

# Modifying Surface Resistivity and Liquid Moisture Management Property of Keratin Fibers through Thiol–Ene Click Reactions

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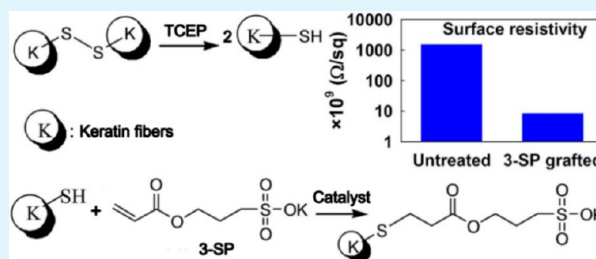
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**ABSTRACT:** This paper reports on a new method for improving the antistatic and liquid moisture management properties of keratinous materials. The method involves the generation of thiols by controlled reduction of cystine disulfide bonds in keratin with tris(2-carboxyethyl) phosphine hydrochloride and subsequent grafting of hydrophilic groups onto the reduced keratin by reaction with an acrylate sulfonate or acrylamide sulfonate through thiol–ene click chemistry. The modified substrates were characterized with Raman spectroscopy and scanning electron microscopy and evaluated for their performance changes in liquid moisture management, surface resistivity, and wet burst strength. The results have revealed that the thiol–acrylate reaction is more efficient than the thiol–acrylamide reaction, and the keratinous substrate modified with an acrylate sulfonate salt exhibits significantly improved antistatic and liquid moisture management properties.

**KEYWORDS:** keratin modification, thiol–ene chemistry, antistatic, surface resistivity, liquid moisture management, wool



## 1. INTRODUCTION

Keratin fibers are predominantly composed of hydrophilic proteins; however, their fiber surfaces are generally hydrophobic in nature due to the presence of a high degree of disulfide cross-linkage in the exocuticle and bound fatty acids on the fiber surfaces.<sup>1,2</sup> As a result of this unique structure, keratin fibers can absorb considerable amounts of water vapor, with a moisture regain over 10% under the standard conditions (25 °C and 65% relative humidity). Their surfaces however exhibit a water-repellent characteristic and are prone to developing a frictional static charge during processing and end-use applications. For instance, severe friction between the wool scales often leads to highly charged wool substrates, which is problematic. Many treatments have been developed to overcome the static charge problems, such as mild oxidation, chlorination, various topical treatments and coatings, plasma treatments, and enzyme treatments.<sup>3–6</sup> However, to date, none of these approaches are able to offer a robust and satisfactory solution. The main focus of this study is therefore to develop a new hydrophilic and antistatic finish for keratin fibers with an improved effectiveness and durability and minimal negative effects on the fibers.

It is well known that keratin fibers inherently contain free thiol groups and cystine disulfide bonds which can be readily cleaved by reducing agents to form more thiols.<sup>8,9</sup> This offers great opportunities for keratin fibers to be modified and functionalized through the thiol–ene reactions. This reaction scheme is receiving increasing attention in organic synthesis, polymerization, and surface modification due to its attractive attributes of click chemistry and versatility.<sup>10–14</sup> The reactions

are readily accomplished in a wide range of conditions but most commonly performed under radical and nucleophilic conditions.

The generation of thiols through reductive cleavage of native disulfide (S–S) bonds in protein or keratin can be achieved by many reducing agents, but tris(2-carboxyethyl)phosphine hydrochloride (TCEP) is often preferred due to its strong reducing power, high stability, high selectivity, wide applicable pH range, and odorless nature.<sup>7–9</sup> The reduction process by TCEP is presented in Scheme 1, where disulfide links between keratin proteins (K) are reduced to yield reactive thiol groups. The associated nucleophilic thiolate anions derived under the nucleophilic conditions are highly motivated species that can be utilized in a wide range of processes with high yield reactions under relatively benign conditions.<sup>10–12</sup>

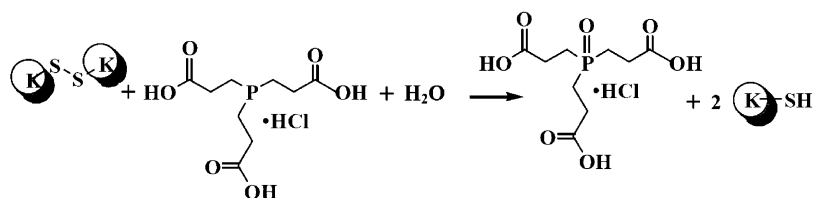
Although TCEP reduction of disulfide has been widely used in protein folding–unfolding mechanisms,<sup>8</sup> and for facilitating complete reduction and dissolution/digestion of proteins,<sup>9</sup> it has not been used in fiber pretreatment for fiber modification purposes. The use of TCEP in large quantities in a mill environment is considered possible. Like all other reducing agents currently used, it can be readily deactivated to minimize and readily control the potential effect of discharge on the environment. Any difference in the chemical cost may also be largely reduced when the demand is high. The technical challenge in this case is to control the reduction process,

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Scheme 1. Reduction of Cystine Disulfide Bonds with TCEP

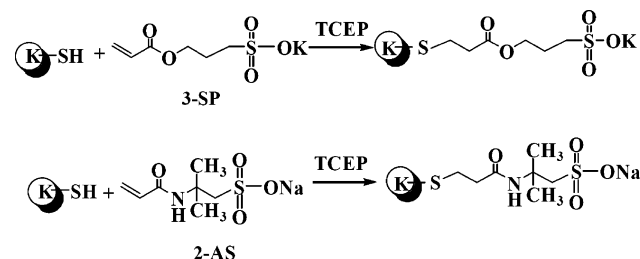


allowing the generation of sufficient thiols while preventing excessive loss of the mechanical properties of the keratin fibers.

In this paper, we report a facile treatment of keratin fibers in an aqueous medium, which involves the generation of thiols by controlled reduction of cystine disulfide bonds in keratin with TCEP, and subsequent grafting of functional groups onto the reduced keratin through nucleophile-catalyzed thiol-ene reactions. Acrylate and acrylamide compounds containing a sulfonate group, a strong hydrophilic group, were used as the ene substrate in this study to modify the hydrophilicity and surface resistivity of keratin fibers.

The specific reactions of the cysteine thiol residues were on reduced keratin with the selected acrylate and acrylamide sulfonate compounds: 3-sulfopropyl acrylate potassium salt and 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt are illustrated in Scheme 2. In the presence of a nucleophile, such

Scheme 2. Thiol-Acrylate Reaction (a) and Thiol-Acrylamide Reaction (b)



as TCEP, a thiol group is added to the electron-deficient C=C bond of the acrylate or acrylamide molecule, forming a thiol-acrylate or thiol-acrylamide dimer. The grafted hydrophilic sulfonate groups on keratin fibers are expected to permanently alter the hydrophilicity and the surface resistivity of the fiber substrates.

Wool was used as a representative example of keratin fibers in this investigation. The modified wool substrates were characterized by Raman spectroscopy, as well as scanning electron microscopy (SEM), and evaluated for their performance changes in liquid moisture adsorption, surface resistivity, and wet burst strength.

## 2. MATERIALS AND METHODS

**2.1. Materials.** A Merino wool plain weave fabric of 190 g/m<sup>2</sup> was used in this study as a representative keratin substrate. Tris(2-carboxyethyl)phosphine hydrochloride was purchased from Soltec Ventures (Beverly, USA). 2-Acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution (50 wt % in H<sub>2</sub>O) and 3-sulfopropyl acrylate potassium salt were obtained from Sigma Aldrich. All chemicals were analytic grade reagents and used without further purification.

**2.2. Treatments.** The pretreatment solution was prepared by dissolving TCEP in a water:ethanol (1:1 v/v) mixture to form either 20 mmol/L or 50 mmol/L TCEP solutions. The pH was adjusted to 2.5, 5.0, and 7.0 with a Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> buffer, as needed. Wool

fabrics were treated in the TCEP solutions at room temperature for different periods of time at a liquor ratio of 1:50 where a gentle shaking action was applied using an orbital mixer at a speed of 100 r.p.m. After the pretreatment, the wool samples were rinsed with deionized water, dried in the air, and stored in sealed plastic bags before being analyzed or used for further treatments. In the subsequent process, the TCEP pretreated wool fabrics were immersed in a solution containing either 10% 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (2-AS) or 10% 3-sulfopropyl acrylate potassium salt (3-SP), in the presence of a catalytic amount of TCEP. The pH of the treatment solution was adjusted to 7.0 with a Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> buffer, and the liquor ratio was 50:1. The treatment was carried out at room temperature for 24 h under gentle stirring.

**2.3. Characterization.** **2.3.1. Raman Spectroscopy.** Raman spectra were obtained at a resolution of 4 cm<sup>-1</sup> using a Bruker RFS-100 FT-Raman spectrometer (Karlsruhe, Germany) equipped with an Adlas Nd:YAG laser operating at 1.064 μm and a liquid nitrogen cooled Germanium diode detector. Fabric samples were held on a mirrored backing, while solids and liquids were held in glass vials. All spectra were collected in 180° backscatter geometry. Data acquisition was performed using Bruker OPUS software (version 3.1). For fabrics, 512 scans were collected at a laser power of 500 mW. To improve the signal to noise ratio, three spectra collected from different areas of each fabric were co-averaged to produce a final spectrum for analysis. For liquids and solids, 256 scans using 250 mW laser power were co-averaged. A Blackman-Harris three-term apodization function was used.

All spectroscopic data manipulation was carried out using Grams AI software. Raman fabric spectra were generally normalized on the intensity of the amide I mode at 1654 cm<sup>-1</sup> as it is not affected by the presence of the monomer in either the unreacted or bound state. When protein conformational changes were being compared, normalization was carried out using the 1445 cm<sup>-1</sup> C-H bending mode as associated with amino acid side chains which are not affected by chemical reaction or conformation. All peak intensity comparisons were made at the peak maxima using a consistently defined two-point baseline. Similar results were obtained when peak areas were used.

**2.3.2. Physical and Mechanical Property Evaluation.** Secondary electron images of the substrate surfaces were obtained from uncoated samples at a 1.2 kV accelerating voltage using a Hitachi S4300 scanning electron microscope (Tokyo, Japan).

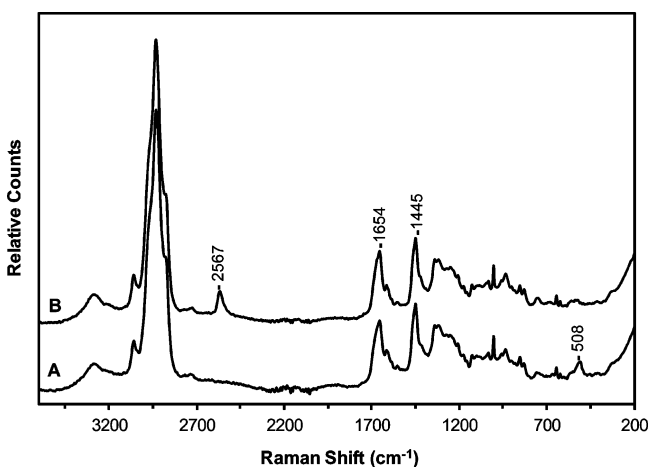
A moisture management tester (MMT) was used for quantitatively assessing liquid moisture transfer characteristics of the treated and untreated substrates in multidirections, according to the AATCC test method 195-2009. A volume of 0.22 mL of normal saline test solution (9 g/L of sodium chloride) was dispensed freely onto the center of the top surface of the fabric under test. As the solution moves through the fabric, the MMT records and measures the liquid moisture transport behavior during the first 120 s.

The antistatic properties of the substrates were assessed using a surface resistivity tester developed by CSIRO in accordance with European Standard EN 1149-1. The specimens were conditioned for at least 24 h prior to testing, which was carried out at a temperature of 23 ± 1 °C and a relative humidity of 25 ± 5%. A potential of 100 ± 5 V was applied for 15 ± 1 s to determine the resistance using a digital ohmmeter. The antistatic property of the wool fabric was evaluated on the basis of surface resistivity ρ in ohms per square (Ω/sq), which is calculated as R(Ω) × Ks, where R is the measured resistance and Ks is the electrode factor which was determined to be 5.698.

The wet burst strengths of the treated and untreated fabric samples were tested according to AS2001.2.4-1990, Determination of bursting pressure of textile fabrics-Hydraulic diaphragm method. For each sample, four tests were conducted, and the results were reported as the averages obtained.

### 3. RESULTS AND DISCUSSION

**3.1. Generation of Keratin Thiols with TCEP.** The treatment of wool with TCEP is critical for generating sufficient thiol groups on the fiber surface for the subsequent grafting reactions while retaining the integrity and mechanical properties of the fibers. To determine the suitable treatment conditions, wool was first treated with 20 and 50 mmol/L TCEP at different pHs for 24 h, using the procedures described in the Materials and Methods section. The treated samples were then analyzed by Raman spectroscopy. Figure 1 shows the



**Figure 1.** Raman spectra obtained from (A) untreated and (B) TCEP reduced wool fabric.

Raman spectra of an untreated and a TCEP-treated wool (with 20 mmol/L TCEP at pH 5) sample, where the S–H and S–S stretching modes are observed at 2567 and 508  $\text{cm}^{-1}$ , respectively.<sup>14</sup> It is evident that the S–S intensity in the treated sample is substantially lower than that of the untreated sample, indicating an effective reduction of cystine disulfide by the TCEP treatment.

By calculating the intensity changes of the disulfide stretching vibration before and after the treatments, the percentages of

disulfide bond cleavage under different treatment conditions were obtained and presented in Figure 2(a).

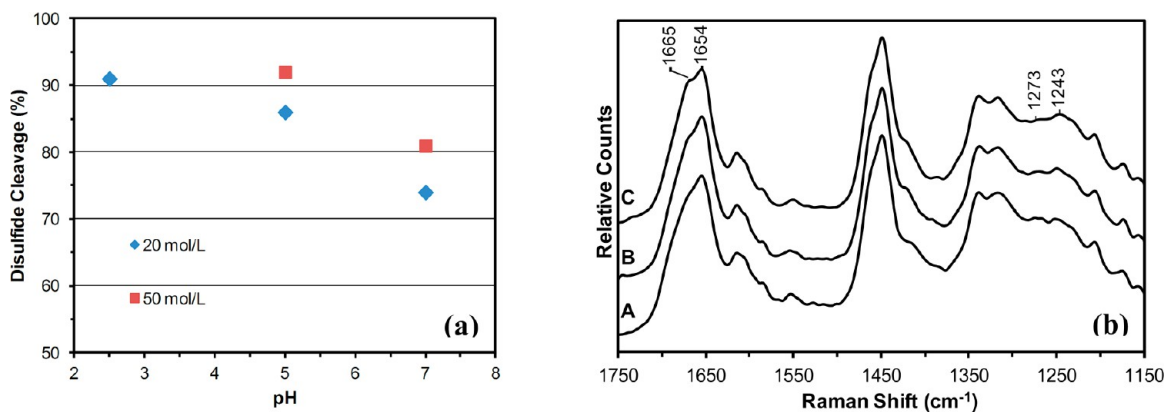
It should be noted that these Raman analyses were conducted a few days after the TCEP treatments. Due to potential oxidation of thiol groups in air, it is probable that the % cleavage has been underestimated. It is also possible that the % cleavage is underestimated from the way that the baseline was defined in the disulfide stretching region as there is likely to be weak underlying vibrational modes present in this region. Nevertheless, the results show that most of the disulfide bonds are cleaved by this treatment, and the % cleavage increases with decreasing pH from 7.0 to 2.5. An increase in TCEP concentration from 20 to 50 mmol/L only resulted in a slight increase in the level of disulfide bond cleavage.

It is also interesting to note that the wool fabrics treated at pH 2.5 exhibited significant changes in the amide I band shape indicative of changes in the protein conformation (Figure 2(b)). This change is also noticeable in the wool fabrics treated at pH 5.0 but not as near as dramatic. Analysis of the amide I and III regions suggests a decrease in  $\alpha$ -helical content (1654 and 1273  $\text{cm}^{-1}$ ) and increase in disordered protein (1665 and 1243  $\text{cm}^{-1}$ ).<sup>15</sup> This may account for the increased level of reduction observed at the lower pH which is not expected based on the known reactivity of the reagent. Furthermore, the reduction of disulfides by TCEP proceeds readily at pH 2.5, and thiolate–disulfide interchange is effectively prevented because only low levels of thiolate are present, which is also consistent with the study of Burns et al.<sup>9</sup>

On the basis of these observations, the treatment with 20 mmol/L TCEP at pH 5.0 was selected and used in further investigation.

Figure 3a and Figure 3b illustrate the effect of the treatment time on disulfide bond cleavage and wet burst strength of the treated samples, respectively. It can be seen that the % of the disulfide bond cleavage increases with increasing TCEP treatment time, but the wet burst strength of the treated sample reduces as the treatment time increases. However, the strength loss within the first 2 h is relatively small. After 2 h treatment, the disulfide bond cleavage is over 80% and the strength loss is around 24%, which is still acceptable. Substantial strength loss around 50% is observed when the TCEP treatment time is over 6 h.

On the basis of the results in Figure 3, two hours of the TCEP treatment have been considered suitable, by which



**Figure 2.** Effect of the treatment pH on (a) percentage of disulfide cleavage and (b) protein conformation—comparison of the amide I and III regions of the Raman spectra obtained from wool fabrics: (A) untreated and TCEP reduced at (B) pH 5 and (C) pH 2.5.

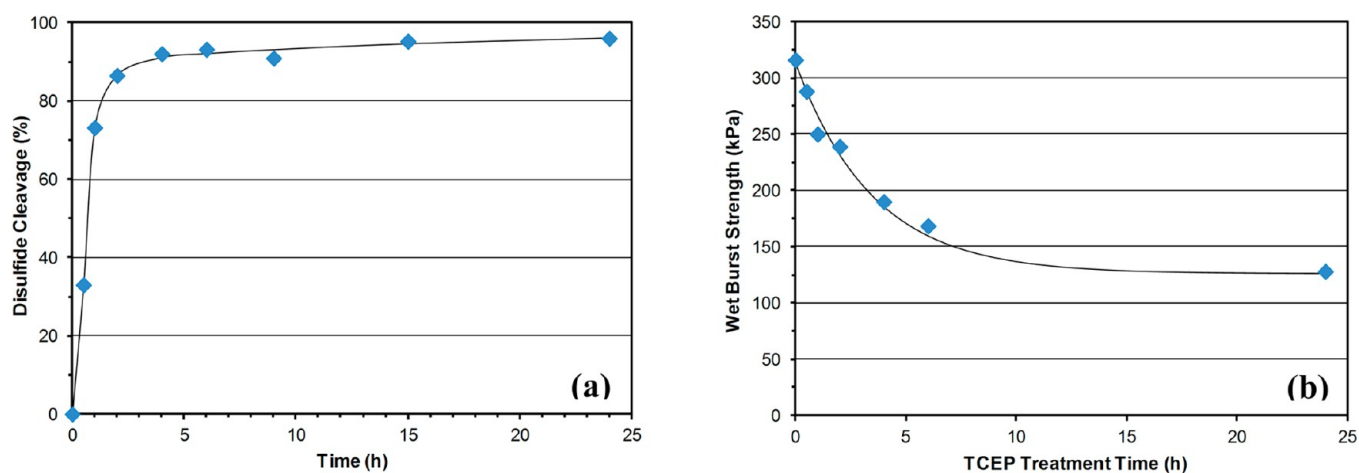


Figure 3. Effect of TCEP treatment time on (a) the percentage of disulfide cleavage and (b) wet burst strength of the treated wool fabrics.

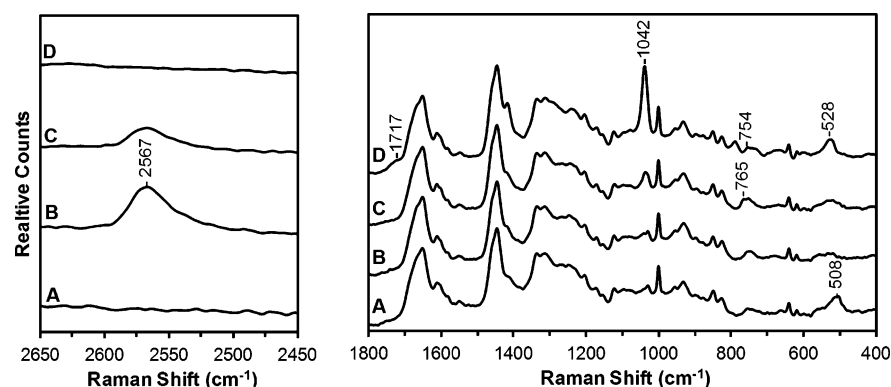


Figure 4. Raman spectra obtained from wool fabric: (A) untreated, (B) TCEP reduced, (C) acrylamide, 2-AS treated, and (D) acrylate, 3-SP treated.

sufficient thiol groups (disulfide cleavage) and acceptable mechanical properties can be obtained.

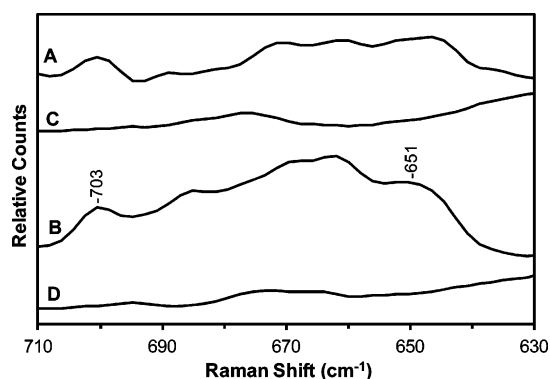
**3.2. Modification of the TCEP Reduced Wool.** The TCEP reduced wool samples were subjected to a further treatment with an acrylate or acrylamide compound containing a sulfonate group. The hydrophilic sulfonate groups are expected to be grafted onto the reduced wool through thiol-ene click reactions. The modified wool samples were characterized by Raman spectroscopy and infrared and evaluated for their physical and mechanical properties.

**3.2.1. Spectroscopic Analysis.** Raman spectra obtained from untreated (A), TCEP reduced (B), acrylamide (2-AS) (C), and acrylate (3-SP) (D) treated wool fabrics are shown in Figure 4.

The left panel of Figure 4 shows the S-H stretching region of the spectra, while the low-frequency region is shown in the right panel. Compared to the TCEP treated fabric (Figure 4 B), the S-H stretching mode observed at 2567 cm<sup>-1</sup> reduces by 53% in the fabric treated with the acrylamide (Figure 4 C). The loss in S-H intensity is not accompanied by an increase in intensity of the S-S stretching vibration (508 cm<sup>-1</sup>) suggesting that disulfide bonds are not being reformed. In the case of the acrylate treated fabric (trace D), the S-H stretching vibration is not observed suggesting complete reaction. Unfortunately the S-S stretching vibration cannot be assessed analytically due to overlap with a strong band in the spectrum of the parent compound at 528 cm<sup>-1</sup>, so it is not possible to determine the extent, if any, that disulfide bonds have reformed. The sulfonate symmetric SO<sub>3</sub><sup>-</sup> stretching vibration is observed at 1042 cm<sup>-1</sup> in the Raman spectra obtained from the treated fabrics (traces

C and D). This band is 4 times more intense in the spectrum obtained from the acrylate treated fabric (trace D) which suggests a much higher rate of reaction for this compound with the thiol groups. The acrylate carbonyl can be observed at 1717 cm<sup>-1</sup> (trace D) which is where it is observed in the parent compound (not shown).

Two different types of C-S-C stretching vibrations are expected in the spectra obtained from the treated fabrics. The C-S stretching vibrations associated with the sulfur of the sulfonate group are observed (see Figure 4, traces C and D) at 765 and 754 cm<sup>-1</sup>.<sup>16</sup> These frequencies are also in agreement with where these vibrations are observed in the parent compounds (not shown). If the H<sub>2</sub>C=C- group has reacted with the thiols on the wool, a CH<sub>2</sub>-S-CH<sub>2</sub> linkage is expected. The C-S-C stretching vibrations are observed at 715 and 652 cm<sup>-1</sup> in the spectra of *n*-dipropyl and *n*-dibutyl sulfides.<sup>17</sup> Through the use of spectral subtraction (Figure 5) weak peaks were identified near 703 and 651 cm<sup>-1</sup>. These features are not present in the spectra of the parent compounds and have thus formed during the reaction. H<sub>2</sub>C=C- group bands are observed in the Raman spectrum obtained from the parent compounds at 3107 (CH<sub>2</sub> symmetric stretch), 3031 (C-H stretch, 2-AS), 1625 (C=C stretch), and 1412 (CH<sub>2</sub> deformation) cm<sup>-1</sup>.<sup>18</sup> These features are not observed in the Raman spectra of the treated wool fabrics. The analysis of the Raman spectra obtained from the treated fabrics is consistent with the monomers being covalently bound to the wool by the H<sub>2</sub>C=C- groups reacting with the thiol groups. On the basis



**Figure 5.** Spectral residuals obtained from subtracting the TCEP reduced wool fabric spectrum from the spectra obtained from the acrylamide, 2-AS treated (A) and acrylate, 3-SP treated (C) wool fabrics. The corresponding spectra obtained from the parent compounds, scaled on the C–H stretching bands of the residuals, are shown as traces B and D, respectively.

of this finding, the treatments would be expected to be durable under normal laundry conditions.

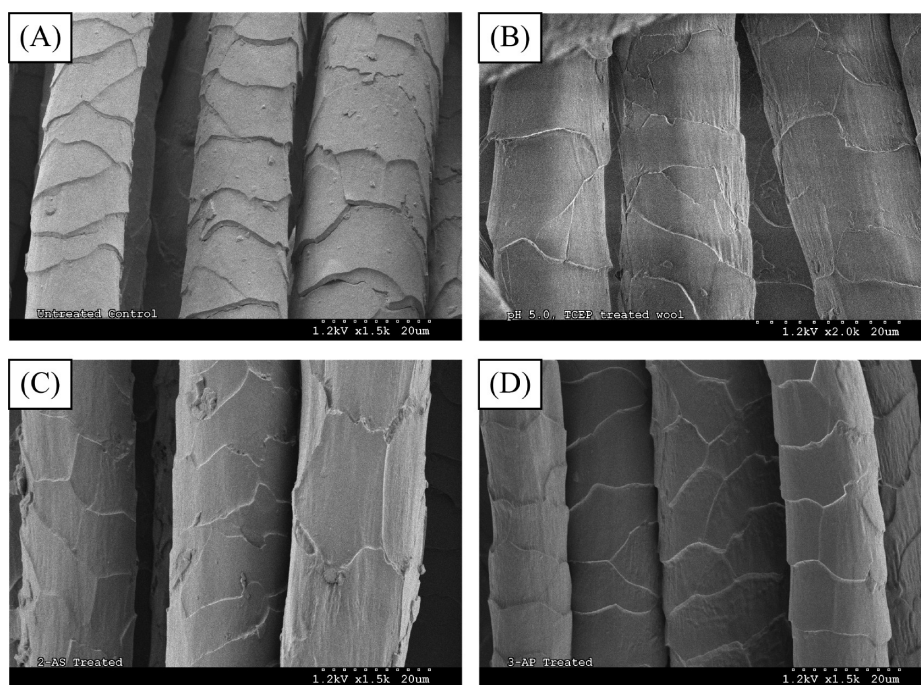
**3.2.2. Surface Morphologies.** The surface morphologies of the treated substrates were examined by SEM. Compared to the untreated wool fibers with smooth scales and sharp edges (Figure 6A), the TCEP pretreated wool exhibits some etching effects with lines or wrinkles noticeable on the fiber surface (Figure 6B). There are no significant changes on the fiber surfaces observed after further treatment with acrylate and acrylamide, as shown in Figure 6 (C and D).

**3.2.3. Liquid Moisture Management.** The liquid moisture management properties of the fabrics, which determine the comfort levels of the fabrics, were evaluated by using an MMT, where the dynamic responses of the substrates towards liquid

moisture were recorded in the first 2 min, as described in the Materials and Methods section.

The MMT results in Table 1 summarize the performance differences of the samples in terms of wetting time, spreading speed, absorption rate, and wetted radius on the top and bottom of the fabrics. It can be seen that TCEP treated wool exhibits an increased water spreading rate and reduced wetting time and absorption rate, in particular on the top surface, compared to the untreated control. This is mainly attributable to the cleavage of cystine disulfide crosslinks in the wool cuticle by TCEP. The introduction of hydrophilic sulfonate groups onto the fiber surface subsequent 2-AS or 3-SP treatment further improved the capability of the fabrics to transfer liquid moisture, as evidenced by a further reduced wetting time and absorption rate, and enhanced the water spreading speed. However, the TCEP–2-AS sample is still unable to transfer the liquid moisture from the top to the bottom within the 2 min of the measurement time. A much superior performance is realized on the TCEP–3-SP modified fabric with overall improved liquid moisture management properties. This is likely due to the much higher grafting density observed for 3-SP than 2-AS on the TCEP reduced wool under the treatment conditions examined.

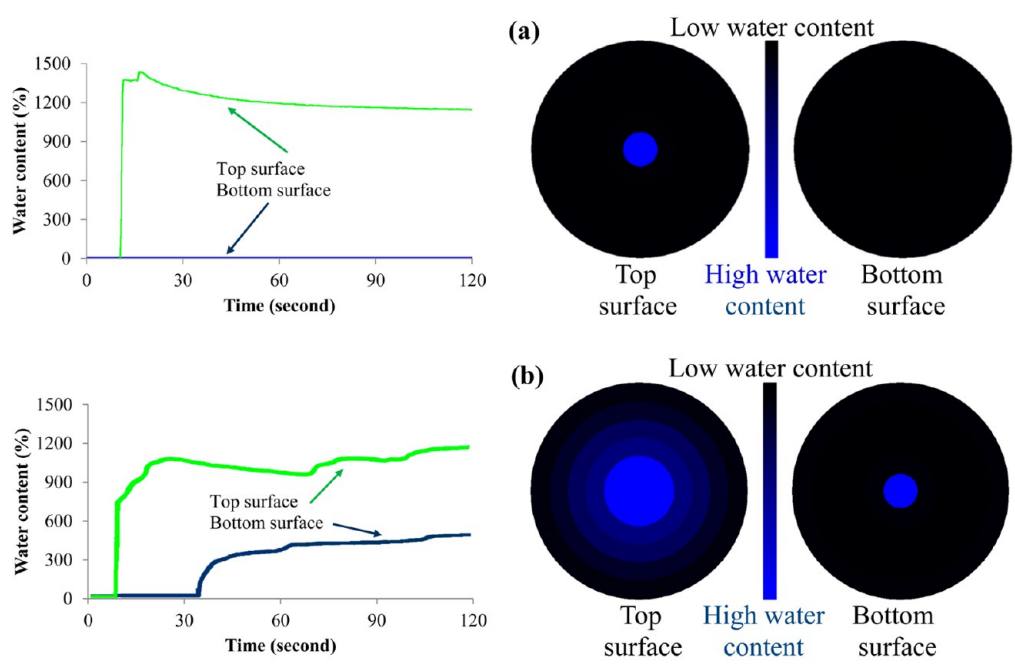
More comprehensive comparisons are presented in Figure 7, where the water content–time and water location–time profiles for the top and bottom surfaces of the untreated and TCEP–3-SP treated fabrics are illustrated. It is known that the maximum moisture absorption rate (%/s) of a fabric is defined based on the initial slope of the water content–time curve on a fabric surface.<sup>19</sup> It can be seen that water dispensed onto the untreated fabric (Figure 7a) remained on the top surface for 16 s and was confined in a 5 mm maximum wetted radius with very limited water spreading. The absorption rate on the top surface is very high as evident by the steep initial slope. There was no liquid moisture transferred to the bottom surface at the



**Figure 6.** SEM images of wool fibers: (A) untreated, (B) TCEP pretreated, (C) combined treatments of TCEP and 2-AS, and (D) combined treatments of TCEP and 3-SP.

Table 1. Liquid Moisture Management Properties of the Treated and Untreated Fabrics

wool sample	wetting time (s)		absorption rate (%/s)		wetted radius (mm)		spreading speed (mm/s)	
	top	bottom	top	bottom	top max	bottom max	top	bottom
untreated control	16	120	460	0	5	0	0.3	0
TCEP treated	8	120	105	0	5	0	0.6	0
TCEP-2-AS	7	120	54	0	5	0	0.8	0
TCEP-3-SP	7	33	67	14	10	5	0.8	0.2



**Figure 7.** Water content and water location vs time on the top and bottom surfaces of the (a) untreated and (b) TCEP-3-SP treated fabrics during the MMT testing.

end of the 120 s measurement. As such, the water content on the bottom surface was 0, as were the absorption rate, wetted radius, and spreading speed. Similar phenomena were also observed for the TCEP and TCEP-2-AS treated samples (Table 1).

In contrast, the TCEP-3-SP treated sample (Figure 7b) was fully wetted to a 10 mm radius on the top surface, with further water spreading into a larger radius (>20 mm). It was also observed during the MMT measurement that the liquid passed through the fabric and fully wetted the bottom of this fabric in a 5 mm radius. This has clearly demonstrated a significantly improved moisture management capability of the TCEP-3-SP fabric.

**3.2.4. Antistatic Property.** Antistatic property is directly related to the surface resistivity of a substrate. The lower the surface resistivity the better the antistatic property is. A substrate with a surface resistivity lower than  $1 \times 10^{12} \Omega/\text{sq}$  would exhibit a certain degree of antistatic effect, and when the surface resistivity is in the range of  $10^9$ – $10^{10} \Omega/\text{sq}$ , the substrate would show a very good antistatic effect.<sup>20</sup> Table 2 presents the test results obtained from the treated and untreated wool substrates, as well as the classification scales of antistatic performance based on the surface resistivity. It is evident that the untreated wool fabric has a high surface resistivity, over  $10^{12} \Omega/\text{sq}$ , indicating a very poor antistatic property, while the TCEP treatment alone reduced the surface resistivity down to  $7 \times 10^{11} \Omega/\text{sq}$ . The subsequent treatment

**Table 2.** Antistatic Properties of the Treated and Untreated Wool Fabrics

samples	surface resistivity ( $\Omega/\text{sq}$ )	surface resistivity range and antistatic assessment <sup>20</sup>
untreated control	$1.48 \times 10^{12}$	$>10^{12}$ insufficient
TCEP treated	$7.04 \times 10^{11}$	$10^{11}$ – $10^{12}$ sufficient
TCEP-2-AS	$5.28 \times 10^{11}$	$10^{11}$ – $10^{12}$ sufficient
TCEP-3-SP	$8.34 \times 10^9$	$10^9$ – $10^{10}$ very good

with 2-AS yielded a substrate of  $5.3 \times 10^{11} \Omega/\text{sq}$ . Although both of the treated samples possess sufficient antistatic behavior, the most profound antistatic performance was achieved by the grafting treatment with 3-SP, which effectively reduced the surface resistivity of wool by over 2 orders of the magnitude.

For comparison purposes, a bleached cotton knitted fabric ( $200 \text{ g}/\text{m}^2$ ) was also tested under the same conditions. The surface resistivity measurement obtained was  $1.26 \times 10^{10} \Omega/\text{sq}$ . It is well known that bleached cotton has an excellent hydrophilicity, which renders it a reasonably good antistatic property. In comparison, the surface resistivity of the TCEP-acrylate modified wool (about  $8 \times 10^9 \Omega/\text{sq}$ ) is even lower than that of the bleached cotton, indicating a very good antistatic performance. As discussed earlier, the significantly superior results obtained with the acrylate treatment are due to the higher grafting density of the acrylate than that of the acrylamide. These results are consistent with those observed in

the MMT test results. The results have clearly demonstrated that the cleavage of disulfide crosslinks and a high amount of hydrophilic groups on the surface contribute to the improved antistatic effect.

**3.2.5. Wet Burst Strength.** Necessary care and attention need to be taken to minimize any strength loss caused by the treatments. Table 3 presents the wet burst strength measure-

**Table 3. Wet Burst Strength of the Treated Substrates**

samples	wet burst strength (kPa)	strength loss (%)
untreated control	316	-
TCEP treated	235	25.4
TCEP-2-AS	238	24.4
TCEP-3-SP	253	19.7

ments obtained from the treated and untreated substrates. As the results show, the burst strength of the TCEP pretreated fabric is about 25% lower than that obtained from the untreated fabric. Disulfide bond cleavage is mainly responsible for the strength loss of the fibers. The subsequent grafting treatments did not cause any further reduction in the wet burst strength of the fibers. The sample treated with the acrylate (TCEP-3-SP) actually showed a slight improvement in strength compared to the TCEP pretreated sample rendering a final strength loss within 20% of the untreated fabric. This is likely attributed to the higher degree of thiol-acrylate bonds and/or thiol-acrylate oligomer being formed in the 3-SP treated wool fiber. In fact, almost all wet processing of wool involves a certain degree of fiber strength loss. For example, dyeing often results in a strength loss of 10% or more. The strength losses determined for the treated samples can be considered to be in the acceptable range for domestic textile applications. There is scope to further reduce this loss by optimizing the extent of reduction in the initial treatment step.

#### 4. CONCLUSIONS

This paper introduces an effective and facile method to modify the antistatic and liquid moisture management properties of keratinous materials. Although wool was used as a representative example in this study, the method developed is applicable to all keratinous materials.

The results of this study have demonstrated that the pretreatment of a keratin fiber with TCEP is feasible. With proper selection of the treatment conditions, effective cleavage of cystine disulfide bonds in a keratin fiber can be achieved to yield sufficient cysteine thiols while maintaining acceptable fiber mechanical properties. Hydrophilic groups can be successfully grafted onto the TCEP reduced fiber by reaction with an acrylate sulfonate or acrylamide sulfonate through thiol-ene click chemistry. The thiol-acrylate reaction is more efficient than the thiol-acrylamide reaction. As a result, the keratinous substrate modified with 3-sulfopropyl acrylate potassium salt exhibited significantly improved liquid moisture management property and reduced surface resistivity, leading to a substantially improved antistatic property and comfort level. The surface resistivity of the modified wool is even lower than that of a bleached cotton. The study has also indicated that this novel approach will offer more opportunities to develop high-performance and functional products made from keratinous materials.

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##### Notes

The authors declare no competing financial interest.

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