# Effect of surface treatments on physicomechanical, stainresist, and UV protection properties of wool fabrics

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# Abstract

The surface of wool fabrics is frequently modified to make them shrink-resistant, water repellent and also to improve their handle properties. In this work, we investigated the effect of common surface modification treatments on fabric stain-resistance, hydrophilicity and UV absorption performance. The surface of wool fabrics was modified by chlorination and also by reacting the chlorinated wool fabrics with a polyamide, a fibre-reactive amino-functional siloxane and a fluorocarbon polymer. The surface of the various treated fabrics was characterised by ATR-FTIR, contact angle measurement and scanning electron microscopy. The effect of surface modification on the tensile strength, surface hydrophilicity, stain-resistance, and UV absorption capacity of the fabric was investigated. It was found that all the treatments except the treatment with the amino-functional siloxane polymer slightly improved the tensile strength of the fabric. The chlorination treatment and the treatment with

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the polyamide resin made the fabric hydrophilic, and fluorocarbon and silicone resin treatment made the fabric hydrophobic.

*Keywords*: Wool fabric; stain-resistance; hydrophilicity; UV-absorption; contact angle; ATR-FTIR

# **1. Introduction**

Wool fibre is the most commonly used animal fibre and is popular because of its good wrinkle resist, stain-resist, warmth, antistatic, flame-retarding, wrinkle-resist, moisture management, and heat insulation properties. Of the natural fibres, wool fibre possesses the highest elasticity. However, fabrics made from wool fibre sometimes have poor dimensional stability, high shrinkage and felting, and also poor handle properties. The physical structure of the outer scaly surface of the wool fibre contributes to its shrinkage and felting. Under mechanical agitation, specifically inter-fibre friction and pressure in the presence of heat and moisture, the scale edges of one fibre mesh with the inter-scale space of an adjacent fibre like a 'ratchet' mechanism. Because of this phenomenon, wool fibres interlock, and are unable to return to their original positions. As a result, this felting shrinkage becomes irreversible. Felting is advantageous for some purposes such as the finishing of blankets, some apparel and felted rugs, but is a serious problem for other apparel as it not only causes substantial shrinkage but also changes the appearance of the fabric [1,2].

Wool fibre is an assembly of cuticle and cortical cells held together by the cell-membrane complex. The outer surface of wool fibre has cuticles which protect the fibre from the surrounding environment. The dyeing and diffusion properties of wool are governed by this cell-membrane complex which is composed of mainly internal wool lipids [3]. These internal

wool lipids form stable liposomes and are arranged in the fibre as bilayers [4,5]. The presence of phospholipids in the bilayers affects the permeability behaviour of dyes within the wool fibre [6]. As the wool fibre is composed of many amino acids, their behaviour is amphoteric. The isoelectric point of wool fibre in aqueous medium is 5; below the isoelectric point the fibre is cationic and above the fibre is anionic [7]. This means that below pH 5, the wool fibre binds acid dyes. The cuticle is also comprised of three layers; the endocuticle (the inside layer), the epicuticle (the outside layer) and the exocuticle between them. There is a polyethylene like fatty acid layer of 18-methyleicosanoic acid (18-MEA) which is bound to the epicuticle through thioester bonds [8–10]. The wool fibre surface is hydrophobic because of this 18-MEA layer [11]. The removal of this covalently-bound lipid by oxidative (e.g. chlorination, radiation, plasma, etc.) [12–14], reductive [15], enzymatic [16] and chlorinated solvent treatment makes the wool fibre surface hydrophilic [17–19].

The most popular treatment to make wool fabrics shrink-resistant and machine washable is the so-called 'chlorine-Hercosett' process [20]. In this process, wool fibres are chlorinated in acidic conditions that not only make the fibre surface hydrophilic by removing the hydrophobic 18-MEA layer but also erode the edge of the scales [14]. The chlorinated fibres are then treated with a fibre-reactive polyamide resin called Hercosett, which covers the interscale spaces of the fibre, thereby preventing the meshing of scales of one fibre with the scales of an adjacent fibre, therefore reducing felting shrinkage of the fabric during washing. Some other treatments, such as plasma treatments alone or in combination with the treatments with chitosan and  $\beta$ -cyclodextrin, have been investigated to modify the surface of wool [21-23].

Staining is a common occurrence that can jeopardise the aesthetics of the apparel or interior textiles. Therefore, wool fibres are sometimes treated with fluorocarbon polymers to provide long term performance against staining. To improve the handle properties and also to

make the fabric soft, wool fabrics are commonly treated with various silicone resins that give wool fabric a silky handle.

However, these surface treatments may affect other physicochemical properties of the wool fibre. The chlorinated treatment and also the cationic polyamide resin treatment may increase the staining propensity of wool fabric. Many beverages and soups contain food colourants, and these natural colourants are mainly anionic in nature. The chlorination treatment may expose cationic amino groups because of the removal of the 18-MEA layer, and/or the treatment with cationic Hercosett resin produces a cationic layer on the surface of the wool fibre that may bind anionic food colours. The chlorination treatment and the subsequent treatment with sodium metabisulphite break down some of the disulphide bonds of wool fibre resulting in decrease in the tensile strength of the fibre. Until now no systematic investigation has been carried out to identify the effect of these common treatments on the stain-resist, mechanical and surface properties of the wool fibre.

In this work, we investigated changes in surface properties that occur due to various finishing agents applied on wool and also how they affect wool fabrics' stain-resistance. Wool fabrics were treated with a range of common polymeric finishes applied on wool, such as amino-functional siloxane, polyamide-epichlorohydrin and fluorocarbon polymers, and their effect on stain-resist, mechanical and surface morphology of the wool fibres have been investigated.

# 2. Experimental

# 2.1. Materials

The wool fabric used was 210 g/m<sup>2</sup> 2/2 twill woven having 34 ends per cm and 24 picks per cm, purchased from South Canterbury Textiles, Timaru, New Zealand. Basolan MW-P, a reactive amino-functional siloxane polymer, was purchased from BASF Chemicals (Germany). Hercosett 125, a polyamide-epichlorohydrin resin, was purchased from Ashland Chemicals (USA). Rucostar EEE6, a C6-based reactive fluorocarbon polymer, was purchased from Rudolf Chemie GmbH (Germany). Dichloroisocyanuric acid and acetic acid were purchased from Sigma-Aldrich Chemicals (USA). Teric GN9, a non-ionic surfactant, and Sandozin MRN, a non-ionic surfactant, were purchased from Huntsman Chemicals (USA) and Clariant Chemicals (Switzerland), respectively.

## 2.2. Treatments of wool

# 2.2.1. Chlorination and treatment with Hercosett

Bleaching and the treatment with Hercosett were carried out in an Ahiba Turbomat (Model 1000, Ahiba A.G., Zurich, Switzerland) laboratory dyeing machine at 1:20 materials to liquor ratio using filtered tap water. Prior to the chlorine-Hercosett treatment, the wool fabric was scoured with 2 g/l Teric GN9 at 50°C for 20 min to remove processing lubricants used during spinning of wool yarn. The wool fabric was then treated with 2% on the weight of wool fibre (owf) dichloroisocyanuric acid at pH 3 at room temperature (20 °C) for 30 min and then treated with 2 g/l sodium metabisulphite to neutralise the residual chlorine. A part of the chlorinated fabric was then treated with 3% owf Hercosett at 58 °C for 15 min at pH 8.5 to 9.0 (adjusted with sodium bicarbonate). After completion of the treatment, the samples were washed twice in fresh water and then neutralised with acetic acid.

#### 2.2.2. Treatment with Basolan MW-P and Rucostar EEE6

The treatments with Basolan MW-P and Rucostar EEE6 were carried out by exhaust treatment using the same Ahiba laboratory dying machine used for the chlorine-Hercosett treatment. The applied doses of silicone and fluorocarbon polymers were 3% owf. The dyebath was filled with water and dosed with 0.2 g/l Sandozin MRN (wetting agent) and the required quantity of fluorocarbon/silicone resin. The pH was adjusted to 4.5 with acetic acid. The temperature was then raised to 60°C at 2°C/min and held for 30 minutes. After completion of the exhaust treatment, the bath was cooled to 45°C at 2°C/min. The bath was then dropped and the samples were squeezed to remove the extra liquor. They were then dried and cured at 120°C for 3 min in a curing oven. The samples were then washed in water to remove the wetting agent, neutralised with sodium carbonate solution and then dried again.

#### 2.3. Surface characterisation

The surface of various treated fabrics was characterised by ATR-FT-IR, scanning electron microscopy and also by contact angle measurement. A Perkin-Elmer Fourier transform infrared (FTIR; Model System 2000) spectrometer with an attenuated total reflectance (ATR) attachment using zinc—selenium crystal was used for infrared studies to characterise the surface of various fabrics. For each sample, 64 scans were carried out and the averages are reported here. The surface of the chlorinated wool fabric and also the wool fabrics treated with Hercosett, Basolan MW-P and Rucostar EEE6 were characterised by field emission scanning electron microscopy (FE-SEM). The treated wool fabric samples were scanned by secondary electrons on a JEOL FESEM (Model: 6100, JEOL Ltd., Tokyo, Japan). The composition of the surface of various treated wool fabrics was evaluated by energy dispersive X-ray (EDX) using JEOL SEM (model 7000F) at 15 kV. KSV CAM 200 Contact Angle Measurement Apparatus (made by KSV Instruments, Finland) was used to measure the contact angle. The contact angle

calculation was performed by applying the spherical approximation of the drop by curve fitting based on the Young-Laplace equation by using the software (KSV CAM 200) supplied with the equipment. UV absorption was measured using a UV-visible spectrometer (Model: Evolution 220, TM Instruments, USA).

## 2.4. Mechanical properties

The tensile strength and elongation properties of the treated wool fabrics were assessed by using an Instron tensile strength tester (Model 4204) at 20 °C and 65% relative humidity according to ASTM Test Method D5035-06: Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method). The sample size was  $25.4 \times 152.4$  mm, and the gauge length was 100 mm. The samples were conditioned at the above-mentioned temperature and humidity for 3 days. At least 10 samples were tested for each treatment and the averages are reported here.

# 2.5 Assessment of stain-resistance against Acid Red 40, red wine and mustard oil

Stain resistance of the treated wool fabrics was assessed according to AATCC Test Method 175-2008 *Stain resistance: Pile Floor Coverings* against C.I. Acid Red 40 and red wine staining agents. For each treatment two fabric samples of  $100 \times 100$  mm size were placed into a conditioned room ( $65\pm2\%$ RH,  $20\pm1^{\circ}$ C) for 24 hours. For blank staining, distilled water with pH 2.8±1.0 adjusted by citric acid was used. One fabric sample was blank-stained and two samples were stained with either red wine or C.I. Acid Red 40. The stain applicator was placed in the centre of each fabric sample, 20 ml of stain solution was poured into the centre of the applicator and the top was pressed with the flat of the inside of the hand. The applicator was

carefully removed and the stained fabric samples were left in the conditioned room for 24 hours, then rinsed under running tap water, dried in the oven at 80°C and returned to the conditioned room. Colour measurements of unstained and stained conditioned samples were carried out with a Mahlo spectrophotometer (under D65 illuminant and 10° observer). At least two samples were tested for each treatment and the averages are reported here. UV absorption was measured using Evolution 220 UV-visible spectrometer. For the mustard oil staining the test method was based on the AATCC Test Method 130-1990 Soil Release: Oily Stain Release *Method.* Two fabric samples of  $100 \times 100$  mm size were placed into a conditioned room (65 ± 2%RH,  $20 \pm 1$ °C) for 24 hours. Using a plastic dropper 1 ml total of mustard oil was applied in drops to the centre of the fabric sample. A square of glassine paper was placed over the sample with a flat bottomed cylinder weight  $(2.268 \pm 0.045 \text{ kg})$  placed on the glassine paper directly over the stained area and allowed to sit undisturbed for  $60 \pm 5$  seconds. With the weight removed and glassine paper discarded the stained fabric samples were left in the condition room for 24 hours, then washed in a Wascator at 41°C as specified by the Woolmark 7A wash cycle using 'Softly' wool detergent. The samples were then dried in the oven at 60°C with air circulation and returned to the condition room.

# 3. Results and discussion

#### 3.1. Stain-resist performance

Table 1 shows the stain-resist performance of control and various treated wool fabric samples against red wine and C. I. Acid Red 40. Colour difference value ( $\Delta E$ ) compared to untreated and unstained wool fabric shows the severity of the staining. The higher the colour difference the greater the severity of the staining. It can be seen that the control wool fabric showed the lowest colour difference for both stain types. The chlorination treatment slightly increased the

colour difference, i.e. slightly increased the staining propensity, but still showed the second lowest colour difference. On the other hand, chlorine-fluorocarbon (Rucostar) treated wool fabric showed the highest colour difference and the chlorine-Hercosett-treated wool fabric showed the second worst performance. The stain-resist performance of chlorine-Basolan MW-P treated fabric was in-between the chlorinated and chlorine-Hercosett treated wool fabric.

Fig. 1 shows optical images of control wool fabric and also wool fabrics treated with various finishes stained with C.I. Acid Red 40 after rinsing and drying. It is evident that stain did not spread in the case of control fabric and most of the staining solution was removed during rinsing. On the other hand, in the case of chlorinated wool fabric samples, stain solution spread throughout the fabric samples as the hydrophilicity of the fabric increased with the chlorination treatment, resulting in the absorption of more staining dyes during the test compared to the control fabric, and also less staining dye removal during rinsing as they penetrated to the centre of the fibre. It is evident that the chlorine- Basolan MW-P treatment improved the hydrophobicity of the surface of the treated fabric and therefore the acid dye stain solution spread considerably less compared to the chlorinated fabric. In the case of fluorocarbon-treated wool fabric, the staining solution didn't spread much. As the stain solution did not spread, the concentration of dye in the stained area was much higher compared to the other samples where the staining solution spread throughout the fabric during the 24 hour stain development period, which resulted in the increased staining intensity reported in Table 1. During rinsing, very little dye was removed due to the strong hydrophobicity of the fluorocarbon polymer-treated treated fabric. In the case of C.I. Acid Red 40, stain-resist performance was in the order of control>chlorinated only> Basolan>Hercosett>Rucostar.

Fig. 2 shows the stain-resist performance of various treated wool fabrics against red wine. It can be seen that red wine spread in the case of all fabrics but the least spreading was observed for the chlorinated fabric treated with Rucostar EEE6. The surface tension of water and ethanol at 20 °C is 72.75 and 22.31 mN/m respectively [24]. As ethanol has both hydrophilic and hydrophobic groups, therefore polyphenol containing ethanol in the red wine was able to penetrate into the hydrophobic wool fibre, and stained from inside. It can be seen that in the case of red wine, the untreated control fabric showed the best stain-resist performance and the fluorocarbon treated fabric showed the worst performance in terms of stain intensity. Most of the red wine stain was removed during rinsing for the control fabric, where for the Hercosett, Basolan MW-P and Rucostar EEE6, less red wine staining dye was removed during rinsing. Although in terms of colour difference, the fluorocarbon polymer treatment (Rucostar EEE6) showed the worst stain-resistance, the stain didn't spread much. Conversely, the chlorine-Hercosett treated fabric showed marginally better stain-resistance but the red wine stain spread over the entire fabric sample. The order of stain-resist performance against red wine was similar to the stain-resist performance shown against C.I. Acid Red 40.

Fig. 3 shows stain-resistance performance of various treated wool fabrics against mustard oil. The strain-resistance trend was similar for the various treated wool as shown for the stainresistance against C.I. Acid Red 40 and red wine. During application, absorption and stain spreading was observed in the all but the fluorocarbon treated fabric where the oil formed a bead on the surface. After the weight was applied further spread of the stain was observed and in the case of the fluorocarbon treated fabric the oil stain had penetrated into the fabric structure and showed the greatest contrast in colouration compared to the other samples, due to the smaller more concentrated appearance of the stain. Subsequent to the washing there had been increased stain spread in all samples. The control fabric was least stained and the fluorocarbon treated fabric was the worst stained with mustard oil. The chlorine-Hercosett treatment showed again the second worst resistance against mustard oil. Overall, these results indicate that common finishing treatments used for wool worsens their stain-resist performance.

## 3.2 UV Absorption

UV absorption capacity of apparel fabrics is an added advantage as it protects the wearer from harmful UV radiation. Fig. 4 shows the UV absorption spectra of the control fabric and also wool fabric treated with various finishes. It can be seen that the untreated wool fabric shows the lowest UV absorbance. The removal of the 18-MEA layer by chlorination increased the UV absorption. However following this by treatment with Hercosett 125 did not further change the UV absorption of wool. The treatment with Basolan MW-P further improved the UV absorption of wool fabric. The highest absorption of UV was achieved by the treatment with Rucostar EEE6.

## 3.3. Tensile strength

Fig. 5 shows the mechanical properties of wool fabric before and after treatment with chlorine and also of the chlorinated fabric treated with Basolan MW-P, Hercosett 125 and Rucostar EEE6. The lowest average tensile strength was shown by the chlorinated wool fabric treated with Basolan MW-P and the highest by the wool fabric treated with Hercosett 125. The average tensile strength of the control wool fabric was 16.7 kgF which increased to 17.5 after the chlorination treatment. The removal of the 18-MEA layer probably increased the inter-fibre friction in the yarns of the wool fabric which increased the tensile strength. The

coating of wool fabric with silicone polymer (Basolan) was expected to increase the tensile strength but interestingly it caused a decrease. The treatment with silicone polymer probably made the fibre surface slippery, which reduced the inter-fibre friction resulting in a decrease in tensile strength. The treatment with Rucostar EEE6 also didn't increase the strength compared to the control, because of the same reason observed for the treatment with Basolan, but made the surface less slippery compared to the Basolan treatment and therefore the reduction of inter-fibre friction was not as much as observed for the treatment with Basolan. The chlorine-Hercosett treatment further improved the tensile strength of the treated wool fabric due to the reinforcement of wool fibres by polyamide coating and showed the highest tensile strength of the treatments investigated here.

#### 3.4. Contact angle

Table 2 shows dynamic water contact angles and also the shape of water droplets after various times. The untreated control wool fabric showed contact angle 118.2 to 118.9° which is consistent with the water contact angle observed for untreated fabric by other researchers [25,26]. The hydrophobic layer formed by the 18-MEA by thioester bond gives the fabric some level of hydrophobicity. The chlorination treatment made the fabric super-hydrophilic and it was not possible to measure the contact angle as the water droplet was soaked by the fabric immediately after placing it. It is known that chlorination treatment removes the 18-MEA by breaking the thioester bonds and exposes hydrophilic amino and carboxyl groups of wool keratin making the fabric surface highly hydrophilic.

The silicone resin treatment (Basolan MW-P) again made the chlorinated fabric hydrophobic by forming a hydrophobic layer of silicone resin. The highest contact angle was shown by the wool fabric with the fluorocarbon polymer treatment (Rucostar EEE6) which made the fabric superhydrophobic (the surafce showing contact angle more than 130° is treated as a superhydrophobic surafce).

#### 3.5. Surface morphologies

Fig. 6 shows the surface morphology of control and various treated wool fabrics. The control wool fabric shows typical scaly structure of wool with some contaminants on the surface of fibre which could be debris of damaged scales. On the other hand, the surface of chlorinated wool fabric is comparatively clean compared to the surface of control fabric. The height of scales looks slightly decreased after the chlorination treatment and there is little debris of damaged scales visible. The chlorination treatment didn't cause any visible damage in the wool fibre. The treatment with Basolan MW-P formed uniform coating on the surface of wool fibre but the thickness of the coating is quite small as they didn't fully cover the scales of wool fibre. On the other hand, Hercosett resin covered the scales of wool fibre and was uniformly distributed on the surface of wool fibre. The best and most uniform coating of wool fibres was observed in the case of the treatment with Rucostar EEE6 as the scaly structure of wool fibre is hardly visible as the resin almost covered the entire fibre surface.

Fig. S1 (Supplementary Information) shows the EDX spectra of surface of wool fabrics treating with various polymeric finishing agents. It is evident that all the treatments changed the elemental compositions of the wool fibre surface (Table S1 in Supplementary Information). The greatest effect was observed in the case of the sulphur content of the fabrics, which considerably increased for the Basolan MW-P treatment but decreased for the other treatments with Hercosett and Rucostar EEE6. It indicates that Basolan MW-P may have thiol groups to form bonding with the thiol groups of wool and therefore the treated fabric showed an increase in the sulphur content. The Basolan MW-P treatment showed the

presence of silicone element in the fabric as it is a silicone elastomeric polymer, but the control and the other fabrics treated with Hercosett and Rucostar EEE6 showed absence of silicone in them. The change in C, H and S content of wool fabric suggests the presence of those polymers on the surface of the treated wool fabrics. The EDX cartography of carbon, oxygen, sulphur and silicone elements was performed on various surface treated wool fabric samples to determine the localisation of the treatments on the fabrics (Fig. S2, Supplementary Information). The image of Basolan MW-P treated fabric shows that the polymer evenly spread on the surface of the chlorinated wool fabric.

# 3.6. Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy

Fig. 7 shows the ATR-FTIR spectra of control, chlorinated and chlorinated wool fabrics coated with various polymers. The FTIR spectrum of control wool shows typical wool keratin IR bands of amide I, amide II and amide III peaks at 1350, 1450, and 1610 cm<sup>-1</sup>, respectively. The broad peak at 3340 cm<sup>-1</sup> could be attributed to the hydroxyl groups of certain amino acids of wool. The spectrum of chlorinated wool also shows the same peaks shown by the spectrum of the control wool fabric but also shows an extra peak at 1019 cm<sup>-1</sup>, which shows the formation of Bunte salt, which indicates that some of the disulphide bonds of wool fibres were broken down and converted to Bunte salt by the chlorination treatment. The spectrum of Basolan-treated wool shows a new band at 800 cm<sup>-1</sup>, which is due the –Si-O-Si– bonds of polysiloxane polymer.

# 4. Conclusions

We demonstrated that common finishing treatments used for wool fabrics can greatly affect their surface characteristics and also affect their stain-resistance, UV absorption, tensile strength and surface hydrophobicity. All of the treatments investigated worsened stainresistance against C.I. Acid Red 40, red wine and mustard oil. The greatest effect was shown by the fluorocarbon polymer treatment and the least effect was shown by the chlorination treatment. These findings will help the manufacturer to select appropriate treatments to tackle the negative effects imposed by these finishing treatments.

# Acknowledgement

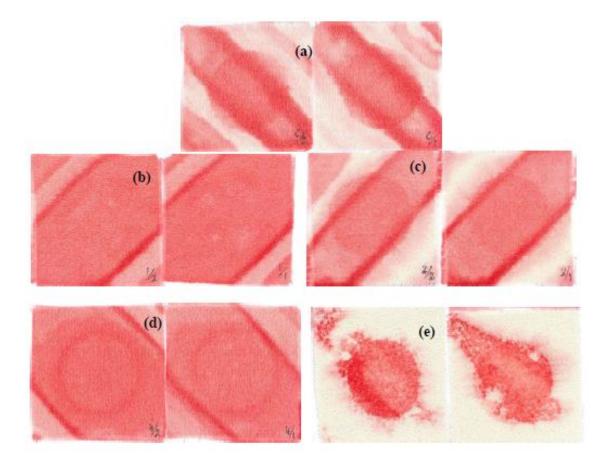
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# References

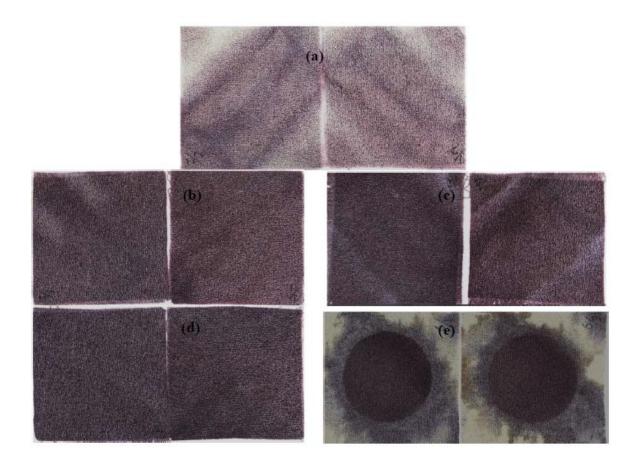
- C.S. Whewell, L. Rigelhaupt, A. Selim, Mechanism of milling shrinkage of wool fabrics, Nature 154 (1944) 772–772.
- [2] J.B. Speakman, E.Stott, A contribution to the theory of milling Part I A method for measuring the scaliness of wool fibres, J. Text. Inst. 22 (1931) 339–348.
- [3] J.D. Leeder, The cell membrane complex and its influence on the properties of the wool fibre, Wool Sci. Rev. 63 (1986) 3–35.
- [4] L. Coderch, A. de la Maza, A. Pinazo, J.L. Parra, Physicochemical characteristics of liposomes formed with internal wool lipids, J. Am. Oil Chem. Soc. 1996, 73, 1713–1718.
- [5] A. Körner, S. Petrovic, H. Höcker, Cell membrane lipids of wool and human hair from liposomes, Text. Res. J. 65 (1995) 56–58.

- [6] M. Marti, L.I. Barsukov, J. Fonollosa, J.L. Parra, Physicochemical aspects of the liposome-wool interaction in wool dyeing. Langmuir 20 (2004) 3068–3073.
- [7] A.M. Sookne, M. Harris, Electrophoretic studies of wool, Text. Res. J. 9 (1939) 437–444.
- [8] A.P. Negri, H.J. Cornell, D.E. Rivett, The nature of covalently bound fatty acids in wool fibres, Aust. J. Agric. Res., 42 (1991) 1285–1292.
- [9] A.P. Negri, H.J. Cornell, D.E. Rivett, Effects of proceeding on the bound and free fatty acid levels in wool, Text. Res. J. 62 (1992) 381–387.
- [10] D.J. Evans, M. Lanczki, Cleavage of integral surface lipids of wool by aminolysis, Textile Res. J. 67 (1997) 435–444.
- [11] C.M. Carr, I.H. Leaver, A.E. Hughes, X-ray photoelectron spectroscopic study of the wool fibre surface, Textile Res. J. 56 (1986) 457–461.
- [12] M. Naebe, P.G. Cookson, J. Rippon, R.P. Brady, X. Wang, Effects of plasma treatment of wool on the uptake of sulfonated dyes with different hydrophobic properties, Text. Res. J. 80 (2010) 312–324.
- [13] J. Shao, C.M. Carr, C.P. Rowlands, J. Walton, XPS, SIMS, and ESR studies of UV/ozone-irradiated silk and wool, J. Text. Inst. 90 (1999) 459–468.
- [14] A., Körner, Naithani, V.K. Partial release of covalently bound 18-methyleicosanoic acid from wool cuticle with primary alcohols, J. Text. Inst. 90 (1999) 14–18.
- Y.K. Kamath, S.B. Ruetsch, Reduction induced surface modification of human hair, J.
  Cosmet. Sci. 61 (2010) 1–12.
- [16] S, Hutchinson, D, Evans, G, Corino, J. Kattenbelt, An evaluation of the action of thioesterases on the surface of wool, Enzyme Microb. Technol. 40 (2007) 1794–1800.
- [17] C. Dauvermann-Gotsche, A. Körner, H. Höcker, Characterisation of 18-methyleicosanoic acid-containing proteolipids of wool, J. Text. Inst. 90 (1999) 19–29.

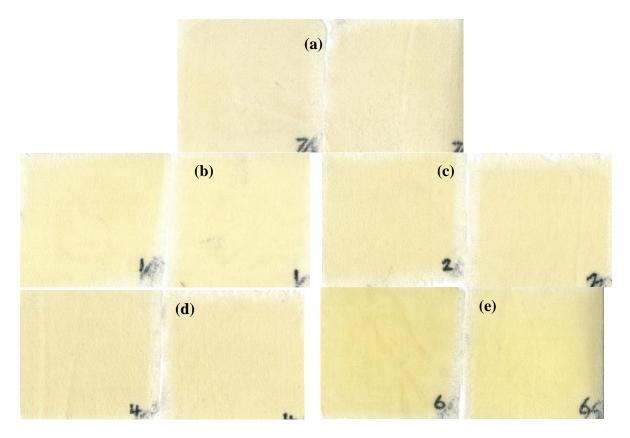
- [18] S.J. Meade, J.M. Dyer, J.P. Caldwell, W.G. Bryson, Covalent modification of the wool fibre surface: Removal of the outer lipid layer, Text. Res. J. 78 (2008) 943–957.
- [19] L.N. Jones, D.E. Rivett, The role of 18-methyleicosanoic acid in the structure and formation of mammalian hair fibres, Micron 28 (1997) 469–485.
- [20] W. de Fries, U. Altenhofen, J. Föhles, H. Zahn, A protein chemical investigation of the chlorine-Hercosett process, J. Soc. Dyers Colorists 99 (1983) 13–16.
- [21] M. Molakarimi, M. Khajeh Mehrizi, A. Haji, Effect of plasma treatment and grafting of β-cyclodextrin on color properties of wool fabric dyed with Shrimp shell extract, J. Text. Inst. 107 (2016) 1314–1321.
- [22] A. Haji, M.K. Mehrizi, J. Sharifzadeh, Dyeing of wool with aqueous extract of cotton pods improved by plasma treatment and chitosan: Optimization using response surface methodology, Fiber. Polym. 17 (2016) 1480–1488.
- [23] A. Haji, S.S. Qavamnia, Response surface methodology optimized dyeing of wool with cumin seeds extract improved with plasma treatment, Fiber. Polym. 16 (2015) 46–53
- [24] G. Váquez, E. Alvarez, J.M. Navaza, Surface Tension of Alcohol + Water from 20 to 50 °C, J. Chem. Eng. Data, 40 (1995) 611–614.
- [25] M.M. Hassan, Binding of a quaternary ammonium polymer grafted-chitosan onto a chemically modified wool fabric surface: assessment of mechanical, antibacterial and antifungal properties, RSC Adv. 5 (2015) 35497–35505.
- [26] Tang, B., Wang, J., Xu, S., Afrin, T., Tao, J., Xu, W., Sun, L., Wang, X. Function improvement of wool fabric based on surface assembly of silica and silver nanoparticles, Chem. Eng. J. 185-186 (2012) 366–373.



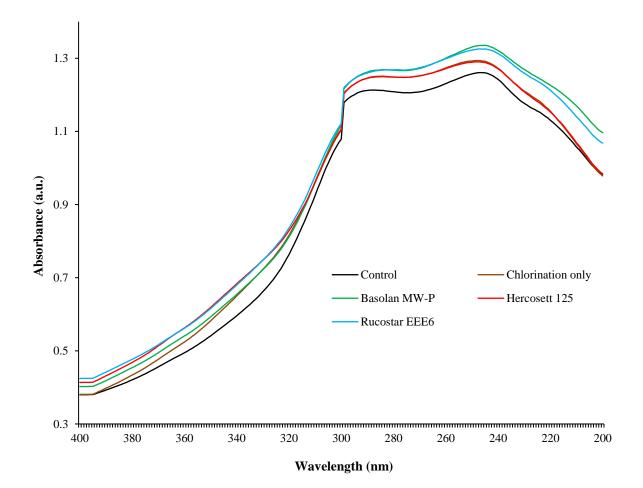
**Fig. 1.** Stain-resist performance against C. I. Acid Red 40 of control (a), chlorinated (b) and also the chlorinated wool further treated with Basolan MWP (c), Hercosett (d) and Rucostar EEE6 (e).



**Fig. 2.** Stain-resist performance against red wine of control (a), chlorinated (b) and also the chlorinated wool further treated with Basolan MWP (c), Hercosett (d) and Rucostar EEE6 (e).



**Fig. 3.** Stain-resist performance against mustard oil of control (a), chlorinated (b) and also the chlorinated wool further treated with Basolan MWP (c), Hercosett (d) and Rucostar EEE6 (e).



**Fig. 4.** UV absorption spectra of control, chlorinated and also the chlorinated wool further treated with Basolan MWP Hercosett, and Rucostar EEE6.

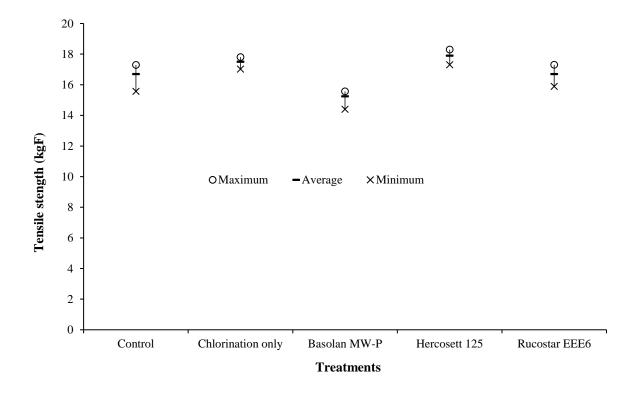
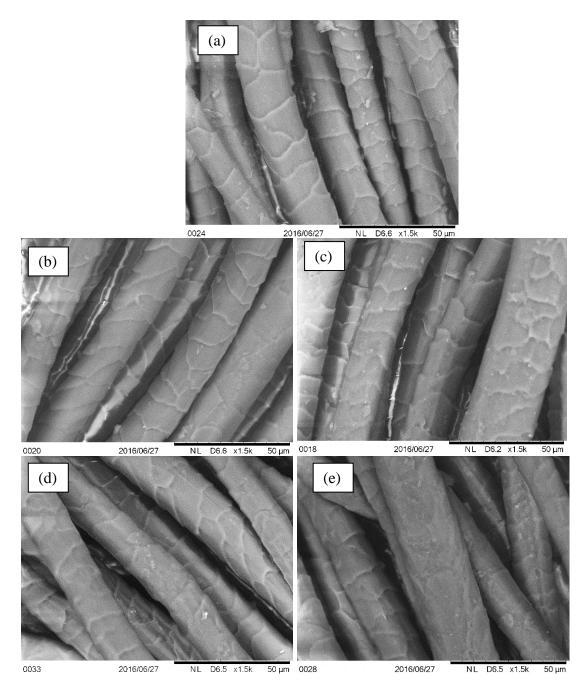
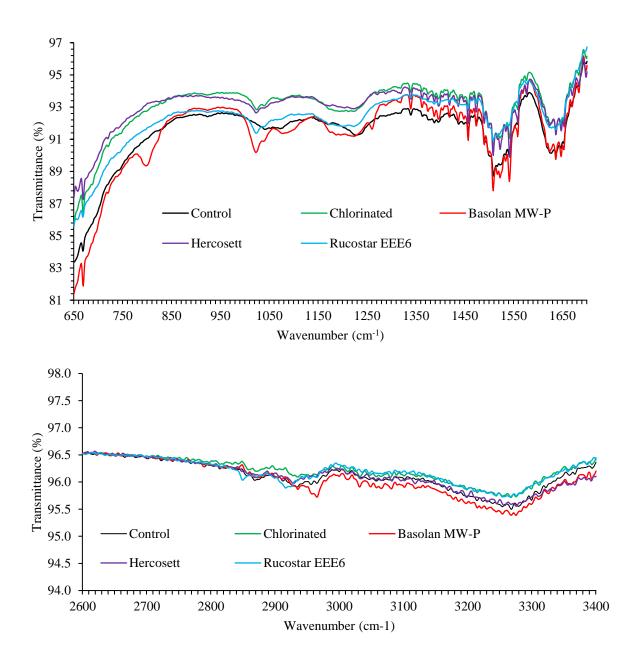


Fig. 5. Tensile strength of control and various treated wool fabrics.



**Fig. 6.** SEM images of control (a), chlorinated (b) and also chlorinated wool fabrics treated with Basolan MW-P (c), Hercosett (d) and Rucostar EEE6 (e).



**Fig. 7.** FT-IR spectra of control and chlorinated wool fabric and also chlorinated wool fabrics treated with various finishes.

# Table 1

*CIE*  $L^*a^*b^*$  values and colour difference of various treated wool fabrics stained with C. I. Acid Red 40 and red wine.

Treatments	CIE L*a*b* values			Colour difference $(\Delta E)$
	L*	a*	b*	_ ()
Acid Red 40				
Control	59.412	39.154	16.638	45.626
Chlorinated	59.832	39.402	16.518	46.276
Chlorine-Basolan	60.238	38.06	16.736	46.62
Chlorine-Hercosett	58.536	40.63	17.368	50.08
Chlorine-Rucostar	58.478	39.658	20.19	54.822
Red Wine				
Control	56.658	8.14	0.92	32.982
Chlorinated	43.856	11.542	0.182	47.98
Chlorine-Basolan	38.768	12.272	-0.622	50.494
Chlorine-Hercosett	40.324	10.218	-0.444	48.594
Chlorine-Rucostar	34.712	13.952	-0.812	57.854

# Table 2

Dynamic contact angle of control, chlorinated and also chlorinated wool fabrics treated with various finishing agents.

