrobial mechanism by leather treated with chitosan and crosslinked CS/GA@AgNPs (d) ZOI of leather samples against S. aureus (Xiang et al., 2018).](image)

![Fig. 13. Schematic illustration of fragrance release from vanillin treated fabrics (Fan et al., 2018).](image)
The superhydrophobicity can also improve the water repellency of superhydrophobic coating on the leather to make a self-cleaning surface and garment is maintaining it hygienic/clean as washing leads to the removal of oils present in the leather which in turn crack out after drying (Mahi Leather, 2020). This problem can be addressed by creating a removal of oils present in the leather which in turn crack out after drying.

3.3. Self cleaning leather

3.3.1. Realization of self-cleaning effect through superhydrophobic surfaces

One of the major challenges while using leather products (footwear and garment) is maintaining it hygienic/clean as washing leads to the removal of oils present in the leather which in turn crack out after drying (Mahi Leather, 2020). This problem can be addressed by creating a superhydrophobic coating on the leather to make a self-cleaning surface that is capable of taking away all the dirt by gentle application of water. The superhydrophobicity can also improve the water repellency of leather making it durable and long lasting. Superhydrophobicity is an ability of the surface to repel water with a contact angle more than 150° (Law, 2014). This is generally achieved by modulating the surface roughness and lowering of the surface energy. Chemically, this is accomplished by introducing long chain alkyl groups or by using fluorinated polymeric materials (Yin et al., 2020; Zhang et al., 2017; Lee et al., 2013). In leather manufacturing, superhydrophobicity is imparted in finishing process by coating the superhydrophobic material on leather surface. With the recent rise on EPA restriction on use of fluorinated polymers (Federal Register, 2020), the quest for alternative superhydrophobic coatings incorporating nanoparticles functionalized with long chain alkyl groups has been a topic of interest.

Kayaoglu et al., formed thin layer of hydrophobic polydimethylsiloxane on leather surface through plasma polymerization (13.56 MHz RF, variable power up to 100W) by employing hexamethyldisiloxane (HMDSO) as monomer and argon gas as carrier (Kayaoğlu and Oztürk, 2013). Stain removal studies conducted using a standard reciprocating crockmeter showed that the optimized conditions for the plasma polymerization was HMDSO treatment for 90 s at 80 W power. This gave a maximum contact angle of 107.02° with an absorption time of 2800 s. Even though the contact angle of untreated sample is 113.11°, it had a very low absorption time of 60 s.

Later, Ma et al., demonstrated a facile spraying method for creating superhydrophobic surfaces on the leather matrix (Ma et al., 2015). In this work, 2% w/w water based polyacrylate emulsion was applied initially to reduce the capillary action of leather surface followed by ethanolic suspension of hydrophobic silica nanoparticles (1% w/w) to improve the water repellency and subsequently dried at room temperature. The contact angle increased from 123.3° to 128.9° (1 coat of silica) to a maximum of 170.3° on applying 8 coats of hydrophobic silica material. Further, they demonstrated that with increasing the treatment up to 10 coats, the contact angle reduced due to the loss of micro/nano roughness caused by denser packing of silica particles in the coatings. The destroyed superhydrophobic surface after mechanical abrasion was restored by simple and facile spraying of ethanolic solution of hydrophobic silica nanoparticles as shown in Fig. 14. Similar repellency property was also demonstrated with polyurethane and epoxy emulsions in the place of polyacrylate emulsion.

Recently, carbon nanotubes have been given more importance in the field of material chemistry owing to its superior thermal, mechanical and electrical properties as platform for the synthesis of functional materials. Krishnamurthy et al., introduced superhydrophobicity into single walled carbon nanotubes (SWCNT) through copper catalyzed alkyne-azole cycloaddition (CuAAC) reaction (Krishnamurthy et al., 2017). Initially, SWCNT were nitrated by radical addition method using sodium nitrite and nitric acid to obtain SWCNT-n(NO2) which was then hydroxylated in aqueous alkaline solution to obtain SWCNT-n(OH). SWCNT-n(OH) was reacted with 3-azidopropyltrimethoxysilane to form azide functionalized SWCNT which was further reacted with 2, 5-diethynylbibithiophene and 1,4-diethynyl -2,5-bis(hexyloxy)benzene to form hydrophobic SWCNT. The modified SWCNT was coated on leather surface by drop casting method. The water contact angle was measured to be 163° with dynamic advancing contact angle of 160° and receding contact angle of 156° (Fig. 15). But, the other properties required for a leather coating such as fastness properties were not reported in the work.

Similarly, Ayyappan et al., synthesized polymeric nanconjugates (PNC) of Multi Walled Carbon Nanotubes (MWCNT) (PNC-1 & PNC-2) and fullerene (PNC-3 & PNC-4) with methacrylic acid as monomers as superhydrophobic material for leather finishing (Ayyappan et al., 2020). PNC-1 & PNC-3 is based on methacrylic acid and PNC-2 & PNC-4 is based on methylmethacrylate. AFM studies showed better roughness for MWCNT based PNC than fullerene ones. Especially, PNC-2 has root mean square roughness of 30.7 nm with height variation of 370 nm. Similar roughness was also observed when visualized under HR-SEM. Dispersion uniformity of PMAA based conjugate was poor than PMMA which is due to the hydrogen bonding between carboxylic acids present in polymer chain. Also, it was found that fullerene based nanoconjugates

Fig. 14. Proposed approach towards creating superhydrophobic surface using silica nano particles (Ma et al., 2015).
showed poor distribution, which was attributed to the restricted interaction with the polymer due to its buckyball structure. HR-TEM analysis showed PMMA thickness of 17–20 nm whereas PMAA thickness was around 11–15 nm. Water contact angle (WCA) of the leather surface coated with PNC-1 to 4 were found to be 111°, 158°, 101° and 123°. Highest WCA of PNC-2 also corroborated with roughness values from AFM and HR-SEM.

The manufacturing cost and color are major drawbacks of using CNTs based hydrophobic material in leather manufacturing. Since, the CNTs based materials are dark black in nature it’s not suitable for pastel shades. Though there are so many superhydrophobic materials that are available in the market, the issue in using them in the leather matrix is their incompatibility with the binders that are used in leather finishing process. To overcome this, researchers are trying to make different kind of film forming polymers that are compatible with the superhydrophobic material without compromising the inherent properties of leather matrix.

3.3.2. Realization of self-cleaning effect through photo-catalysis

Several, photocatalysts such as metal oxides are known to degrade organic molecules and thus they are particularly used very much to decolorize the dye containing wastewater emanating from textile and leather industries (Akpan and Hameed, 2009; Sirirerkratana et al., 2019). The similar concept was explored to decolorize the stains on leather surface by coating photocatalysts along with polymeric film forming material to realize self-cleaning effect.

Petica et al., developed a visible light active nitrogen-iron doped TiO$_2$ nanoparticle as photocatalyst and coated on leather surface along with resin based film forming material (Petica et al., 2015). Further, the efficiency in removing stains of methylene blue (MB) dye and ball pen ink was studied by visual examination and color difference measurement under visible light irradiation (Fig. 16). The increased photocatalytic activity is attributed to the formation of oxygen deficient sites in the grain boundaries of polycrystalline materials and doping nitrogen in the part of such oxygen-deficient sites are important as a blocker for reoxidation (Ibara et al., 2003). In case of Fe$_3$O$_4$ doped TiO$_2$, Fe$_3$O$_4$ ions can act as trap and prevent the recombination of holes and electrons, thus enhancing the photocatalytic activity (Goswami and Ganguli, 2012). Results showed complete disappearance of the MB and ball pen ink spot within 30 h of visible light irradiation on Fe–N–TiO$_2$ nanoparticle coated leather. This proved that integration of photocatalyst capable of absorption in visible range of EMR spectrum can be a facile system for fabricating a self cleaning leather. Gaidau et al., demonstrated similar self cleaning effect by using silica doped TiO$_2$ nanoparticles that was prepared by hydrothermal method (Gaidau et al., 2017).

But these methods of self cleaning still raise a question of what will happen to the dyestuffs and the binder itself which are also organic.

Fig. 15. [Top left] Schematic representation of synthesis of superhydrophobic SWCNTs. [Top right] FTIR spectra of (a) SWCNT-n(OH) (b) azide-functionalized SWCNTs and (c) copolymer of SWCNTs (Arrow marks indicating the disappearance of azide functional group after polymersiation reaction) [Bottom left] Contact angle of water droplet on glass surface after drop casting and drying with (a) THF (b) Pristine SWCNTs (c) SWCNT-n(OH) (d) click copolymer of SWCNTs. [Bottom right] XPS spectra of copolymer of SWCNTs (Krishnamurthy et al., 2017).

Fig. 16. Visual examination of MB spot and ball pen ink line degradation on leather surface treated with Fe–N–TiO$_2$ (Top) and untreated control leather (Bottom), under Visible light irradiation (Petica et al., 2015).
components that are used in leather finishing process. The mechanism has to be further explored to study the selective effect of stain removal in presence of dyestuffs in leather finishing coats.

3.4. Thermal management in leather

With the increasing demands on energy savings, researchers are trying to integrate personal thermal management technologies on the daily use fabrics to mitigate the problem. This includes cooling, heating, insulation and thermo regulation techniques (Wu et al., 2019; Hu et al., 2020). Thus, leather industry is also looking at enhancing the thermal comfort of the users by incorporating such technologies into leather products. Skin/hide is well endowed with a highly dense fibrous structure of type-1 rod like collagen protein, with pores ranging from micro to macro size (Fig. 17). This property can be attributed mainly to the hierarchical ordering of the collagen starting from a nanoscopic to macro size (Fig. 17). This property can be attributed mainly to the hierarchical ordering of the collagen starting from a nanoscopic to macro size (Fig. 17). This property can be attributed mainly to the hierarchical ordering of the collagen starting from a nanoscopic to macro size (Fig. 17). This property can be attributed mainly to the hierarchical ordering of the collagen starting from a nanoscopic to macro size (Fig. 17).

These pores are capable of efficiently trapping stagnant air, that can provide thermal insulation by suppressing the thermal transfer by conduction and convection. In addition to this, it has a strong multiple diffuse reflectance ability, letting it to reflect NIR waves (0.9–2.3 μm) up to 80% (Wang et al., 2015; Liu et al., 2016). But, due to the presence of large amount of polar groups –NH₂/-OH and amide I/amide II, it absorbs the IR radiation (2.5–4.0 μm and 5.5–7.5 μm). Low thermal conductivity and high reflectance of IR waves, makes it a suitable candidate for the fabrication of thermo regulating materials.

Wang et al., demonstrated that glutaraldehyde tanned leather can effectively prevent the absorption of the IR radiation (2.5–4.0 μm) by blocking the polar –NH₂ groups (Wang et al., 2019). Still FTIR spectroscopy confirmed the absorption of infrared radiation in the region of 5.5–7.5 μm. Since, SiO₂ know to reflect IR radiation effectively, the glutaraldehyde tanned leathers were treated with ethyl silicate and pH was adjusted to 9.0 which induced in-situ formation of SiO₂ nanoparticles (leather/SiO₂) (Liu et al., 2014). This was further brush coated with SiO₂/polyurethane and marked as SiO₂-leather/SiO₂. Leather surface coated only with SiO₂/polyurethane was used as control (leather-SiO₂). The in-situ nanoparticle formation enhanced porosity from 52.4 to 61.4% thereby reducing thermal conductivity from 0.07 Wm⁻¹K⁻¹ to 0.04 Wm⁻¹K⁻¹ by letting more stagnant air to be trapped in pores. Further, the brush coated SiO₂- leather/SiO₂ (thickness of 100–300 μm) showed significant reduction in thermal diffusivity from 1.24 × 10⁻⁷ to 0.92 × 10⁻⁷ m²/s. But as the flexibility of leather was affected, the thickness of coating was optimized at 200 μm. This method was thus effective in blocking thermal energy transmission through conduction, convection and radiation. But in case of leather-SiO₂, it exhibited lower porosity of 32.9% and had higher thermal diffusivity (1.54 × 10⁻⁷ m²/s) and thermal conductivity (0.079 Wm⁻¹K⁻¹). Thus, a simple coating of SiO₂ will not be sufficient for effective thermal regulation (Fig. 18). Additionally, the reflectivity and scatterance of leather was analyzed as per Kirchoff’s law (ε value is inversely proportional to the reflectivity and scatterance) and the results showed a decrease from 0.94 for pristine leather to 0.87 in case of leather-SiO₂ and 0.63 for leather/SiO₂.

Alternatively, Renzi et al., achieved thermal regulation property using Phase Changing Material (PCM) (Izzo Renzi et al., 2010). PCM can absorb or release sufficient amount of energy at certain temperature to provide heating or cooling effect making them a good candidate for fabrication of thermoregulating fabrics. Microencapsulated PCMs Ty65 (18 °C) and MPCM 28 (28 °C) of size 5 μm–40 μm was coated on leather by a wet soaking/dry coating method and the later showed better adherence. Thermoregulation property of the treated leather was analyzed using a Peltier device connected to an infrared thermocamera. On visualizing the coated (SX) and uncoated sides (DX) of leather, upon cooling cycle the SX side appeared green from red and DX side cyan, showing that the SX side slowed down the cooling process while DX sides cooled much faster (Fig. 19 transition from step 1 to 2). Here, PCM on SX side acted as thermal buffer by releasing the stored heat energy and thus effectively slowing down the cooling process. Similarly, on heating cycle, the SX side turned green from blue while the DX was yellow (Fig. 19 transition from step 3 to 4). This again showed the thermal buffering of PCM on SX side by slowing down the heating process by absorbing the heat energy for melting process. This proved the thermoregulating property of PCM coated leather. A similar model was also demonstrated by fabricating a thermoregulating jacket.

Similar kind of study was conducted by Prakash et al., wherein n-octadecane based PCM was encapsulated into melamine formaldehyde resin and used as synthetic tanning agent (syntan) in post tanning process (Prakash et al., 2014). Briefly, oil-in-water emulsion of...
n-octadecane using SDS as surfactant was added dropwise into melamine-formaldehyde pre-polymer and stirred for 2 h at 70 °C followed by drying to obtain PCM based syntan. Similarly, control melamine formaldehyde syntan was prepared without adding PCM. The PCM based syntan showed high enthalpy of transition in DSC thermo-gram compared to that of control syntan confirming the successful encapsulation of PCM into melamine formaldehyde resin. 5% of the PCM syntan and control syntan was used in post tanning process. The thermoreponsive function of PCM treated and control leather was studied by exposing both the leather to thermal radiation for 60 s. Infrared thermocamera images of PCM treated leather showed less dissipation of heat energy compared to that of control leather. This may be due to the absorption of heat energy by PCM for melting process to occur. This proved the thermo regulation property of the prepared syntan.

Currently, these kind of materials have been gaining much importance owing to the advantages offered like energy saving and providing thermal comfort to the users by reflecting the sunlight in various ways. More research on developing such materials is expected to use technologies like conductive nanomaterials and also by employing passive cooling and heating systems to selectively play with the thermal regulation properties of the leather matrix.

3.5. Flame retardant leather

Since, the post tanning process of leather manufacturing uses several polymeric fillers and lubricants, in the event of fire hazard these organic compounds will easily catch fire and release toxic gases and smoke (Bacardit et al., 2010; Leather International, 2007). Thus, fire resistant property of a material is very critical in ensuring the personal safety of the users particularly automotive upholsteries where a possibility for a fire accident is very high. Usually, polybrominated diphenyl ether (PBDE) based flame retardants were used but they were soon replaced due to its toxic nature and its strong persistent presence in the natural environment. Researchers are trying to introduce non toxic flame retardant materials into the leather matrix, so that it can avoid the spread of fire and minimize the damage. This technology can be employed in making garments for fire fighters and also it can be exploited for defense personnel.

Phosphorous based flame retardants are of current interest due to its low toxicity compared to that of the brominated flame retardants. Mohamed et al., proposed a method of using Pyrovatex CP, a phosphorous based flame retardant along with etherified methylolated melamine (EMM) along with the finishing formulation by a pad-dry-cure technique (Mohamed and Abdel-Mohdy, 2006). Such treatment increased the Limiting Oxygen Index (LOI) of untreated leather from 36
to 44 in case of treated leather. Jiang et al., demonstrated a technique of using intumescent flame retardant (IFR) in leather processing (Jiang et al., 2015). A water soluble IFR was prepared and further reacted with montmorillonite (MMT) in the presence of surfactant and collagen to form OMMT-IFR nanocomposites. The flame combustion time reduced from 55 s to 4.2 s for 9% w/w OMMT-IFR treated leather in vertical burning test. Cone calorimetric tests which provides results that can be extrapolated to real life situations showed a reduction in peak heat release rate ($214.7 \text{ kW/m}^2$) by 41.7%. Also, the total smoke production reduced (from 0.628 m$^2$/kg to 0.363 m$^2$/kg) by 42.2%, demonstrated the flame retardant property of the treated leather. The flame retardant mechanism was attributed to the degradation of OMMT-IFR composite to its individual constituents which further decomposes into carbon sources, acids and also release non combustible gases. Further, at high temperatures of 200–250 °C, MMT decompose into $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ can react with acids from IFR to generate aluminosilicophosphate layers that can promote dehydration and charring. Thus, the combined effect of IFR and MMT acts as flame retardant system for leather. Yang et al., and Xu., et al., synthesized melamine based flame retardants similar to the previous study without adding MMT and collagen and was incorporated into leather matrix by simple absorption in aqueous medium (Yang et al., 2016; Xu et al., 2017). The LOI value increased from 24.0 to 34.1% with a flame retardant dosage of 8%.

Sanchez-Olivares et al., used Sodium-MMT alone as flame retardant in post tanning process of leather manufacturing (Sanchez-Olivares et al., 2014). The burning length of the untreated leather was found to be at 16.4 cm, which is higher than the maximum burning length of 15.2 cm for aeronautical applications. In case of 3% Na-MMT treated leather, the burning length reduced to 13.3 cm making it suitable for any kind of automotive upholstery. The flame retardant property was assigned to the formation of protective char layer that can act as thermal barrier reducing the transfer of heat, oxygen and mass during the combustion process (Gilman, 1999; Gilman et al., 2000).

Duan et al., used phosphorous flame retardants (PFR), nitrogen & phosphorus intumescent flame retardant (NPIFR) and nitrogen and phosphorus flame retardant (NPFR) as re-tanning agent in leather processing (Duan et al., 2019). All the fire retardants used in the study was based on dimethyl phosphate and the scheme of synthesis of the same is explained in the Fig. 20. The cone calorimetry test showed an increase in time to ignition from 87 s (control) to 136, 125 and 105 s for PFR, NPIFR and NPFR treated leather, respectively. Fire growth index (FGI – larger the FGI, the easier the material burns) of the samples reduced from 7.5 (control) to 3.5 (PFR), 2.0 (NPIFR) and 1.0 MJ/m$^2$s (NPFR). Even though the FGI was low for NPIFR and NPFR, the total smoke production was very high at 25.4 and 28.4 m$^2$ compared to that of control (12.3 m$^2$) and PFR (5.4 m$^2$). Thus, all the fire retardants had a good flame retardancy properties but comparatively PFR treated leather had better properties with low smoke production.

As a new class of materials, Layered double hydroxides (LDH) are emerging halogen free flame retardants and are tried as replacement for...
halogenated and phosphorous compounds. As name suggests, LDH are layered anionic compounds with thermally degraded metal hydroxides of large surface area that are capable of showcasing good flame retardancy (Kalali et al., 2016; Li et al., 2016).

Lyu et al., prepared flame retardant lubricant (Fatliquor) by incorporating $[\text{Mg}_4\text{Al}_2\text{(OH)}_12]^{3+}(\text{CO}_3)^2-\cdot4\text{H}_2\text{O}$ (MgAl-LDH) into Zanthoxylum bungeanum Maxim seed oil (ZBMSO) (non-edible oil) (Lyu et al., 2019). ZBMSO was first decolorized and the acid number was reduced by treatment with glycerol (58.88–12.86 mg KOH/g) to make it a suitable for fatliquor preparation to obtain modified ZBMSO (MZBMSO). To improve the compatibility of LDH with MZBMSO (C18 chain length), it was pretreated with sodium stearate and introduced into the MZBMSO oil to prepare MZBMSO-sLDH nanocomposites. The reduction in after flame time (70 s–37 s), length of charring (81 mm–35 mm), mass loss (60.32–30.29%) and smoke density index (25–6) along with increased limiting oxygen index (23.6%–28.0%) confirmed the flame retardant efficiency of the prepared fatliquor. The mechanism of flame retardance studied by TG-FTIR showed reduction in release of the flammable components. The absorbance intensities for the flammable gases (hydrocarbon, aromatic, carbonyl and ether compounds) reduced in case of nanocomposite treated leather and it was attributed to the increased strength of leather char residue due to the presence of LDH (Babu et al., 2017; Gao et al., 2014). Also, SEM analysis showed intact fibres coated with dense continuous char capable of blocking the penetration of heat and oxygen into collagen fibres in case of nanocomposite treated leather whereas broken porous residues capable of combusting easily were visualized in control leather (only MZBMSO treated) (Fig. 21). These properties confirmed MZBMSO-sLDH nanocomposites can be an effective method for imparting flame retardance to leather matrix.

Similar to the previous reported work, Lyu et al., have used oxidized sodium alginate (OSA) as LDH modifier in the place of sodium stearate (Lyu et al., 2020). The LDH was exfoliated in formamide by ultra-sonication. Sodium alginate is a green dispersant and the pendant –COO$^-$ groups present in sodium alginate can be exploited to assemble with the exfoliated LDH nanosheets and thus stabilize the exfoliated structures in aqueous medium with good dispersibility (Kang et al., 2014). The exfoliated LDH showed better dispersion in water along with OSA at mass ratio up to 1:0.2 (OSA: LDH). Additionally, the presence of reactive aldehyde groups in OSA helped in better fixation of MZBMSO/OSA-LDH on to amine group of collagen fibres which results in reduction of potential fogging value from 18.5 to 10.35 mg by preventing migration of oil molecules and strong adsorption capacity of OSA-LDH. In case of control leather, the high antifogging value was attributed to simple electrovalent interaction between the polar groups of oil and amine group of collagen, which will lead to easy migration of oil molecules up on heating. The flame retardancy characteristics were a bit lower compared to previous study which can be attributed to low loading of LDH (1.5%) in the current study while it was 4% in previous study. The possible modes of interaction hypothesized by the authors is given in the picture given below (Fig. 22).

4. Implications for theory and practice

Having discussed on the various aspects such as method adopted for the synthesis of functional materials, their mode of incorporation into leather matrix, the mechanism behind realizing the intended property and their effect on the properties of the final leather in the previous sections and a brief summary of it is given in the Table 1. Nevertheless, it leaves us with a question of How well they would work in an industrial scale? Their applicability for large scale manufacturing is still lagging behind considering various parameters such as studies on upscaling experiments, cost and toxicity of the raw materials used in the synthesis process. Only with these information, it will be possible to explore the sustainability of the proposed methods. This can be easily achieved by having a collaboration between the research institutes, the leather chemical manufacturing industries and a leather industry. In such collaborations, the R&D institutes and the chemical manufacturing firms can actively involve in the design and development of the newer products and assessment of the same at lab scale and pilot scale levels. Whereas, the leather manufacturers can validate the developed technology in an industrial scale and ease the process of commercialization. With the challenges faced in the situations like the COVID-19 pandemic, the validation of such technologies for pilot scale and industrial scale trials should be given higher priority to fulfill the demands of the customer.

Fig. 21. Schematic representation of the flame retardance mechanism by MZBMSO-sLDH nanocomposites (Lyu et al., 2019).
5. Conclusions

COVID-19, though proved to be disastrous to the economy, it has inculcated an awareness among the people to use bio-safe materials in every aspect of life. Leather industry, a consumer-focused sector, is on the lookout for manufacturing products that can offer such comfort to its users. Apart from this, for the leather industry to compete with the fast-growing synthetic materials, it has to integrate itself with scientific innovations and move forward towards fabricating advanced functional materials. Keeping that in mind, this review article provided an overall view on the need for the development of biosafety and functional leather highlighting the significant progress made in the past decade and the main outcomes of this review are.

➢ Various possible options that are well researched and can provide solutions for several issues by adopting the technological interventions from different fields are discussed.
➢ Diverse novel methods that are developed to incorporate functional materials into the leather matrix.
➢ A comprehensive view on the mechanism behind and factors involved in the production of advanced leather materials.
➢ Demonstration of the leather as an excellent base material for the fabrication of several multifunctional materials which can open up new avenues for the leather industry to explore.

But some of the critical factors that need to be addressed includes.

➢ Majority of the paper did not validate the practical applicability and sustainability of the proposed solution. The scientific minds working for the development of new avenues for leather market should keenly look into the intricacies of the leather manufacturing and develop technologies that can be easily up-scaled for its commercial exploitation.
➢ Also, the cost involved in fabrication of such materials were not established which is a crucial factor when it comes to a mass production industry such as leather. This again should also go along the concept of sustainability wherein the raw materials chosen for the study may not only be economic but also be from a renewable source and non-toxic in nature.
➢ It will be of great significance if the techno-economic feasibility studies of the developed technologies are taken into account in an elaborated manner.
➢ Additionally, most of the experiments were done only in laboratory scale and thus there is an ambiguity of whether similar results can be reproduced when they are tried out in industrial scale.
➢ Finally, the toxicity of the fabricated materials was not discussed in some of the works which can impede the process of adopting such emerging and need of the hour technologies in the near future.
➢ The leather fraternity should also focus its research into the development of similar functional materials using the proteinous waste generated by the industry which can also come under the scope of waste to wealth approach and push forward towards the cleaner and sustainable development of leather based materials creating an impeccable model for a circular economy.

Apart from the above reviewed materials, more and more functional leather capable of radiation shielding, self-healing etc., are also emerging, exhibiting the versatility of the leather. These materials were tried out as sustainable options for lead aprons with improved durability and comfort. Thus, understanding the above stated challenges that are faced in the fabrication of functional leather based materials can help researchers come out with multifunctional materials and can also guide them to work hand in hand with industry partners to facilitate the upscaling process paving way for the development of next-generation leather materials.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence
| Mode of application | Material/chemical used | Mechanism of functional material | References |
|---------------------|------------------------|----------------------------------|------------|
| **Antimicrobial leather based on antibiotics incorporation** | PU with rose benzal and benzophenone | Radical/ROS generation and H₂O₂ production by irradiation of photoactive antimicrobial agents with UV light. | Hong and Sun (2010) |
| **Coating** | Sulfanilamide covalently linked to PU | Microbial urease enzyme triggered release of sulfanilamide biocide from the polyurethane backbone of the finish film. | Xu et al. (2013) |
| **Coating** | Acryloylated ciprofloxacin and acrylic acid | Broad spectrum antimicrobial activity of the ciprofloxacin present in the acryloylated ciprofloxacin-acrylic acid copolymer. | Chang et al. (2017) |
| **Antimicrobial leather based on metal oxide incorporation** | TiO₂ and ZnO nanoparticles in PU and acrylic polymer | Photocatalytic activity of metal oxide nanoparticles upon irradiation. | (Chen et al., 2010) (Liu et al., 2014) (Bao et al., 2017) |
| **Drumming** | Silver doped hydroxyapatite | > Conversion of zerovalent Ag to Ag⁺ ion upon oxidation and its interaction with negatively charged sulfur containing bacterial cell membrane leading to the destabilization of outer membrane and plasma membrane rupture leading to the depletion of intracellular ATP. | Liu et al. (2017) |
| **Drumming** | Polyethylene glycol grafted chitosan | > Polyethylene glycol attachment enhanced the solubility of chitosan and making it compatible to be applied at different stages of leather processing. | Luo et al. (2016) |
| **Drumming** | Silver nanoparticle supported PEGylated chitosan | Contact killing mechanism by cationic charged chitosan. | (Fernandes et al., 2013) (Ocak et al., 2015) |
| **Antimicrobial leather based on chitosan incorporation** | Chitosan in formic acid and chitosan formate | Sustained release of vanillin molecules from Layer By Layer deposition method. | (Bielak et al., 2020) (Eke Bayramoglu et al., 2006) (Bayramoglu, 2007) (Sirvaityte et al., 2011) (Sirvaityte et al., 2012) (Bielak et al., 2016) |
| **Drumming** | Essential oils | Antimicrobial activity of raw natural oils such as ➢ Oregano oil ➢ Eucalyptus oil ➢ Lavender oil ➢ Thyme oil ➢ Cinnamon oil | Velmurugan et al. (2015) Velmurugan et al. (2017) Fan et al. (2018). |
| **Drumming - Post-tanning** | Lemongrass oil/lavender & orange | Release of scented oil encapsulated in chitosan-polyacrylic acid nano spheres. | Velmurugan et al. (2015) Velmurugan et al. (2017) |
| **Coating** | Vanillin | Sustained release of vanillin molecules from Layer By Layer deposited solutions of polyacrylate resin, vanillin, silicon dioxide and solution of chitosan in acetoc acid. | Velmurugan et al. (2015) |
| **Self cleaning leather: Realization of self-cleaning effect through superhydrophobic surfaces** | Hexamethyldisiloxane | Plasma induced polymerization of HMDI/DDA creating a hydrophobic layer on the surface. | Kayaoglu and Ozturk (2013) |
| **Coating** | Polyacrylate resin and Silica nanoparticles | Micro/nano roughness created by denser packing of hydrophobic silica particles on the leather surface through Layer By Layer deposition method. | Ma et al. (2015) |
| **Coating** | Single walled carbon nanotubes | Introduction of hydrophobic alkyl groups by copper catalyzed click reaction on the azide functionalized SWCNT. | Krishnamurthy et al. (2017) |
| **Coating** | Multi walled carbon nanotubes | Surface roughness created by nano conjugates of polyethyleneacrylate containing MWNTs and fullerene. | Ayyappan et al. (2020) |
| **Self cleaning leather: Realization of self-cleaning effect through photo-catalysis** | Nitrogen and Fe doped TiO₂ | Degradation of dye stains by the radical generated from photocatalyst upon irradiation. | Petica et al. (2015) Gaidau et al. (2017) |
| **Coating** | Silicon doped TiO₂ | Deactivation of dye stains by the radical generated from photocatalyst upon irradiation. | Kayaoglu and Ozturk (2013) |
| **Thermal management in leather** | Glutaraldehyde and SiO₂ | Reflection of IR radiation by SiO₂ combined with the blocking of polar amine groups by glutaraldehyde. | Wang et al. (2019) |
| **Immersion coating and Drumming - Post Tanning** | Phase Changing Materials (PCM) | Absorption and release of energy by melting and recrystallization of PCM. | (Izzo Renzi et al., 2010) (Prakash et al., 2014) |
| **Flame retardant leather** | Pyrovatex CP and etherified methylated melamine | Gas phase generation of radicals by phosphorous based flame retardants. | (Mohamed and Abdel-Mohdy, 2006) (Duan et al., 2019) |
| **Drumming** | Dimethyl phosphate | Intumescent flame retardant forms of a swelled matrix and undergoes carbonization forming an insulating protective layer. | |
| **Drumming** | Dimethyl phosphate | Release of non-combustible nitrogen gas from the nitrogen rich flame retardants during degradation. | |

(continued on next page)
the work reported in this paper.

Acknowledgements
The first author thanks Council of Scientific and Industrial Research (CSIR) for providing Senior Research Fellowship (SRF) to carry out this work. CSIR-CLRI communication no. R/2020/INO/CLRI-SRF/1403.

References
Akpan, U.G., Hameed, B.H., 2009. Parameters affecting the photocatalytic degradation of dyes using TiO2-based photocatalysts: a review. J. Hazard Mater. 170, 520–529. https://doi.org/10.1016/j.jhazmat.2009.05.039.
Aksoy, A., Kaplan, S., 2013. Production and performance analysis of an antibacterial foot sweat pad. Fibers Polym. 14, 316–323. https://doi.org/10.1007/s12221-013-0316-x.
Ará, K., Hamam, M., Akiba, S., Kolke, K., Okioka, K., Hagura, T., Kamiya, T., Tomita, F., 2006. Foot odor due to microbial metabolism and its control. Can. J. Microbiol. 52, 357–364. https://doi.org/10.1139/w05-130.
Ayyappan, V.G., Prakash, D., Jaisankar, S.N., Sadhukhan, N., Alam, M.S., Samanta, D., 2020. Nanoconjugates of methacrylic polymers: synthesis, characterization, and immobilization to leather. J. Appl. Polym. Sci. 137, 48627. https://doi.org/10.1002/app.48627.
Babu, H.V., Coluccini, C., Wang, D.-Y., 2017. 8-functional layered double hydroxides (LDHs): Development, application, and challenges. Int. J. Nanomedicine 12, 700–707. https://doi.org/10.2147/IJN.S114495.
Barghoorn, E.S., 1950. Histological study of the action of fungi on leather. J. Am. Leather Chem. Assoc. 45, 524–536. https://doi.org/10.1021/jacs.000020z.
Bayramoglu, E., 2007. Unique biocide for the leather industry. J. Am. Leather Chem. Assoc. 102, 347–352.
Bielach, E., Marcinikowska, E., Sygula-Cholewińska, J., 2016. Antibacterial activity of leather lining materials with addition of silver nanoparticles. Int. J. Mol. Sci. 17, 1041. https://doi.org/10.3390/ijms17041041.
Bielach, E., Marcinikowska, E., Sygula-Cholewińska, J., 2017. The durability of antimicrobial effect of leathers finished with orcinol-oil. J. Am. Leather Chem. Assoc. 112, 377–386.
Bielach, E., Marcinikowska, E., Sygula-Cholewińska, J., 2020. Investigation of finishing of leather for inside parts of the shoes with a natural biocide. Sci. Rep. 10, 5467. https://doi.org/10.1038/s41598-020-60285-y.
Bryskier, A., 1993. Fluorquinolones: mechanisms of action and resistance. Int. J. Antimicrob. Agents 2, 151–183. https://doi.org/10.1016/0924-8579(93)90052-7.
Chang, J., Yang, Y.T., Yang, J.C., Wu, H.D., Tsai, T., 2008. Absorption and emission spectroscopic shifts of brown ring associated with DMPC liposomes. Lignes Pigments 79, 170–175. https://doi.org/10.1016/j.dyepig.2008.02.003.
Chang, J., Chen, Y., Zhao, S., Guan, X., Fan, H., 2015. Poly(N-acryloyl ciprofloxacin-co-acrylic acid) grafted magnetite nanoparticles for microbial decontamination of collagen solution: have we conquered the problem of antimicrobial residues? Polym. Chem. 6, 8150–8160. https://doi.org/10.1039/C5PY01091H.
Chang, J., Yang, G., Zheng, Q., Wang, Z., Xu, Z., Chen, Y., Fan, H., 2017. Poly (N-acryloyl ciprofloxacin-Co-acrylic acid)-incorporated waterborne polyurethane leather coating with long-lasting antimicrobial properties. J. Am. Leather Chem. Assoc. 112, 15–22.
Chen, Y., Yan, L., Wang, R., Fan, H., Zhang, Q., 2010. Antibacterial polyurethane synthetic leather coating with in-situ generated Nano-TiO2. Fibers Polym. 11, 689–694. https://doi.org/10.1007/s12221-010-0689-1.
Covington, A.D., Wise, W.R., 2020. Tanning Chemistry: the Science of Leather, second ed. RSC Publishing.
Duan, B., Wang, Q., Wang, X., Li, Y., Zhang, M., Diao, S., 2019. Flame retardance of leather with flame retardant added in retanning process. Res. Phys. 15, 102177. https://doi.org/10.1016/j.ijcerl.2019.102177.
Eke Bayramoglu, E., Gulumser, G., Karaboz, I., 2006. Ecological and fungicidal influence for the leather industry: essential oil of Origamia minutiforum. J. Am. Leather Chem. Assoc. 101, 96–104.
Emam, H.E., Manian, A.P., Sirotek, B., Duelli, H., Redl, B., Pipal, A., Bechtold, T., 2013. Treatments to impart antimicrobial activity to clothing and household cellulose-texiles - why "Nano"-silver? J. Clean. Prod. 39, 17–23. https://doi.org/10.1016/j.jclepro.2012.08.038.
Famá, L., Rejo, P.G., Bernal, C., Goyanes, S., 2012. Biodegradable starch based nanocomposites with low water vapor permeability and high storage modulus. Carbohydr. Polym. 87, 1899-1903. https://doi.org/10.1016/j.carbpol.2011.10.007.
Fan, Q., Ma, J., Xu, Q., An, W., Qiu, R., 2018. Multifunctional coatings crafted via layer-by-layer spraying method. Prog. Org. Coating 125, 215–221. https://doi.org/10.1016/j.porgcoat.2018.09.015.
Fernandes, L.P., Amaral, J.S., Pinto, V., Ferreira, M.J., Barreiro, M.F., 2013. Development of chitosan-based antimicrobial leather coatings. Carbohydr. Polym. 98, 1229–1235. https://doi.org/10.1016/j.carbpol.2013.07.030.
Ferrero, F., Perioloato, M., Ferrario, S., 2015. Sustainable antimicrobial finishing of cotton fabrics by chitosan UV-grafting: from laboratory experiments to semi-industrial scale-up. J. Cleaner Prod., Integr. Clean. Prod. Sustain. Strat. 96, 244–252. https://doi.org/10.1016/j.jclepro.2013.12.044.
Galdau, C., Peticas, I., Ignat, M., Popescu, L.M., Păulescu, R.M., Tudor, I.A., Pătescu, R., 2017. Preparation of silica doped titania nanocomposites with thermal stability and photocatalytic properties and their application for leather surface functionalization. Arab. J. Chem. 10, 985–1000. https://doi.org/10.1016/j.arabjc.2016.09.002.
Gao, Y., Wang, Q., Wang, J., Huang, L., Yan, X., Zhang, X., He, Q., Xing, Z., Guo, Z., 2014. Synthesis of highly efficient flame retardant high-density polyethylene nanocomposites with inorganoly-layered double hydroxides as non-foiler using solvent mixing method. ACS Appl. Mater. Interfaces 6, 5094–5104. https://doi.org/10.1021/am502655a.
Gentleman, E., Lay, A.N., Dickerson, D.A., Nauman, E.A., Livesay, G.A., Dee, K.C., 2003. Mechanical characterization of collagen fibers and scaffolds for tissue engineering. Biomaterials 24, 3805–3813. https://doi.org/10.1016/S0142-9612(03)00206-0.
Ghavempour, S., Mortazavi, S.M., 2015. Microwave curing for applying polymeric nanocapsules containing essential oils on cotton fabric to produce antimicrobial and fragrant textiles. Cellulose 22, 4065–4075. https://doi.org/10.1007/s10570-015-0765-1.
Gilman, J.W., 1999. Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites. Appl. Clay Sci. 15, 31–49. https://doi.org/10.1016/S0169-1317(99)00019-8.
Gilman, J.W., Jackson, C.L., Morgan, A.B., Harris, R., Manias, E., Giannelis, E.P., Wuthenson, M., Hilton, D., Phillips, S.H., 2000. Flammability properties of Polymer -Layered-silicate nanocomposites. Polyypropylene and polyurethane nanocomposites. Chem. Mater. 12, 1866–1873. https://doi.org/10.1021/cm001760u.
Gimenez-Arzua, A., Silvestre, J.F., Mercader, P., De la Cuadra, J., Ballester, L., Gallardo, F., Pujol, R.M., Zimerson, E., Bruze, M., 2009. Shoe contact dermatitis from dimethyl fumarate: clinical manifestations, patch test results, chemical analysis, and source of exposure. Contact Dermatitis 61, 249–260. https://doi.org/10.1111/j.1600-0536.2009.01628.x.
Goswami, P., Ganguli, J.N., 2012. Evaluating the potential of a new titanina precursor for the synthesis of mesoporous Fe-doped titanina with enhanced photocatalytic activity.
