Antimicrobial bioactive materials and treatments for leather preservation

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Leather materials are good media for the growth of various microorganisms. The damage resulting from the activities of micro-organisms such as bacteria, yeasts and moulds is a big problem faced by the leather sector. In order to combat microbial growth, it is necessary to find out an antimicrobial material for leather that is both economical and environmentally friendly. In this chapter, the natural bioactive materials such as plant extracts, essential oils, chitosan and its derivates and the effects of these antimicrobial materials, and antimicrobial treatments applied on leather to prevent microorganism activity are described.

Keywords: Antimicrobial, Leather, Chitosan, Essential oil, Plasma technology

1. Introduction

Various species of micro-organisms are known to occur on leather material and the damage resulting from the activities of micro-organisms such as bacteria, yeasts and moulds is a big problem faced by the leather sector. Leather materials can not only be carriers of microorganisms, but also are good media for the growth.

Bacteria, yeasts and moulds segregate enzymes able to degrade macromolecules like proteins, fats and carbohydrates to smaller units that can be absorbed through the cell membranes and serve as nutrients [1]. Several extracellular enzymes may remain active long after the death of their producer organisms [2]. When microbes grow to high numbers in leather, they can cause unwanted odour and compromise the health. These problems are caused mostly by bacteria in the processes before tanning, while in tanning and later processes, fungi cause the most problems.

The fungi hydrolyse the oils in the leather and can cause the leather to harden. The leathers may show no visible signs of damage, but their resistance to stretching is lower and they are damaged in terms of their usage characteristics, but the main damage is staining and bad smells in the places of production [3]. Fungi mostly show activity on the surface of leathers, and although they are mostly removed in later processing, the damage they do cannot be hidden. It has been found that different kinds of fungi in pickled and chromed leathers cause different pigmentations [4]. Fungal growth on pickled hides, wet blue leather and vegetable-tanned leather can cause some of the defects such as stains, protein material loss, deterioration of grain layer, and modification of the physical and mechanical properties of resistance [5].

In order to avoid microbial damages, the use of fungicides is recommended during the pickling stage [6]. However, a various antimicrobial agents that used in leather industry have high costs and an adverse effect on the environment. Besides, the various biocides with active substances which are on the market do not have the same effects on every microorganism species. For this reason it is important to determine which species is causing damage and to select and use the specific type of biocide which will inhibit that particular species. In addition, a good leather biocide should have high activity and a broad antimicrobial spectrum, will not conflict with the leather or the processing chemicals, will be stable on the leather, not leach colours, be acceptable environmentally, will be of low toxicity to people, and be reasonably priced.

2. Tannins, plant extracts and essential oils used for leather preservation

Some substances used in tanning process have an adverse effect on growth of microorganisms, so that sulphide-lime liquors are inhibitory because of high alkalinity and the sulphide present. Chromium formulations and tanning agents, especially in fresh or more concentrated solutions, prevent especially the growth of bacteria. Nevertheless, the effect of these agents varies greatly and depends on whether they are of vegetable or synthetic origin, as well as on the type of tannin [7].

Tannins of quebracho, mimosa, gall-nut, chestnut and valonia were added to the float for 8h and 24h soaking processes in order to examine the effect of these tannins on bacteria. Subsequently, gall-nut and chestnut extracts were observed to be effective against bacteria in the float during 8h soaking process, while gall-nut was found to be more effective than other vegetable tannins in 24h soaking period [8].

Tannic acid (TA) is a vegetable tanning material showing no toxicological effect in comparison with the biocides used in the leather industry which cause harm to human health and to the environment. Tannic acid was added in varying proportions to the pickling float and it was found that a proportion of 3% of TA to the pickling bath was more effective than other concentrations against the micro-organisms such as *Bacillus cereus* (ATCC 11778), *Salmonella typhimurium* (CCM 5445), *Proteus vulgaris* (ATTC 6889), *Enterobacter aerogenes* (ATCC 13048), *Pseudomonas* *aeruginosa* (ATTC 27853), *Escherichia coli* (ATTC 25922), *Staphylococcus aureus* (ATCC 6538), *Neisseria canis*, *Aspergillus niger*, *A. fumigatus*, *A. flavus*, *Penicillium granulatum*, *P. granulosum*, *Geotricum candidum*, *Yarrowia lypolitica* and *Rhodotorula rubra* (DSM 70403), and it was determined that tannic acid could be used in the pickling process as an alternative antimicrobial agent [9].

In other study, tannic acid (0.5%-1%) has performed better antimicrobial activity during the first 8 hours of soaking process when compared to commercial bactericide. Besides, it was advised to apply the tannic acid in lower concentrations with the maximal inhibitory effect on microorganisms due to its polyphenolic structure [10].

The antimicrobial activity of eight different commercial vegetable tanning extracts (1% and 5%) used in the leather industry against bacterial and fungal isolates from tannery processes such as beamhouse, tanning, and post-tanning processes was determined. The antimicrobial activity of the extracts was assessed by the disc diffusion method. It was observed that all of the extracts were more effective against the bacterial isolates than the fungal isolates [11].

From the ancient time people have used the unique properties of plants or plant extracts in the treatment of wounds or injuries. Some plants could prevent the microbial growth due to the phenolic compounds they consist of. Nowadays, most of medicine contain plant extracts or essential oils. So far, there are several studies in the literature dealing with the development of antimicrobial leather using plant extracts or essential oils.

Along with its use in the fields of medicine and cosmetics, the plant *Aloe vera* has been used in the textile and leather sector for its antibacterial and antiviral properties. The researchers showed that leathers treated with ethanol and water-based extracts of *Aloe vera* had antimicrobial effects against various Gram positive and Gram negative bacteria as well as against *C. albicans* [12].

The antimicrobial activity of samples of raw skin and chrome tanned leather treated with *Pseudeverina furfuracea* (L.) Zopf acetone and chloroform extracts was tested against seven bacteria, six fungi and *Candida albicans*; and it was reported that both extracts showed inhibition zones of between 11.0 and 31.0 mm for the raw skin and between 11.2 and 29.0 mm for the chrome tanned leather, for the bacteria and fungi respectively [13].

The effect of *Quillaja saponaria* saponin, a plant-derived biosurfactant, as an antimicrobial soaking agent in leather manufacturing was investigated and it was found that the total protein content of soaking liquor was increased at higher sapogenin contents in spite of decreased microbial growth which was an indication of antimicrobial soaking character of saponins [14].

The chlorophyll extracted from spinach leaves was used in the soaking process and its effect on the total aerobic mezophyll bacteria was determined in comparison with the effect of bactericides [15].

Bayramoğlu (2004) researched the use of the essential oils of *Origanum minutiflorum* (oregano), *Laurus nobilis* (bay laurel), *Foeniculum vulgare* (fennel) and *Schinus molle* (California pepper) against the fungi which constitute the greatest problems in leather production, *Aspergillus niger*, *Alternaria alternata*, *Penicillium rubrum* and *Trichoderma viride*. According to the findings of the study, the essential oil of oregano had a greater antifungal effect than the others, and leathers treated with 2% oregano oil were found to be even more resistant to certain experimental fungi than were samples containing commercial fungicides [16].

In another study, an investigation was made of the antibacterial effects of wet-blue sheepskins treated with the essential oils of *Origanum minutiflorum* (oregano) and *Schinus molle* (California pepper) against the bacteria *B. cereus* (CCM 99), *P. aureginosa* (ATCC 27853), *E. coli* (ATCC 27999) and *S. aureus* (ATCC 6538). It was found that oregano oil had a greater antibacterial effect than California pepper oil, and that leathers treated with 1% oregano essential oil were resistant to gram-positive bacteria (*B. cereus and S. aureus*) [17].

1%, 2%, 5% of storax and 1% essential oil of *Origanum onites* mixed with the storax were tested for their antimicrobial activity in comparison with 50% organosulfur compound as commercial bactericides commonly used in the leather industry. It was reported that storax has an antibacterial effect in soaking with increasing concentrating rates and when it was mixed with the oil of oregano, the bactericidal activity was increased. It was found that Sığla storax and oregano essential oil has synergic effect and their mixture can be used as bactericidal agents in leather industry [18].

The essential oil of *Myrtus communis* was used as a bactericide in the soaking process. The effect of 1% myrtle oil was compared with that of a commercial bactericide typically containing 7-25% phenol, 4-chloro-3-methyl. It was reported that *Myrtus communis* oil has an antibacterial effect in soaking and is suitable for the use in leather industry [19].

Samples of shoe leather were immersed in a 5% extract of orange seed oil and agitated for four hours in an orbital shaker. Afterwards, the samples were left in the open air and the growth of fungi on them was observed each day. It was recommended as a result of the study that this oil, which had been shown to have a protective effect against fungi which could cause damage to leather products, should be used at various stages in leather processing or added to shoe polish or other leather treatment agents [20].

Treatment with plant essential oils such as eucalyptus and lavender (*Eucalyptus globulus* and *Lavandulae officinalis*) was investigated as alternative preservatives for various tanned leather. The *L. officinalis* essential oil ensures better antibacterial effect against tested bacteria (*E. coli, P. aeruginosa* and *B. cereus*) than that of *E.globulus*. The received results have shown that leather preserved with 2-(thiocyanomthylthio)benzothiazole (TCMTB) have weaker protection after 24 weeks comparing with the samples treated with essential oil of lavender [21].

The essential oils included cinnamon oil, garlic oil, clove oil and star anise oil were tested in comparison with 2-Thiocyano-methylthlobenzotiazole (TCMTB) containing commercial fungicide to inhibit the growth of moulds on wet-blue leather. It was reported that for garlic oil, clove oil and cinnamon oil, the dosage of 2% is enough to inhibit the growth of all the tested moulds on wet-blue whilst for star anise oil, more than 2% is required. Essential oils show different inhibitory effects on different moulds and in general, *Penicillium citrinum* and *Alternaria alternata* are the species most sensitive to the essential oils, *Aspergillus niger* is rated second, and *Rhizopus stolonifer* is the most resistant and most difficult strain to inhibit by the four essential oils. It was stated that considering the advantages of being eco-friendly natural products and the acceptable economic cost, the essential oils extracted from traditional Chinese medicinal materials have potential as fungicides to be used in leather industry [22].

Gram-positive bacteria were found to be more sensitive to the essential oils of thyme (*Thymus vulgaris*) than Gram-negative bacteria. The bacteria *P. aeruginosa* had a low sensitivity to the action of the selected essential oils of thyme, but the leather samples treated with the essential oils of thyme remained resistant to the action of these bacteria. The leather preserved with TCMTB had weaker protection after four weeks compared to the samples treated with the essential oil of thyme when the amount of the used essential oil was not less than 3% of the wet-blue mass [23].

With the development of encapsulation technology incorporation of essential oils in microcapsules has been developed. A natural polymer gelatine was used for the production of an antifungal lining leather because of its biological degradability and its porous structure as a microcapsule wall material, a material which contained the volatile oil of *Melaleuca alternifolia* as an active ingredient which has antifungal properties against fungi of the feet. It was found that the lining leather which was obtained by using an antifungal agent which was suitable for microencapsulation had a longer lasting antifungal effect against the test micro-organisms which caused fungal infections of the foot [24].

Microencapsulation is an effective method to protect these functional natural biocides from reactions with moisture, light, and oxygen. Thus, incorporation of melamine-formaldehyde microcapsules containing *Melaleuca alternifolia* oil (tea tree oil) as a natural biocide for footwear applications was evaluated. Tea tree oil showed suitable antimicrobial activity against different microorganisms found in foot skin and worn shoes such as *E. coli, B. subtilis, K. pneumoniae, S. aureus* [25].

The microencapsulated clove oil (MCO) shows a good controlled-release property. Results of antimicrobial tests reveal that, although the minimum inhibitory concentrations (MICs) of the microcapsule product are higher than that of crude clove oil, it still has sufficient antimicrobial activity against bacteria, yeasts and moulds. When the PU-MCO was applied in retanning of garment leather, the leather shows good antimicrobial property which persisted for a long time at room temperature and was not significantly affected by perspiration or washing because of the firm physical and chemical combination between the PU (polyurethane) wall material and leather fibres. Thus, a feasible method to prepare an antimicrobial leather with a non-toxic nature and long-term effectiveness was provided by using the microencapsulated natural clove oil [26].

Essential oils have a great potential for preventing micro-organism damage to leather and leather products. As a natural organic material, they can be broken down biologically, and as such present little or no environmental threat. However, they are known for being difficult and expensive to extract.

3. Chitosan and its antimicrobial usage in leather processing

Chitosan, a non-toxic biopolymer with an antimicrobial and antioxidant effect, has recently been used in slimming pills, and has widespread usage because of its properties of absorption and controlling bleeding. It has recently been used in the leather industry as an auxiliary material and in the dyeing process [27-29].

Though the antimicrobial activity of chitosan salts against various bacteria and fungi is known, it is only in the last couple of years that attempts have been made to use chitosan salts on leather materials [30-31].

Antimicrobial leather materials were developed taking advantage of chitosan intrinsic antimicrobial activity and film forming capacity. Among different coating technologies such as drum, calender and spray, which were applied considering the specificities of the leather tanning industry, the best results achieved with the drum. Considering chitosan price (economic reasons) and the obtained results (antimicrobial activity and coating effectiveness), the impregnation in the drum using a chitosan content of 1% (w/v) in a formic acid solution during 2 h, is proposed as the best option for obtaining leather with antimicrobial capacity. Moreover, chitosan coating conferred antimicrobial properties to the treated leathers, with the higher capacity to eliminate *E. coli* [30].

Chitosan formate (CF) retained the original chitosan structure and antimicrobial activity was effectively applied to tanned leather resulting in enhanced antibacterial and antifungal activities of the substrate. Results indicated that the treated leathers showed broad-spectrum antimicrobial activity against all test microorganisms between proportions of 2.0 and 5.0% CF without any significant changes in the leather's physical properties [31].

Poly(ethylene glycol)-grafted chitosan (PEG-g-CS) was prepared as water borne coating for leather surface and the antimicrobial activity of PEGylated CS coating was investigated by measuring its minimum inhibitory concentration and the inhibition zone of coated leather against Gram-negative *E. coli* and Gram-positive *S. aureus*, respectively. Compared to CS coating, such PEGg-CS coating exhibited better antimicrobial property, which indicated the synergetic effect of the antimicrobial property of CS and the antiadhesive property of PEG. It was suggested that PEGylated CS copolymer can be used as efficiently antimicrobial coating for leather product [32].

4. Plasma technology and its antimicrobial effect on the leather surface

Recently, a new technology as plasma technology has gained a great attention. Plasma shows a synergistic sterilisation effect composed of three phases. In the first phase, UV radiation from the plasma breaks up the DNA which is the genetic material of the micro-organism. In the second phase, the chemical compounds in the micro-organism structure which were broken up by the UV radiation separate into chemically unstable volatile molecules (CO, CHx). However, the reactive molecules under the influence of the plasma react with the volatile atoms from the micro-organisms, and stable compounds are formed. During the plasma process, the oxygen in the air is changed under the influence of the plasma into O_3, the water vapour in the air and ozone form H_2O_2 by photodegradation, and this hydrogen peroxide changes to -OH as a result of gene photodegradation. In the third phase, these-OH ions create an oxidative stress effect known as lipid peroxidation. This causes breakdown of the micro-organism's cell membranes and cell walls, which are formed from lipids, fatty acids and proteins. The synergistic effects created vary with increasing duration of plasma [33-37].

Examining the results of the percentage reduction test method chosen to test the antibacterial characteristics of leather, it was seen that a considerable reduction was obtained in the number of colonies on leather exposed for 15 minutes to a plasma process with argon gas, and that the plasma processed leather gained an effective antibacterial quality [38].

It is reported that when plasma processing was applied to leather in the form of corona discharge, an antibacterial effect of over 70% was shown against the bacteria *S. aureus* and *E. coli* according to AATCC test standards [39], and in another study corona discharge and silver nano particles applied in combination had a better antibacterial effect against the bacteria *S. aureus* and *E. coli* on goatskins [40].

A key advantage of plasma sterilization is the ability to achieve sterilization at temperatures less than 50°C. At these temperatures, sensitive structures contaminated with microbials which cannot be exposed to autoclave and oven temperatures will retain their physical attributes [41]. Plasma sterilization also does not expose process operators to harmful gases such as ethylene oxide [42].

5. Antimicrobial materials and mechanisms of action

Antimicrobial agents currently used in leather industry are generally called biocides or disinfectants (due to the application on inanimate objects or surfaces) and take place in the group of preservatives. An antimicrobial material is defined as one which kills micro-organisms or prevents their reproduction. The most important compounds which perform these functions include those below:

- Phenol and its derivatives
- Alcohols
- Metals or heavy metals
- Oxidizing agents
- Isothiazolinones
- Quaternary ammonium compounds
- Alkylating agents
- Chitin and chitosan

Antimicrobial materials differ from one another in terms of the following characteristics as chemical structure, stability, effectiveness, toxicity, reliability and cost.

Metals such as mercury, copper and silver, either as metals or as metallic salts, have antimicrobial effects. Mercury however is very toxic to humans. Copper salts are generally green, and are not desirable for many uses. Silver has been used as an antimicrobial material for 2000 years: the Romans are known to have used silver coins in their drinking water vessels to keep the water fresh and clean [43].

Antimicrobial materials are not all active by the same mechanisms. For this reason it is necessary to understand the differences between them in order to make a suitable choice. Antimicrobial materials exhibit their activities by the following mechanisms [44]:

- Denaturation of proteins
- Disruption of cell wall synthesis
- Disruption of cell membrane permeability and functions
- Disruption of nucleic acid function
- Metabolic antagonistic effects.

Antibacterial agents can affect bacteria in different ways, many of which are not properly understood. Nevertheless, it is possible to make some generalizations. At high concentrations, many agents disrupt the colloidal structure of cell proteins and cause them to coagulate. Others inhibit the DNA replication and transcription by damaging DNA. Some of them specifically break up cell membranes under certain conditions. Many of the cell's basic enzymes carry sulfhydryl (-SH) groups, and these groups can only function in a free and reduced state. It is for this reason that agents which oxidize the sulfhydryl groups or bind to them have a strong preventive effect. Finally, many agents may be effective by antagonistic chemical effects or by disrupting a number of specific enzymatic reactions.

The overall description of the mechanisms is given below:

Protein coagulation

Most or all cell proteins with an enzymatic structure are normally very thinly distributed and are in a colloidal state. If the characteristics of the protein are changed to a significant extent by an antibacterial agent, the proteins coagulate and become non-functional. The changes which occur when white of egg is heated or when milk goes sour are good examples of protein coagulation. However, little is known of the chemical changes which occur before or along with these events. Alcohols and some heavy metals could exhibit this mechanism.

Disruption of the cell membrane or cell wall

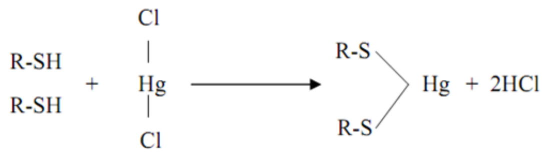
Cell membranes function as a selective barrier, allowing certain dissolved substances to pass, but preventing others. Some compounds are actively passed through the membrane and become concentrated in the cell. At present, the mechanisms which play a role in this are not completely understood, but it is clear that the presence of a healthy undamaged cell membrane is necessary. For this reason, materials collecting on the surface of the cell change the physical and chemical properties of the membrane, and either kill the cell or stop it dividing by disrupting its normal functions. The cell wall functions as a protective structure, protecting the cell from osmotic dissolution. For this reason, agents which disrupt the wall (for example lysozyme) or prevent its normal construction such as penicillin cause cell breakdown. It has been known that phenols depending on the compound and quaternary ammonium compounds are membrane active agents.

Removal of free sulfhydryl groups

Enzyme proteins carrying cysteine have side chains ending with sulfhydryl groups. At the same time, at least one key enzyme has a free sulfhydryl group. Enzymes like this do not function when the sulfhydryl groups are free and reduced. Oxidizing agents disrupt metabolism when they change sulfhydryl groups which are next to them into disulphide links.

$$\text{R-SH + HS-R - 2H R-S-S-R} \quad (1)$$

The ions of many metals, such as mercury, have a damaging effect by joining with sulfhydryl groups in this way:



(2)

Because there are many sulfhydryl enzymes in the cell, oxidizing agents and heavy metals cause damage.

Chemical antagonism

A chemical agent interfering with the normal reaction between a particular enzyme and its substrate is known as chemical antagonism. When such substances join with a part of a holoenzyme, it prevents the normal substrate from joining with the holoenzyme. The substance forming the antagonistic effect joins with the enzyme because it has a particular chemical relationship with a basic region of the enzyme. Enzymes perform their catalytic functions because of their relationships with their own natural substrates, and for this reason any compound which closely resembles the substrate in structure attracts the attention of the enzyme in the same way.

If this relationship is strong enough, this material with the similar structure takes the place of the normal substrate and prevents the correct reaction from taking place. In the case of many holoenzymes, there is a mineral ion which forms a bridge between either the enzyme and the coenzyme or the enzyme and the substrate. Chemical agents which can join quickly with these minerals prevent the coenzyme or the substrate from joining. For example, carbon monoxide and cyanide join with the iron atom in the porphyrin enzyme and thereby obstruct respiration in this enzyme.

For simplicity, antagonistic chemical substances can be divided into two groups, the antagonistic effects of energy-creating functions and the antagonistic effects of biosynthetic functions. In the first of these, there are poisons of respiration enzymes like carbon monoxide and cyanide, and oxidative phosphorylation poisons like dinitrophenol. In the second group, there are substances which are structurally similar to amino acids which are the building blocks of proteins and nucleotides which form nucleic acids. In some conditions, an antagonistic material only prevents the joining of a normal metabolite. In other conditions, the antagonistic material takes the place of a normal metabolite in the structure of a large molecule, and causes it to become non-functional [45].

It is known that microorganisms can adapt to a variety of environmental physical and chemical conditions, and can gain a resistance to extensively used antimicrobials. There is also the challenge of how to design the use of antimicrobials on inanimate substances or surfaces. Many of biocides may be used singly or in combination in a variety of products which vary considerably in activity against microorganisms. Besides, the antimicrobial activity can be affected by many factors such as formulation effects, presence of an organic load, synergy, temperature, dilution, and test method. The resistance of microorganisms to antimicrobials and high costs for overcoming this problem as well as for developing of new effective antimicrobial agents should be taken into consideration in all the fields including leather industry.

6. Conclusion

The collagen network of leather material provides an ideal environment for the rapid growth of bacteria and fungi. Microbial growth leads to material degradation and damage that sometimes irreversible. In order to combat microbial growth, researchers have investigated bioactive antimicrobial materials such as plant extracts, essential oils and chitosan which are environmentally friendly materials and could be used in leather industry. In addition, it was shown that plasma treatment can also be applied to obtain the leather with antimicrobial surface. At last, antimicrobial materials are active by different mechanisms which are described in this chapter in detail.

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