

## Improving the Properties of Chemically Damaged Wool Fabrics with Carbohydrate Polymers

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**ABSTRACT:** Wool is a natural composite material consisting of keratin and keratin-associated proteins as the key molecular components. During wool product processing, a variety of chemical and enzymatic reagents are used, the side-effects of which can include the removal of the outside layers of the fiber (cuticle) and damage within the internal protein matrix of the fiber. This can reduce the mechanical strength and durability of wool fabrics. We report the use of neutral, cationic, and anionic carbohydrate polymers, namely 2-hydroxyethyl cellulose, chitosan and alginate, as repair agents to improve the mechanical properties and morphology of wool fabrics damaged under harsh alkaline conditions. Tensile strength, peel adhesion, scanning electron micrographs, and fabric wettability evaluation reveal the cationic polymer, chitosan, to be most effective at remedying the effects of the alkaline treatment. The improved mechanical properties observed after chitosan treatment may offer viable remediation routes for adding value to processing-damaged wool textiles. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3105–3111, 2013

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### INTRODUCTION

Wool is a natural composite material, with keratin as its basic constituent. Wool that is not under tension exhibits characteristic X-ray diffraction patterns for  $\alpha$ -keratin. This is a crystalline protein with adjacent polypeptide chains crosslinked through disulfide bonds from cystine amino acid residues. This cross-linking plays a significant role in making keratin an insoluble material with high resistance to physical degradation.<sup>1–3</sup> The important histological components of wool are the cortical and cuticle cells, which are linked through the cell membrane complex (CMC), forming a continuous phase in the fiber. The cuticle cells form the outermost part of the fiber surrounding the cortical cells. The surface of cuticle cells is hydrophobic because of the presence of lipids (predominantly the branched-chain lipid, 18-methyl eicosanoic acid) that are covalently bound to the underlying keratin proteins via thioester linkages with cysteine residues. These lipid-to-protein thioester bonds are relatively reactive and can be readily cleaved by alkaline chemical reagents, yielding a hydrophilic and anionic proteinaceous surface with a high concentration of surface thiols.<sup>1,4–6</sup>

A range of alkaline reagents including soaps or detergents are used in wool processing steps such as the scouring of greasy wool, laundering of wool fabrics, and dyeing. This can

progressively remove the lipid layer from the wool cuticle and also cause hydrolysis of peptide bonds and amino acid side-chains. Lipid removal exposes cysteine and other acid amino acid side chains, which oxidize to form cysteic acid,<sup>4,6,7</sup> or hydroxyl, carboxyl, amine and amide groups, creating an anionic wool surface. These chemical changes on the wool surface increase its surface free energy and wettability,<sup>4,6–8</sup> and can negatively impact the mechanical strength and durability of wool fabrics.<sup>9</sup> Wool surface damage may also be caused by the proteolytic enzymes used in wool textile processing, which frequently penetrate through the cuticle and degrade the internal wool structure.<sup>5,10–13</sup> Wool is also damaged by microbes and insects, which secrete enzymes that cause keratin hydrolysis.<sup>14</sup> Such inherent damage caused to wool products during their processing and storage has created a need for reparative technologies to mitigate, or even reverse, the undesirable characteristics typical of damaged wool.

Natural polymers, including carbohydrates, have attracted a great deal of interest in the textile industry as possible substitutes for synthetic polymer coatings. Many of them possess unusual physicochemical and biological characteristics. Polymers such as chitosan are used to improve a variety of fabric properties.<sup>15–21</sup> One application of chitosan treatment with significant potential, but that has not yet been well-developed, is

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restoration of the desirable characteristics in wool fabrics damaged seriously during textile processing. This article describes the behavior of wool fabrics when treated with different carbohydrate polymers after they have been damaged in harsh alkaline conditions with potassium hydroxide. The damage model chosen was an extreme one compared to those expected to be encountered in industry, allowing the ameliorative effects of polymer coatings to be observed in a proof-of-principle context. Three polymers with varying characteristics; chitosan, alginate, and 2-hydroxyethyl cellulose (cationic, anionic, and neutral polymers, respectively) were chosen to study their restorative effects on damaged wool fabrics. In addition to the creation of a novel route for damaged wool fabrics to be recycled and reused, a secondary objective of such research is to introduce new surface properties to wool products.

## EXPERIMENTAL

### Materials

Woven fabric made from 100% nonshrink resistant New Zealand merino wool was used in this research. The fiber diameter was 18.5 micron and the fabric weight was 145 g/m<sup>2</sup>. Chitosan with a deacetylation of 91% and average molecular weight of 890 kDa was extracted from Alaska snow crab (Shanghai Waseta International Trading Company, Shanghai, China). 2-hydroxyethyl cellulose with an average molecular weight of 1300 kDa was supplied by Sigma-Aldrich, St. Louis, MO. Alginic acid (sodium salt) was purchased from Scientific Polymer Products, Ontario, NY. Potassium hydroxide, glacial acetic, and glycerol were obtained from BDH, Poole, UK.

### Damaging Wool Fabrics

The wool fabric samples were immersed in a harsh alkaline environment generated with a solution of 0.1 N KOH at 70°C for 20 min using a constantly shaking water bath. The mass ratio of fabric to solution was 1:100. Once the alkaline treatment was completed, the wool was rinsed thoroughly five times with distilled water and then dried in an air-circulated oven at 60°C for 4 h.

### Treatment of Damaged Wool with Carbohydrate Polymers

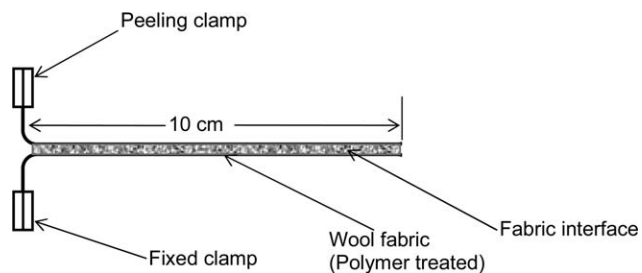
For each treatment, aqueous solution consisting with 1wt % polymer was prepared at 70°C for 3 h under constant stirring. Chitosan was dissolved in 1wt % acetic acid, and alginate and hydroxyethyl cellulose solutions were prepared using distilled water. The damaged wool fabric samples (10 × 10 cm<sup>2</sup>) were immersed in polymer solutions separately and treated at 70°C for 2 h with constant shaking. After polymer treatment, the samples were washed thoroughly with distilled water and dried in an air-circulated oven for 4 h at 60°C.

### Infrared Spectroscopy

Infrared spectra were taken using a Perkin Elmer Spectrum 400 FTIR spectrometer with an attached Spotlight 200 FTIR microscope equipped with a gold mirror. In each case, absorbance spectra of wool fabrics were produced using 50 scans of each sample with a spot size of 100 × 100 μm<sup>2</sup>.

### Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX)

The surface morphologies of the wool fabrics were observed at 130× magnification under a JEOL JSM 7000F field emission,



**Figure 1.** Schematic of the peel test. Two wool fabrics treated with polymers are thermally compressed and separated to measure the fabric interfacial adhesion.

high resolution scanning electron microscope. Prior to analyzing the morphology, fabrics were coated with a thin layer of carbon. The elemental compositions of wool fabrics were determined in an EDX spectrometer attached to the electron microscope. For each fabric, three specimens were scanned and all data were collected in the energy range of 0–20 keV under ×2500 magnification using an accelerating voltage of 10–15 kV and scanned area of 50 × 50 μm<sup>2</sup>. The average values of elemental compositions with standard errors are reported.

### Tensile Properties

The wool fabrics were conditioned and tested according to the ISO 13934-2 method. The tensile properties of the wool fabrics were measured using a universal testing machine INSTRON 4204 (Instron, High Wycombe, UK) with a load cell of 100 N, gauge length of 20 mm and extension speed of 50 mm/min. Each tested specimen had an average length of 100 mm, width of 10 mm, and thickness of 0.20–0.30 mm. For each sample, five test specimens were tested and the stress–strain plot that represents the average results was reported. Prior to testing, all samples were conditioned under a standard atmospheric condition (50 ± 2% relative humidity and 21 ± 1°C) for 24 h.

### Peel Test

The peel test is a widely used method for determining the interfacial adhesion between two polymeric substrates. Prior to testing, the wool fabric samples (10 × 12 cm<sup>2</sup>) were immersed completely in 1 wt % solution of 7 : 3 polymer : glycerol for 30 min with constant shaking and dried in an air-circulated oven at 60°C for 4 h. Two fabrics treated under similar conditions were compressed face-to-face at a press temperature of 120°C, pressure of 3.4 MPa and press time of 3 min using a 0.25 MN platen vulcanizing press (Shanghai Light Industry Machinery Company, Shanghai, China). The adhesion peel strengths were examined according to ASTM Standard D903-98 (2010) using the INSTRON 4204 with a load cell of 10 N, gauge length of 20 mm, and extension of 100 mm/min. Figure 1 shows a schematic representation of the peel test. For each polymer treatment, the interfacial adhesion of KOH-treated fabrics was compared with that of control fabrics. For each sample, five test specimens were prepared with dimensions of 2 × 12 cm<sup>2</sup> and averaged results with standard errors are reported.

### Measurement of Hydrophilicity

The hydrophilicity of wool fabrics was evaluated with respect to the degree of wettability and percent of water absorption. The

wettability of the fabrics was determined by measuring the time for a 10  $\mu\text{L}$  drop of water to soak fully into the fabric when observed at an angle of  $45^\circ$ . For each sample, 10 repeated measurements were carried out to obtain the mean values. The shorter the average wetting time, the greater the fabric hydrophilicity. To measure percent water absorption, the fabrics were immersed in water for 24 h and the weight gain was determined gravimetrically after removing excess surface water using blotting paper. For each sample, five repeated measurements were performed for weight gain.

## RESULTS AND DISCUSSION

### Chemical Changes of Fabrics

Infrared and EDX analytical techniques were used to study the changes in the chemical characteristics of the wool fabrics before and after treatment. In infrared spectra (Supporting Information shown in Figure S1), the fabrics, irrespective of treatment types, showed the characteristic bands of amide I (C=O stretching) and amide II (N-H bending and C-H stretching) in the range of  $1750\text{--}1650\text{ cm}^{-1}$  and  $1530\text{--}1630\text{ cm}^{-1}$ , respectively. The characteristics of the amide I band are associated with the C=O stretching of  $\alpha$ -helix,  $\beta$ -sheet, and random disorder secondary structures of keratin.<sup>22–25</sup> Minor changes of the amide I band with chemical treatment were observed, indicating some conformational arrangement of wool keratins.

EDX evaluation allows profiling of the relative elemental composition of surfaces, and therefore provides insight into molecular changes occurring at the surface. The untreated wool fabric control surface had a relative elemental composition of 80.2% carbon, 17.6% oxygen, and 2.2% sulfur atoms (nitrogen's low energy level prevents its detection with EDX) (Table I). This is comparable with values reported earlier.<sup>14,26</sup> High carbon concentration is due to carbon coating used during SEM/EDX sample preparation. On treatment with KOH, the relative sulfur content of the wool fiber surface was reduced by more than 50%. This is in harmony with earlier studies.<sup>9,27–29</sup> Sulfur reduction is consistent with removal of cuticle-associated high-cysteine proteins<sup>30,31</sup> under alkali conditions, and is indicative of significant surface damage.

Each of the carbohydrate surface treatments had an observable effect on the relative elemental composition of the wool fiber surface, indicating successful polymer application, with the cellulose treatment resulting in a composition that was most similar to the undamaged wool. The chitosan treatment resulted in the greatest

increase in relative carbon abundance at the surface, while the alginate treatment resulted in the largest increase in relative oxygen abundance. The relative increase in sulfur at the surface observed with the chitosan treatment, as compared to the sample that was alkali-damaged only, suggests that the chitosan treatment may be penetrating into the fiber surface, resulting in a higher relative abundance of sulfur-containing moieties from near-surface proteins. This effect is not observed with either the alginate or cellulose treatments, because of poor or no chemical interaction with anionic wool keratin as discussed below.

### Fabric Surface Morphology

Wool fabrics have a large surface area in relation to their bulk properties, influencing their behavior as textiles. As shown in the SEM images (Figure 2), the untreated wool surface consists of flattened cellular sheets of cuticle cells that overlap each other from root to tip along the fiber. The cuticle cells are  $\sim 0.5\text{ }\mu\text{m}$  thick and form a protective sheath around an internal cortex. The cells have sharply defined scale edges, and at the junctions of cells, the surface drops to the level of the next underlying cuticle cell. The junction between the upper and lower scales is distinct and generally small as compared to the cell thickness.<sup>1</sup> The SEM images demonstrate that on alkaline treatment the scales suffer significant degradation and removal along with breaking of keratin integrity, leading to serious fiber damage. This is also undoubtedly accompanied by changes in other key fiber properties, such as strength. Encouragingly, it appears that the wool fiber integrity is partly recovered on treatment with carbohydrate polymers [Figure 2(c), fiber morphology]. It is anticipated that the factors such as hydrophilicity, reduced crystallinity, and negative charges on the keratin backbone of KOH-treated wool fabrics constitute the underpinning drivers for durable coating with positively charged and hydrophilic polymers such as chitosan.

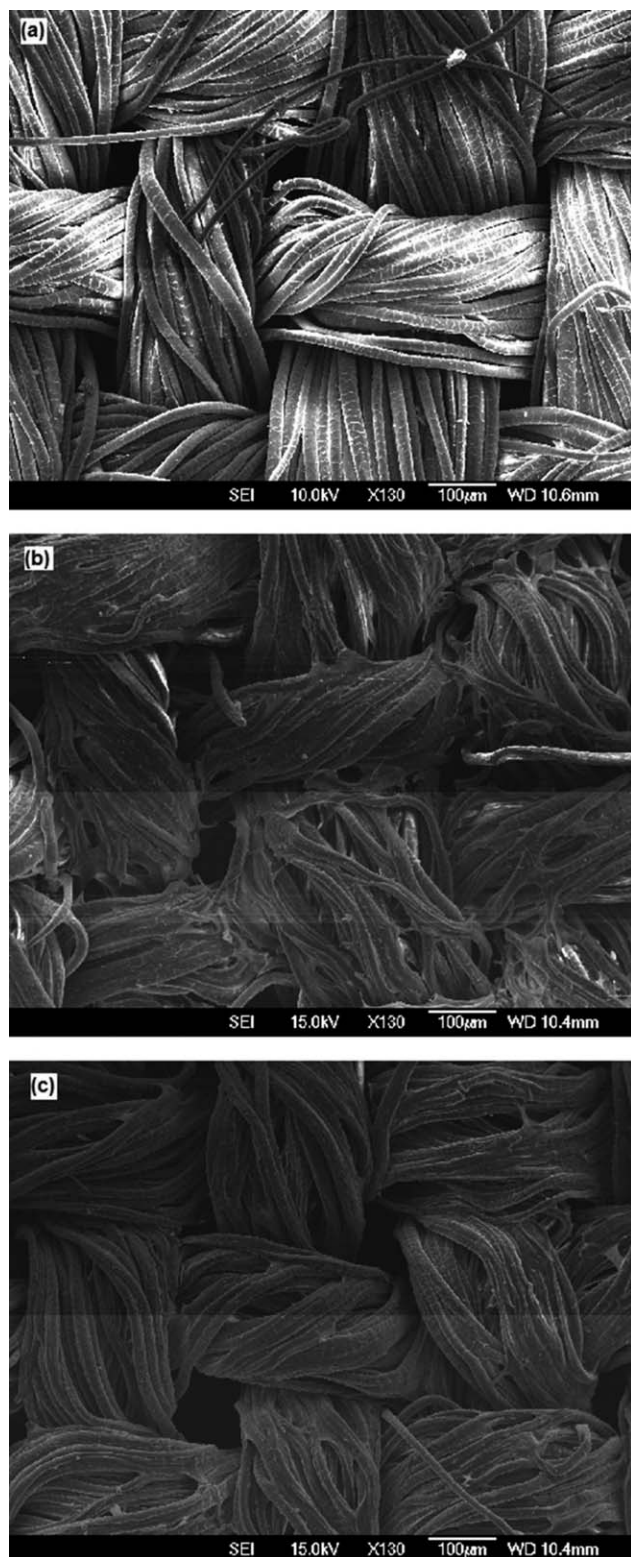
### Surface Wettability Studies

The surface wettability of textiles is an important factor in determining the kinetics of chemical treatment, and their wearing comfort and maintenance. Chemical changes to the surface, or the application of polymers can modify wettability. Wool fibers are highly moisture absorbent because of their proteinaceous nature, and can absorb moisture up to about 30% of their own weight without feeling wet to the touch.<sup>32</sup> However, the surface of wool is hydrophobic in nature, due to the bound surface lipid layer, and has low wettability.

The wettability of the fabric samples was measured in terms of wetting time and percent of water absorption. As anticipated,

**Table I.** Relative Elemental Composition Analysis of Wool Fabric Surfaces Using EDX Spectroscopy

Element (atomic %)	C	O	S	K	Na
Position (keV)	0.277	0.525	2.307	3.312	1.041
Undamaged wool	80.2 $\pm$ 3.6	17.6 $\pm$ 3.6	2.2 $\pm$ 0.4	-	-
KOH-treated wool	78.3 $\pm$ 2.5	19.9 $\pm$ 2.0	0.8 $\pm$ 0.1	0.7 $\pm$ 0.1	-
KOH and alginate	76.9 $\pm$ 4.5	21.2 $\pm$ 3.3	0.9 $\pm$ 0.2	-	0.4 $\pm$ 0.0
KOH and chitosan	82.6 $\pm$ 1.4	15.7 $\pm$ 1.6	1.5 $\pm$ 0.4	-	-
KOH and cellulose	80.2 $\pm$ 4.9	17.3 $\pm$ 4.1	0.9 $\pm$ 0.3	-	-



**Figure 2.** Scanning electron microscopic images of (a) untreated wool; (b), KOH-damaged wool; and (c) KOH-damaged wool treated with chitosan.

untreated wool was highly hydrophobic and had no capacity to absorb water, taking over 1 h for droplets to absorb or evaporate. The KOH treated wool sample showed a significant

increase in wettability. The time to wet reduced to about 5 s for the fabric treated with KOH (Table II), in harmony with previous reports.<sup>6,7</sup> Average water absorption by untreated and KOH treated wool was 43 and 83 wt %, respectively. Although alginate and hydroxymethyl cellulose surface treatments had only a minimal effect on water absorption relative to the alkali-damaged wool, chitosan treatment significantly reduced the water absorption to 64 wt % (Table II). This indicates effective coating or masking of the abraded keratin surface after chitosan treatment, as compared to the hydroxyethyl cellulose and alginate treatments, with a return to surface wettability values closer to that of undamaged wool fabric.

The increased wettability of alkali treated wools can be attributed to the exposure of hydrophilic keratin moieties (through surface delipidation).<sup>26</sup> SEM evaluation (Figure 2) showed that chitosan can effectively coat the fiber surface, and this no doubt led to its reduced hydrophilicity, as chitosan is more hydrophobic than exposed keratin. In terms of restoration of a protective hydrophobic surface, chitosan therefore demonstrated a reparative effect for alkali-damaged wool fibers.

### Mechanical Properties

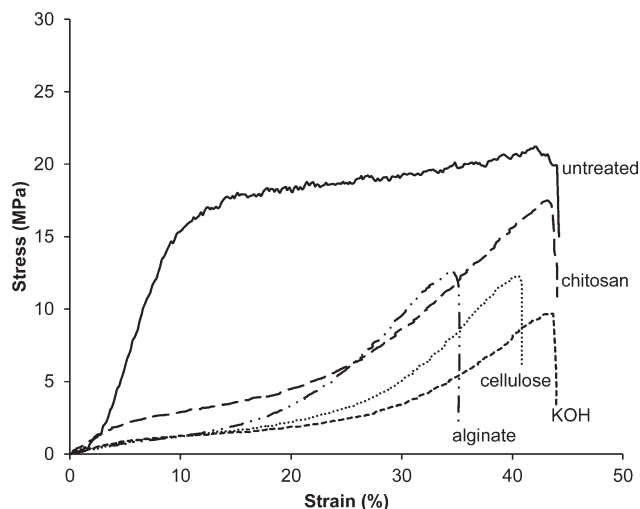
The mechanical performance of the fabric samples was measured in terms of their tensile or stress–strain properties (Figure 3). In wool, cortical cells are held together via the CMC, which is a lightly crosslinked phase that acts as a kind of glue in retaining the mechanical integrity of the fiber. As compared to other regions, the CMC is particularly susceptible to chemical ingress and attack. Alkaline reagents can damage the disulfide bonds of the CMC, after penetrating the wool surface lipid layer. This can lead to disintegration of the fibers by dislodgement of cortical cells, resulting in loss of mechanical strength.<sup>2</sup> This provides an explanation for the decrease in fabric strength observed after treatment with KOH.

Untreated wool fabric had an average tensile strength of 21 MPa, while KOH treated fabric had a tensile strength of only 9.5 MPa (Figure 3). The use of carbohydrate polymers after alkali damage partially restored the fabric strength, particularly when cationic chitosan was used. The treatment of damaged wool fabrics with chitosan resulted in a partial recovery of the strength loss (17.3 MPa), in harmony with previous studies showing improvements in mechanical strength with chitosan treatments.<sup>18,25</sup> This may be attributed to the strong ionic and/or covalent crosslinking of chitosan with the polar groups of wool keratin, creating a durable chitosan surface layer, which can partially remedy the negative effects of alkali exposure on fabric mechanical strength and surface morphology. In contrast, the effects of anionic (alginate) and neutral (hydroxyethyl cellulose) polymers on recovering the wool strength were less significant. The alkali treatment also significantly reduced the tensile modulus or stiffness of wool fabrics, which remained unchanged or marginally increased on treatment with carbohydrate polymers. The low fiber modulus is attributed to the damage of CMC glue during alkali treatment. The chemical structures of the three polymers and the possible interaction mechanism of chitosan with alkali treated wool fabrics are shown in Figure 4.

**Table II.** Wool Fabric Surface Wettability, as Measured Using Wetting Time and % (w/w) Water Absorption.

Sample	Wetting time (s)	Standard error	Absorption (%)	Standard error
Undamaged wool	n/a	n/a	42.7	±1.8
KOH-treated wool	6.7	±1.3	83.4	±0.9
KOH and alginate	5.3	±0.8	79.9	±0.7
KOH and chitosan	164.2	±37.1	64.1	±1.3
KOH and cellulose	4.0	±0.9	80.0	±1.0

Of the three polymer coatings, chitosan stands out as best at remedying the effects of alkali (KOH) damage.



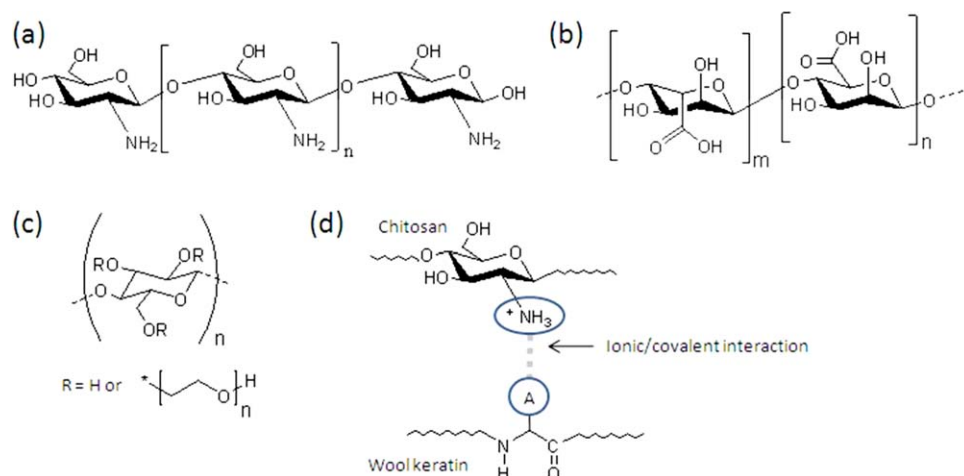
**Figure 3.** Stress–strain properties of wool fabric samples.

### Peel Adhesion Test

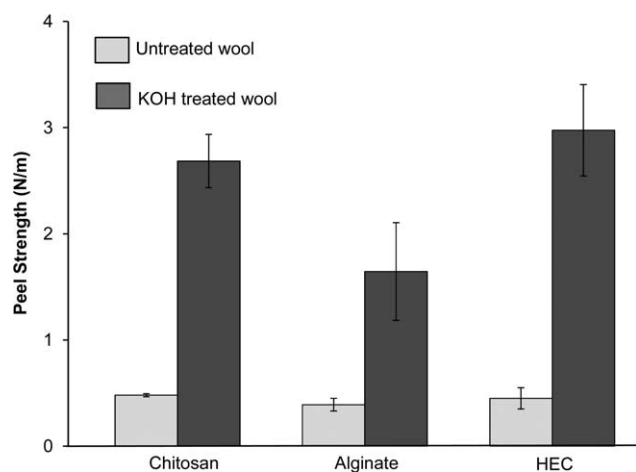
The interfacial adhesion between polymer treated fabrics was estimated via peel strength measurement (Figure 5), which predicts the durability of polymer coatings on fabrics. The greater

the interfacial adhesion, the higher the peel strength value. The structure and other properties such as polarity of the coating polymer, and the surface properties of the fabric are critical factors in determining the peel strength.

Without surface lipid-removal by alkali pretreatment, wool fabrics showed an average peel strength of 0.5 N/m, irrespective of polymer treatment. In contrast, fabrics treated with polymers after KOH exposure exhibited peel strengths 3–6 times greater than without alkali exposure (Figure 5). On treatment with chitosan, alginate and hydroxyethyl cellulose, the fabrics exposed to KOH showed mean peel strengths of 2.7, 1.7, and 3.0 N/m, respectively. This demonstrated that interfacial adhesion between damaged wool fabrics is affected by the properties of polymers applied to the surface. Alkali treatment makes the fabric surface anionic because of the exposure of moieties such as thiol, sulfonic, and carboxylic groups of the underlying keratin. Therefore, the significant increase in peel strength caused by treatment with chitosan is likely due to strong ionic and/or covalent interactions with the keratin matrix (Figure 5). In addition to chemical interactions, polymer molecules increase peel strength more effectively when they are of large relative molecular size, due to mechanical inter-locking. Accordingly, damaged fabric treated with a high molecular weight polymer, hydroxyethyl cellulose (1300 kDa), also exhibited high peel



**Figure 4.** (a) Cationic chitosan, (b) Anionic alginic acid, (c) Neutral 2-hydroxyethyl cellulose, and (d) Possible mechanism of the interaction of chitosan with keratin that leads to improvements in the physical characteristics of alkali-damage wool fabrics. “A” represents groups such as —SH and/or —SO<sub>3</sub>H, —COOH on the surface of chemically damaged wool. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 5.** Peel strengths of wool fabrics, showing high interfacial adhesion between damaged fabrics after treatment with chitosan, alginate, and 2-hydroxyethyl cellulose. Error bars represent standard error of the mean.

strength values. The low peel strength of alginate treated fabrics indicates poor interfacial adhesion with wool, which is likely due to less stable interactions due to the anionic character of both alginate itself, and the damaged wool surface. As shown in Figure 5, the peel strength values for alkali damaged fabrics had high standard errors, indicating uneven removal of surface fatty acid layers. This in turn has contributed to a patchy exposure of the reactive (anionic) fiber surface moieties, resulting in an unevenly dispersed polymer surface coating.

## CONCLUSIONS

In studying the capacity of carbohydrate polymers to improve the properties of wool fabric damaged in harsh alkaline conditions, the cationic polymer, chitosan, demonstrated the most encouraging results in terms of post-treatment fiber properties. Compared to anionic (alginate) and neutral (2-hydroxy ethyl cellulose) polymers, chitosan was highly effective in improving the mechanical performance of the damaged wool. In addition, compared to alkali damaged wool and fabrics treated with alginate and hydroxyethyl cellulose, chitosan treated fabrics showed high wetting times, indicating that chitosan formed a better protective coating on the wool surface. Infrared spectra revealed that alkali treatment causes some minor changes to the amide I band pattern, indicating some conformational rearrangement of keratin secondary structure, which was affected only marginally by treatment with carbohydrate polymers. SEM evaluation revealed that carbohydrate polymer treatments resulted in robust surface coating, and improved the fiber integrity of the damaged wool fabrics.

Regarding probable mechanisms of action, the results indicate that negatively charged sites on the wool fiber, caused by lipid removal during alkali treatment, facilitate the formation of strong ionic and/or covalent interaction of chitosan with keratin. When compared with polymers of differing in their ionic characteristics (anionic alginate and neutral hydroxyethyl cellulose), the cationic chitosan was found to be the most effective in improving critical textile properties such as mechanical strength, fiber integrity, and surface wettability after severe alkali

damage. The encouraging improvements in important textile parameters observed in treated fabrics in this study provided proof-of-concept for the suitability of chitosan-like cationic polymer treatments for both new wool surface treatment applications, as well as the recycling and reparation of damaged wool products.

Future projects recommended to take this closer to application in industry would examine the response to treatment of less severely damaged textiles that might be realistically expected to be fully repairable, and would look at how to optimize chitosan and other cationic polymer treatment protocols.

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