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Protein Fibre Surface Modification

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1. Introduction

Many natural fibres, including wool, cashmere and silk, are protein-based materials; the dry weight of wool is almost entirely derived from proteins (Maclaren & Milligan 1981). As such, they possess an inherent structural and chemical heterogeneity not found in synthetic polymers. Although typically less heterogeneous than biological fibres, the rapidly emerging range of commercially available protein-based biomaterials also contain a wide range of functionality derived from their constituent primary and secondary protein structure.

The response of fibres to processes such as dyeing and finishing treatments correlates directly to their structural and chemical properties, and this is particularly true for surface treatments. Due to its barrier function in the fibre, modification of the surface has a profound impact on processing and performance. Keratinous fibres such as wool and cashmere have an outer lipid layer which results in a hydrophobic surface. Recently a range of innovative and novel fibre surface technologies has been developed, many of which involve altering surface properties by the removal of the lipid layer, which exposes a proteinaceous surface with a variety of reactive chemical moieties. Treatments that can be covalently bound to fibre surface components, rather than simply physically applied to the surface, offer the potential for superior durability.

The surface modification of proteinaceous fibres has a long history. These include plasma applications, which expose and generate functional groups on the protein surface, etching into the surface of the cuticle scales, to improve properties such as surface wettability, dyeability, shrink-resistance and felting-resistance. Chemical approaches utilised include ozone treatments, which cause oxidation of the surface and altered ionic balance, leading to a more plastic and reactive fibre surface and shrinkage control; chlorination, which improves sorption characteristics and reduces shrinkage; hydrogen peroxide treatment; and acid anhydride acetylation of silk and wool, which improves the textile response to dyeing, shrink resist, and setting treatments. Enzymatic treatments have been utilised to decuticulate the surface and improve properties such as shrink resistance. More recent developments include reaction of functional chemical agents or branched molecules to exposed reactive groups on the fibre surface, enabling the attachment of covalently-bound smart treatments, or the amplification of reactive groups for increased functionality.

This chapter outlines developments in the area of targeted surface modification of protein-based fibres and textiles, including summarising applications and future directions. It is not

intended to cover every aspect of fibre surface modification, but rather focus on key types of surface modification that exploit the unique properties of proteinaceous fibres.

2. Physical modification

The increasing pressure for environmentally friendly processing approaches has motivated the textile industry to exchange aqueous treatments involving potential chemical pollutants and effluents with high adsorbable organic halide (AOX) contents for physical 'dry' processes, such as plasma and UV/ozone treatment. With respect to dyeing, the nature of physical modification to protein fibre surfaces and where this occurs in production are important and must be taken into consideration.

2.1 Plasma

Plasma treatments, which utilise a gaseous electrical discharge, are reported to be surface specific for protein fibres (Höcker 2002) and offer significant potential in terms of being simple, clean, solvent-free and relatively inexpensive. These treatments can be used to modify surfaces by the deposition of polymers or can 'clean' the surface by surface etching. Plasma treatments are increasingly replacing wet (chemical) textile treatments to achieve outcomes such as shrink-resistance and improved dyeability. Plasma and corona treatments oxidise the surface of protein-based textiles, generate chemically active radicals, induce functionalisation, and etch the surface (Höcker 2002; Ceria *et al.* 2010). Those utilising certain gases may result in the deposition of atoms from those gases, such as fluorine (Höcker 2002). The effects of plasma treatments are restricted to the wool surface, and are therefore unlikely to result in changes to the bulk properties resulting from damage to the interior of the fibres.

Within the context of the textiles industry, plasma means the products of the interaction of an electromagnetic field with gas; namely, a partially ionised gas that contains ions, electrons and neutral particles (Kan & Yuen 2007). At gas pressures similar to atmospheric pressure and high voltage, corona discharge is generated. At gas pressures of 0.1-10 MPa at lower voltage, glow discharge is generated (Rakowski 1997; Kan & Yuen 2007). Atmospheric corona discharge plasmas lack uniformity due to their filamentous nature (Prat *et al.* 2000). Glow discharge is most commonly referred to when plasma textile processes are described. Many plasma treatments have employed low pressure (vacuum) systems to keep the plasma stable, called cold plasma or non-equilibrium plasma. Lowered pressure also assists with the penetration of plasma effects through the thickness of a textile (Poll *et al.* 2001). Atmospheric pressure plasma systems, however, have an industrial advantage for large-scale textile applications because of the expense, time and space involved in maintaining a vacuum (Sugiyama *et al.* 1998; Demir 2010). These require a source frequency of 1-20 kHz and a carrier gas of helium (Prat *et al.* 2000). Microwave-induced glow-discharge plasma can be kept stable at atmospheric pressure (Sugiyama *et al.* 1998). Several types of discharge may be used to generate plasma, including direct current discharge, radio-frequency discharge, and microwave.

In wool, plasma treatment oxidises and partially removes (ablates) the hydrophobic surface lipid layer (both the loosely adhering lipids and those covalently bound). The disulfide bonds in the surface protein layer of wool (epicuticle) are also oxidised (Höcker 2002). The surface is the only part of the fibre affected; this becomes rougher (surface area increases), while its protein contents are hardly affected (Höcker 2002). The free radicals that remain on the wool surface following ablative plasma treatment stimulate the formation of functional groups and of bonds between the fibre surface and customised surface coatings (Kan &

Yuen 2007). As an alternative to ablation, with the use of carbon- and hydrogen-rich plasma gases, polymers may be deposited on the surface (Kan & Yuen 2007).

The physical changes (roughening) caused by ablative plasma treatments result in altered yarn strength, frictional and spinning properties and decreased felting behaviours (Höcker 2002). A detrimental effect is a firm or harsh handle (Rakowski 1997). The chemical changes (surface oxidation and the loss of surface-bound fatty acids) result in improved dyeing and resistance to shrinkage (Rakowski 1997). Shrink-resistance is obtained at levels comparable to those obtained from other treatments (like chlorination, reduction and resin application) by the addition of resin, causing surface smoothing. Dyeing depth, speed and bath exhaustion are also improved (Höcker 2002). Atmospheric pressure plasma treatment is also seen to improve the dyeability of mohair (Demir 2010). An unusual application of wool plasma treatment is the deposition of antibacterial polymers for woollen wound dressings using fluorinated post-discharge plasmas (Canal *et al.* 2009).

Due to the wide variety of techniques utilised to treat protein-based fibres with plasma, it can be difficult to compare the effects reported by different groups. Relating this problem to dyeing, Naebe *et al.* showed that the effect of plasma on dyeing depended on the dye used – with hydrophobic dyes unaffected by plasma treatment, and hydrophilic dyes greatly affected (Naebe *et al.* 2010). One general feature of plasma-based approaches to modifying the surface of protein materials is the high level of surface oxidation observed after treatment (Meade *et al.* 2008b).

Hydrophilicity can be a desirable attribute for textiles, allowing improved dyeing, and enhancing comfort and wear properties. The natural hydrophobic surface of wool makes it practically impossible to print wool fabrics without prior treatment. Plasma treatment improves fabric wettability, and also reduces felting (Kan & Yuen 2007). This can be accomplished by the removal of surface lipids (oxygen plasma) or by the deposition of hydrophilic monomers, such as the plasma-assisted deposition of acrylic acid (Kutlu *et al.* 2010). Aside from dye properties and processing, the wool dyeing rate is primarily determined by fibre morphology and by the state of adsorbed water in the fibre (Ristić *et al.* 2010). These properties may be modified by a variety of surface treatments. When the outer lipid layer is even partially removed from wool, the wettability and dyeing rate are reduced. Plasma treatments remove this lipid layer and generate functional groups (such as thiols) that are more reactive to certain dyes. Corona discharge has been reported to incorporate oxygen atoms into the fibre and enhances wettability, which increases the acid-dye intensity of printed fabrics (Ryu *et al.* 1991). Combining plasma treatments with chitosan results in increases in colour intensity and dyeability over those observed with either treatment alone (Ristić *et al.* 2010).

2.2 UV/Ozone

UV/ozone (UVO) treatments also achieve textile improvement effects able to compete with aqueous treatments. UV radiation at certain frequencies generates atomic oxygen and ozone from molecular oxygen (at 184.9 nm) and atomic oxygen from ozone (at 253.7 nm). Organic hydrocarbons may also be excited at 253.7 nm. Textiles placed close (within 5 mm) of these UVO sources are cleaned by the reaction of UV-excited surface molecules with atomic oxygen. The volatile reaction products desorb from the surface (Shao *et al.* 1997).

This surface treatment results in more wettable wool, which improves dyeing and printing properties, even at low temperature (Xin *et al.* 2002). The wool also yellows, although this can be lessened when the process is combined with peroxide pad bleaching (Shao *et al.*

2001). This is due to oxidation of the surface layers: Cysteic acid is detected, as disulfide bonds are broken. Carboxylic acid and carbonyl groups are detected at higher levels than after chlorination (Shao *et al.* 1997). The lipids at the surface are modified or volatised. UVO treatment results in a colour yield and dyeability comparable to that obtained after chlorination, permitting printing (Shao *et al.* 1997; 2001).

3. Chemical modification

3.1 Bleaching
Wool bleaching affects the fibre surface, but is not performed specifically to produce functionalised surfaces, so will not be discussed at length in this chapter. Agents utilised in protein-fibre bleaching include hydrogen peroxide, sodium borohydride, sodium bisulfite, thiourea, oxalic acid and blue light (Arifoglu *et al.* 1992; Millington 2005; Yilmazer & Kanik 2009). Bleaching is sometimes combined with additional surface modification techniques such as scale removal (Chen *et al.* 2001).

3.2 Acylation
Acylation may provide a route to water-proofing of materials such as wool and silk. Acylation agents include dodecenylsuccinic anhydride and ctadecenylsuccinic anhydride, anhydrides such as succinic anhydride and phthalic anhydride, and solvents including dimethyl sulfoxide and dimethylformamide (Arai *et al.* 2001; Davarpanah *et al.* 2009).
Wool is noted to gain more weight and acyl content than silk. Silk tensile properties are unaffected, whereas wool displays greater extensibility. Silk and wool both increase in water repellency and decrease in moisture regain and water retention. Deposits are observed (via SEM), which are attributed to the modifying agents (Arai *et al.* 2001). Acylation provides an enhanced surface for the grafting of chitosan to wool or silk to provide antibacterial and anti-felting properties and superior dyeing ability in an environmentally friendly fashion (Davarpanah *et al.* 2009; Ranjbar-Mohammadi *et al.* 2010).

3.3 Chlorination
Chlorination is performed to impart shrink-resistance to wool fibre, sometimes in combination with the applications of resins such as Hercosett or Nopcobond (Van Rensburg & Barkhuysen 1983; Roeper *et al.* 1984). As an industrial process, this is under regulatory pressure because of the AOX released into the waterways, raising environmental concerns.
Chlorination mixtures are generated by the combination of hypochlorite with sulfuric acid, or, for a milder treatment, chlorine gas may be dissolved in water (Van Rensburg & Barkhuysen 1983). Chlorination affects the surface lipid layer. Dyeing properties are also affected due to increased surface adsorption and alterations to the surface lipid layer (Ottmer *et al.* 1985; Baba *et al.* 2001). The changes in surface chemistry lead to more rapid dye exhaustion and dye penetration (Jocic *et al.* 1993).

3.4 Other
Potassium permanganate treatment of wool fibres reduces scale height and smoothes the cuticle, as assessed using 3D-SEM. This is desirable for the elimination of felting and to impart shrink resist. Potassium permanganate treatment provides a more even effect than a comparable proteolytic enzyme treatment (Bahi *et al.* 2007).

3.5 Delipidation

Keratin fibres such as wool, human hair and cashmere are covered in an outer lipid layer which is covalently bound to the surface to form a hydrophobic barrier. The major component of the surface wool lipids is 18-methyleicosanoic acid (18-MEA). 18-MEA is attached to the underlying protein mainly via covalent thioester bonding. A range of treatments have been reported to cleave the thioester bonds to form thiols on the epicuticle surface (Meade *et al.* 2008b). The generation of reactive surface sulfhydryl groups, with the sulfur able to act as a strong nucleophile, make these thiols attractive potential sites for subsequent covalent attachment of novel surface modifications (Meade *et al.* 2008a). Most research and development in this area has been performed with wool, but the principles have potential for application in other mammalian fibres used in textiles.

Wool fibres are comprised of a core of cortical cells surrounded by an outer sheath of overlapping cuticle cells. Each cuticle cell is enclosed within a resistant membrane termed the epicuticle (Höcker 2000). The epicuticle of wool covers the cuticle, and is comprised of both proteins and lipids (fatty acids); the hydrophobicity of the wool surface is largely attributable to this external lipid layer. The fatty acid component of the epicuticle accounts for approximately quarter of the epicuticle mass, with the surface-bound fatty acids forming a hydrophobic surface layer (Meade *et al.* 2008b). The branched chain fatty acid 18-methyleicosanoic acid (18-MEA) has been identified as the major lipid component of the wool surface, comprising approximately 65-70% of the surface lipid content (Negri *et al.* 1991; Ward *et al.* 1993). This 18-MEA is covalently bound to surface proteins via thioester linkages to cysteine, with the epicuticle estimated to have a content of 35% half-cystine (Negri *et al.* 1993; Evans & Lanczki 1997). The identity of the proteins that the surface lipids are bound to, forming proteolipids, is not yet well understood (Dauvermann-Gotsche *et al.* 1999). Thioesters are a relatively reactive group that can be cleaved relatively readily through nucleophilic substitution reactions.

If this outer lipid layer is removed in a controlled manner, it is possible to expose the underlying proteinaceous surface so that there are a variety of reactive functional groups (including hydroxyl, carboxyl and amine moieties) available for potential covalent attachment of surface treatments. There are various alkaline reagents that have been used to release covalently bound surface lipids from wool, yielding a hydrophilic and anionic surface with an increased frictional coefficient (Dauvermann-Gotsche *et al.* 2000).

The use of alcoholic or aqueous alkali conditions cleaves the thioester bonds to form a substituted lipid and a thiol at the epicuticle surface (Negri *et al.* 1991; 1993; Dauvermann-Gotsche *et al.* 2000) The chemical mechanism for nucleophilic substitution of the thioester bond is shown in Figure 1 [modified from Meade *et al.* 2008b].

Alcoholic alkali treatments use sodium butoxide, potassium tert butoxide, potassium hydroxide and hydroxylamine in water or in an anhydrous solvent such as tert butanol, dehydrated butanol, or ethanol (Leeder & Rippon 1983; Brack *et al.* 1996; Taki 1996; Meade *et al.* 2008b). These treatments are applied to control felting shrinkage, to improve polymer application, dyeing and printing, shrink resistance, and electrical conductivity (Leeder & Rippon 1983; Leeder *et al.* 1985). Alcoholic alkali treatment is less damaging than chlorination, as the effects are limited very much to the surface. The cortex is assumed to be unaffected; only the cuticle is removed, or de-scaled (Taki 1996). Lipid material is removed and a polar surface is generated. Covalently bound lipids are removed from the surface, revealing the polar surface of proteins beneath (Leeder & Rippon 1985; Brack *et al.* 1996; Meade *et al.* 2008b). As potassium t-butoxide is not found to be as good at removing the

lipids as is the smaller potassium hydroxide, it is speculated that some lipids may be trapped within the proteins and that agent access plays a part in this difference. Removal of lipids may be made easier by prior fine scale damage (Brack *et al.* 1996). Functional agents revealed by removal of the lipid layer are available for covalent attachment of chosen treatments (Meade *et al.* 2008).
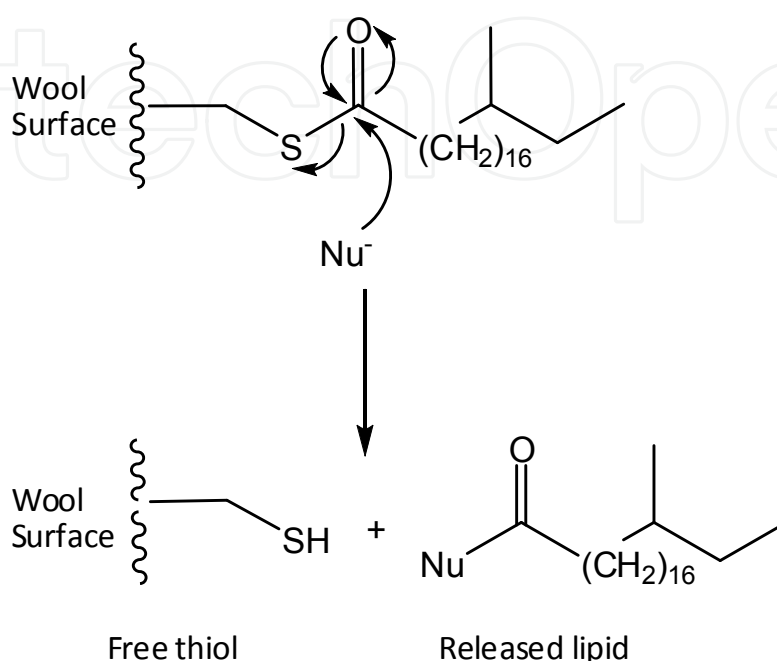

Fig. 1. Nucleophilic cleavage of 18-MEA from the wool protein surface (Meade *et al.* 2008b).

Methanolic potassium hydroxide is particularly effective at removing surface bound lipids from wool, for instance it has been shown to release up to 91% of the surface bound 18-MEA with a simple 90 minute room temperature treatment (Meade *et al.* 2008b) Although this high level of delipidation may be advantageous for subsequent surface treatment, drawbacks include the lack of surface specificity resulting in a harsh fibre and/or fabric handle, as well as general fibre damage. Anhydrous *t*-butoxide in *t*-butanol has the advantage of being a highly surface specific treatment, although it removes less of the surface bound 18-MEA. For instance, a two hour treatment at 60°C removes approximately 40% of the 18-MEA.

Hydroxylamine-based delipidation treatments have been reported using a number of different solvent systems (Dauvermann-Gotsche *et al.* 2000). Aqueous hydroxylamine treatment combined with a non-ionic surfactant has been found to remove 70-80% of surface bound 18-MEA without adversely affecting the handle of the treated fabric (Meade *et al.* 2008b). This treatment generates a significant increase in surface wettability and friction, along with low reported oxidation of surface thiols. Addition of surfactant was found to improve the evenness of treatment across a wool fabric surface, without causing any significant change in the amount of 18-MEA and total fatty acids removed by the treatment (Meade *et al.* 2008b). With its moderate, aqueous conditions, this treatment protocol offers a practical route for the application of surface-specific modification to protein fibres.

These delipidation approaches can act as a pre-treatment for subsequent covalent attachment of novel surface modification reagents.

3.6 Covalent surface attachment

Application of surface-specific smart and functional treatments to impart novel properties to protein materials requires an appropriately activated surface with functional groups accessible for modification. The removal of the surface lipid layer of mammalian fibres before the attachment of the new surface, as described earlier in this chapter, enables enhanced accessibility and functionality. Lipid removal, as opposed to surface oxidation alone, has been demonstrated to be critical for the covalent binding of amine-reactive polymer particles (Pille *et al.* 1998). Covalent surface attachment provides the possibility of high durability to wear and laundering in comparison to conventional technologies based on ionic or other non-covalent forces.

The generation of reactive groups on the surface of protein fibres after disruptive treatments such as UV/ozone treatment or plasma (Xu *et al.* 2007; Rathinamoorthy *et al.* 2009) can be used to aid the covalent grafting of surface treatments, such as Ag-loaded SiO_2 nanoparticles (Xu *et al.* 2007)

Proof-of-principle for the covalent modification of wool fibre surfaces after chemical delipidation with fluorescent and hydrophobic compounds has been demonstrated by Meade *et. al.* (2008a). Evidence for genuine covalent attachment of a chemical entity to wool surfaces after surface lipid removal was achieved by surface treatment with the fluorescent compound 7-fluorobenz-2-oxa-1,3-diazole-4-sulfonamide (ABD-F). The benzofurazan moiety of ABD-F fluoresces only when covalently bound to a thiol group, and therefore evaluation of the specific fluorescence of bound ABD-F after treatment, performed with fluorescence microscopy, was able to demonstrate successful covalent attachment to surface thiols. The degree of modification was assessed using scanning electron, light and fluorescence microscopy, wettability testing and X-ray photoelectron spectroscopy (XPS), and generally good, even surface modification was observed. These treatments also demonstrated good durability to dye dyeing and laundering durability.

Another class of compounds that have been evaluated for covalent surface attachment is epoxides (Meade *et al.* 2008a). Epoxides react with a wide range of nucleophiles including amines, thiols and hydroxyls and provide a potential means to exploit all the available nucleophilic groups present in proteins. After delipidation of wool fibre surfaces with hydroxylamine, which significantly increases surface wettability, covalent attachment of fluoroepoxides was shown to restore surface hydrophobicity. The subsequent wetting time, contact angle measurement and XPS analyses were all consistent with the formation of a new covalently bound hydrophobic surface. This novel treatment approach provides a potential route for generating customisable surface hydrophobicity through careful selection of the specific fluoroexpoxide utilised. Once again, these achievements highlight the potential for customising the properties of protein fibre surfaces.

Microparticles and nanoparticles have also been successfully tethered to the wool surface utilising crosslinkers (Meade *et al.* 2008a). Microencapsulation as a textile treatment technology offers a broad range of applications, but is currently limited for wool and other proteinaceous fibres due to generally poor durability. Covalent attachment of such particles to the fibre surface after delipidation is a potential means to increase treatment durability. To this end, covalent attachment of microparticles and nanoparticles with surface-coated carboxylic and amine surface functionality were investigated utilising both long-range and zero-length crosslinkers. Of the crosslinking technologies evaluated, the crosslinkers 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, known as EDC, and *N*-hydroxysuccinimide (NHS), were observed to be the most effective. Particles applied after removal of surface-

bound lipids demonstrated increased durability relative to particles applied without prior delipidation.

Once surface thiol groups are exposed via alkali delipidation, maleimide-based treatments also provide an excellent potential route to covalent attachment of new surfaces. Maleimide-derivatives have a high reactive specificity for covalent modification of thiol groups. Thiol-specific gold nanoparticles have been shown to bind (via maleimide reactivity) to thiols exposed on the wool surface following lipid removal by hydroxylamine treatment. This thiol-specific reagent, monomaleimideo nanogold, was used to demonstrate the formation of free thiols on the wool surface and their reactivity towards maleimide-containing reagents via visualisation of the nanoparticles using TEM (Dauvermann-Gotsche *et al.* 2000). The ultimate goal of initial removal of the surface lipids is a customised accessible and exposed surface prior to application of a secondary treatment. Once delipidated in a controlled manner, the exposed reactive thiol surface of the underlying epicuticle and other exposed surface moieties such as hydroxyl and amine groups present targets for permanent attachment of new surfaces. Relative to other forms of surface modification that do not involve prior controlled delipidation, modification *via* attachment to thiol and other nucleophilic functionalities after alkaline treatment appears to be a promising route for providing some significant potential benefits for protein fibres. However, further development of this approach is required before cost-effective, commercially applicable treatments become available.

3.7 Deposits/polymers

Polymers and surface coatings are applied to protein-based fibres for a variety of reasons. The deposition of surface coatings may be examined using XPS or SEM. Polyethylene glycols have been applied to various materials, including wool, to improve thermal storage, resistance to oils, pilling and static charge (Vigo & Bruno 1989). In the pad-cure process, these glycols are crosslinked with dimethylol dihydroxyethylene urea in the presence of an acid catalyst. Super-hydrophobic properties can be obtained for wool and wool blends using *in situ* chemical binding of inexpensive silica and polysiloxane materials, yielding nano-rough surfaces (Zhang & Lamb 2009). To generate improved biomaterials from silk fibroin, cyanuric chloride-activated poly(ethylene glycol) has been applied to give increased hydrophilicity, a smoother morphology (SEM), and increased attachment and proliferation of human fibroblasts (Vepari *et al.* 2010).

Chitosan is frequently applied to protein-based fibres, as it provides additional sites for acid dye adsorption (Ristić *et al.* 2010). Incorporating an enzyme in the alkaline peroxide treatment bath has been reported to enhance wool wettability and the effectiveness of subsequently applied chitosan biopolymer. This also significantly enhanced fibre whiteness. This combination of treatments resulted in a highly shrink resistant machine washable wool fabric. The formation of ionic bonds between the new sulfonic groups generated on the wool fibre surface and chitosan are believed to contribute to this excellent shrink resistance. However, if the enzyme concentration in the peroxide bath is too high, the efficiency of the subsequent chitosan application decreases, as does the shrink resistance (Jovanĉić *et al.* 2001). Chitosan is also better deposited on the wool surface after plasma treatment (Ristić *et al.* 2010).

Durable polymer coatings in the form of sol-gels may be deposited on fibre surfaces. Inorganic sol gels based on modified oxides of silica, titanium, or other inorganic oxides can form stable layers of small particle size (<50 nm) that improve textile properties on their own merit, and which can be impregnated with customised functional additives such as UV

absorbers. These treatments can be applied at low temperature, aside from a brief high temperature curing step (Mahltig *et al.* 2005). Tung & Daoud (2009) reported the coating of wool fibres with inorganic titanium dioxide-based anatase sols prepared using either nitric acid (N-sol) or hydrochloric acid (H-sol). Sol-gel treatments of wool have been reported to result in wool yellowing; Tung and Daoud found that this undesirable effect only resulted after N-sol treatment, likely due to the oxidative nature of nitric acid. In contrast, wool fibres treated with H-sol remained white and exhibited an even surface coating. The UV-absorbing properties of titanium dioxide also resulted in improved UV protection after sol-gel treatment. Most interestingly, treatment with these sols provided a self-cleaning function, with coffee and wine stains disappearing during exposure to UV light. The sol-gel coatings on the wool triggered photocatalytic reactions in the presence of oxygen and water that degraded the chromophores in the food stains (Tung & Daoud 2009). This is a very desirable characteristic in high-value protein-based fibres.

4. Enzymatic modification

A wide range of enzymatic approaches have also been trialled for surface-specific modification of protein fibres. Enzyme treatments offer the prospect of replacing environmentally unacceptable processes with more eco-friendly processes for treating protein fibres. Extensive research and development has been conducted with respect for utilisation of enzymes as antifelting agents for wool, as well as for enhancing the fibre surface colour (Das & Ramaswamy 2006).

Biopolishing, or biofinishing, refers to the application of proteolytic enzymes to the surface of fibres in order to remove protruding fibre components and thereby improve key properties such as pilling, felting and shrink resistance (Durán & Durán 2000). Proteases are the main class of enzyme used for modifying protein fibre surfaces. Proteases are proteolytic enzymes, that is, they act by cleaving peptide bonds and thereby degrading proteins. Utilisation of protease enzymes can improve some physical and mechanical properties of protein fibres such as smoothness, drapeability, dyeing affinity and water absorbency.

As enzymes are sterically bulky at the molecular level, they can often be utilised in a relatively surface specific manner, although general weakening of protein fibres is often observed with such treatments. Treatment with proteolytic or lipolytic enzymes therefore often leads to a perceived softening effect in the fibre, and a reduction in perceived harshness in handle, which can be attributed to a reduction in the fibre bending stiffness through structural protein degradation. A limitation of protease-based treatments is that adsorbed proteases can be difficult to remove from treated fibres, and enzyme retained after rinsing and drying has been shown to cause further degradation under ambient storage conditions (Nolte *et al.* 1996; Durán & Durán 2000).

It has been noted that enzyme concentration and reaction time have a significant impact on the location and level of enzymatic modification at a given pH. Polymers applied for complementary shrink-resist finishing can impede enzymatic action, but, generally speaking, dyeing and oxidative processes leave the fibre more susceptible to enzymatic modification (Nolte *et al.* 1996). In one enzyme trialling experiment, wool yarns were treated with varying concentrations of aqueous protease solutions. Dyeing with madder was then performed on the treated yarns. The observed to decrease in direct correlation to the enzyme concentration used. The wash-fastness of the dye was unchanged by the protease pre-treatments, while the lightfastness was increased (Parvinzadeh 2007).

Enzymatic treatments have been evaluated in tandem with plasma surface treatments. In one study, wool fabrics were treated with low temperature oxygen plasma with and without proteolytic enzymes and examined for their physico-mechanical and dyeing properties. Plasma pre-treatment caused a higher rate of weight loss in the subsequent protease treatment. When wool was dyed with a levelling acid dye, equilibrium dye uptake did not change, but the dyeing rate was observed to increase with plasma pre-treatment followed by protease treatment. With a milling acid dye, the plasma/protease combination treatment was shown to increase both dye uptake and dyeing rate over plasma or enzyme treatments alone. These results appear to indicate that while plasma-induced modification is surface-specific itself, plasma pre-treatment facilitates increased penetration of the enzyme into the fibre. Interestingly, an attempt to polymerise the enzyme with a water-soluble carbodiimide did not observably enhance strength retention (Yoon *et al.* 1996).

Incorporating an enzyme in alkaline peroxide treatment baths has been reported to enhance wool wettability and the effectiveness of subsequently applied chitosan biopolymer, significantly enhancing fibre whiteness and shrink resistance (Jovanĉić *et al.* 2001).

Enzymatic approaches have also been evaluated for improving fibre colour, with discoloration often more severe on and near the fibre surface. Typically this has also involved proteases, which can degrade and remove fibre surface components and thereby increase the overall fibre whiteness (Schumacher *et al.* 2001). In one study, the efficiency of various enzymes (xylanase, pectinase, savinase, and resinase) in scouring wool was trialled across a range of specialty hair fibres (llama, alpaca, mohair and camel). Significant colour improvement was noted after treatments with xylanase and pectinase (comparable with soap treatment), but not with resinase (Das & Ramaswamy 2006). Colour improvement in terms of resistance to photoyellowing has also been imparted to wool fibres via the laccase-mediated crosslinking of a naturally occurring antioxidant, norhydroguaiaretic acid (NDGA), to the wool surface, along with improved shrink resistance and antioxidant activity (Hossain *et al.* 2010).

5. Future directions

Global trends indicate that there will be a sustainable and increasing demand for smart and functional textiles. In addition, the move towards natural and sustainable materials continues to gain momentum and is widely expected to be a key driver in consumer decision for decades to come. These factors mean that targeted surface modification of both natural protein fibres and their biomaterial derivatives to provide functional and durable properties will continue to be a growing and exciting area in the global fibre, textile and biomaterial industries.

Recent advances in covalent attachment of new surfaces may provide the platform technologies for a new generation of fibre surface treatments. For protein-based biomaterials, in particular, such durable surface modification provides the potential to overcome current limitations, such as low abrasion and heat resistance. It is anticipated that research performed on the modification of protein fibres, such as wool and silk, will have spill-over application to such biomaterials. However, further research and development is required before these approaches become commercially viable for either natural protein fibres, or fibrous protein biomaterials. In the near future, it is likely that plasma and enzyme-based approaches, with their potential for cost-effectiveness, high throughput processing, and reduced environmental impact, will continue to gain popularity.

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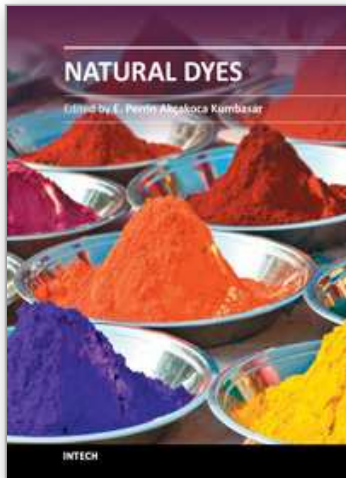
Natural Dyes

Edited by Dr. Emriye Akcakoca Kumbasar

Textile materials without colorants cannot be imagined and according to archaeological evidence dyeing has been widely used for over 5000 years. With the development of chemical industry all finishing processes of textile materials are developing continuously and, ecological and sustainable production methods are very important nowadays. In this book you can be find the results about the latest researches on natural dyeing.

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