

## The Effect of Wool Surface and Interior Modification on Subsequent Photostability

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**ABSTRACT:** Wool surface and interior modification can impart favorable properties, such as felting/shrink resistance, settability, or improved affinity for dyes. However, in principle such modification may have an either beneficial or adverse effect on the subsequent photostability of the modified wool. In this study, a range of representative physical and chemical modification approaches including the use of helium gas plasma, papain, acylation with acid anhydride, and permanganate oxidation were applied to wool fabrics, and the subsequent effects characterized using scanning electron microscopy, FTIR-ATR, contact angle goniometry, fluorescence spectrophotometry, and tensile strength test. The relative photostability of control and treated wool were evaluated in terms of coloration changes under UVA, UVB, and blue light irradiation. We have shown that the subsequent photostability of modified wool fabrics is highly dependent on the modification type, and this factor should be carefully considered in the design and application of wool treatments. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** wool; modification; photostability; color

Received 20 November 2011; accepted 24 February 2012; published online 00 Month 2012

DOI: 10.1002/app.37573

### INTRODUCTION

Wool has a complex morphological and chemical structure, consisting of an outer layer of cuticle scales surrounding an inner cortex. It contains over 170 different proteins and polypeptides containing 20 different  $\alpha$ -amino acids.<sup>1–5</sup> The physical and chemical modification of wool is of particular commercial interest to the wool textile industry. Common targets for improvement include felting or shrink resistance, settability, affinity or resistance for dyes/pigments. To meet these modification requirements, enzymatic treatment, plasma treatment, oxidation, and acylation are commonly applied to wool.

Enzymatic treatment is a potential eco-friendly alternative to the chlorine-based Hercosett process to improve the felting/shrink tendency of wool and has potential use in the industrial sector. It also enables enhancement of the handle, lustre, whiteness, and dye accessibility of wool.<sup>6–9</sup> Industrial low temperature plasma treatment on wool is used to improve felting/shrink resistance, hydrophilicity, and uptake of dyes.<sup>10–14</sup> Surface oxidation, including potassium permanganate treatment, can be utilized to improve the shrink resistance of wool.<sup>15–18</sup> Acylation of wool by reaction with acid anhydride is known to improve the settability and shrink resistance of wool and provide binding sites for other functional groups.<sup>18–24</sup>

Studies on the color stability of wool have demonstrated that wool can be either yellowed by ultraviolet light or bleached by visible light, in particular between 400 and 450 nm.<sup>25–30</sup> The photostability of wool, especially the susceptibility of wool to photoyellowing, is one of the few areas where wool compares relatively poorly to cotton and some synthetic.<sup>25</sup> It is well known that certain common pretreatments of wool, such as chemical bleaching and/or fluorescent whitening treatment can accelerate subsequent photoinduced discoloration of wool.<sup>31</sup> However, few studies have paid attention to the effect of other functional surface and interior modification techniques on the subsequent photostability of wool. Evaluation of the effects of these treatments is therefore of considerable importance, particularly if a photoprotective effect is observed.

In this study, wool surface and interior modification methods including atmospheric pressure helium gas plasma treatment, enzymatic treatment with papain, acylation with succinic anhydride, and chemical oxidation with potassium permanganate have been applied. Physical and chemical changes were characterized using scanning electron microscope (SEM), contact angle goniometry and FTIR-ATR techniques. The intrinsic tryptophan-type fluorescence of different wool fabric samples was also examined, along with the determination of yellowness changes

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under UVA and UVB irradiation and whiteness changes under blue light irradiation.

## EXPERIMENTAL

### Materials

Clean plain-woven wool fabric with a unit weight of 138 g/m<sup>3</sup> was used in this study.

### Enzymatic Treatment

A concentration of 20% papain on weight of wool fabric (o.w.f.) was chosen after our preliminary trials on the efficacy of scale removal in relation to papain concentrations. Papain was dissolved in 0.1M Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub> buffer solution, pH 6.0 and the enzymatic treatment carried out at 65°C in a water shaker bath, at 60 rpm, for 2 h (liquor ratio: 20:1). To deactivate papain, the treated wool fabric sample was soaked in boiling water for 5 min.

### Plasma Treatment

An in-house built laboratory-size Atmospheric Pressure Glow Discharge (APGD) instrument was used to treat wool fabric samples at ambient temperature, using helium as carrier gas.<sup>32</sup> The discharge chamber consisted of two parallel 10 cm × 10 cm copper electrodes separated by a 2.5-mm space. Glow discharge between the electrodes was optimal at 90 V and a frequency of 20 kHz. Before the plasma discharge was initialized, helium gas was flushed into the discharge chamber for at least 3 min to clear air trapped in the reaction chamber. The rate of helium gas flow was maintained at 1500 sccm.

### Acylation

Totally, 40 g/L succinic anhydride was dissolved in dimethyl sulfoxide (DMSO). The treatment was conducted in a 75°C water bath, at 60 rpm, for 2 h (liquor ratio 50 : 1). Acylated wool fabric was thoroughly rinsed with distilled water and DMSO and then incubated in acetone at 55°C for 1 h. The acylation treatment was completed after wool fabric was thoroughly rinsed with distilled water.

### Chemical Oxidation

The oxidation of wool was conducted at room temperature (20 ± 2°C), in 4M sodium chloride containing 4% o.w.f. potassium permanganate (liquor ratio 20 : 1). To remove the brown color of MnO<sub>2</sub> formed on wool fabric, it was treated with 0.05N H<sub>2</sub>SO<sub>4</sub> acid solution containing 5% o.w.f. NaHSO<sub>3</sub>. The oxidized wool fabric was then thoroughly rinsed with distilled water.

### Scanning Electron Microscopy

A JEOL JSM 7000F field emission, high-resolution scanning electron microscope was used to observe the morphological features of control wool and treated wool fabric samples.

### Contact Angle Measurement

A contact angle goniometer (KSV, CAM 100) was used to assess the wettability of wool before and after surface modification. Distilled water was used as test liquid. Statistical analysis was based on 20 measurements from each type of wool fabric sample.

### FTIR-ATR Spectroscopy

The infrared (IR) spectra of control and treated wool fabric samples were obtained by a Perkin Elmer system 2000 spectrometer in ATR reflection mode. An average of 8 scans, 2000 cm<sup>-1</sup>– 800 cm<sup>-1</sup>, using a resolution of 16 cm<sup>-1</sup> was recorded for each sample.

### Fluorescence Measurement

The tryptophan-type fluorescence spectra of control and treated wool fabric samples were measured by a Hitachi F4000 fluorescence spectrophotometer. Fabric samples were positioned behind a quartz window that served to prevent the soft sample from swelling and shadowing the optical path. The excitation wavelength was at 295 nm, with the emission peaking at approximately 340 nm.

### Tensile Strength

According to ASTM D5035, the tensile properties of five types of wool fabrics were measured in the warp direction using an Instron Tensile Tester. The tests were conducted on 3-cm ravelled fabric strips with 22 threads of warp yarns. Five specimens for each type of wool fabric were prepared.

### Irradiation

Irradiation was conducted in a Luzchem LCZ-4X photoirradiator fitted with UVA (Hitachi FL8BL-B), UVB (Luzchem LZC-UVB) or blue light tubes (Luzchem LZC-420). When multiple samples were irradiated at one time, fabric samples were placed on a rotating plate to ensure that equivalent irradiation energy was absorbed by each fabric sample.

### Color Measurement

A Datacolor Spectraflash SF600 spectrophotometer was used to take color measurements from wool fabric samples. A D65 light source, 10° collection angle and a small area view (SAV) aperture were selected. The averages of multiple readings of CIE tristimulus values XYZ were obtained from the spectrophotometer. D1925 Yellowness and CIE whiteness index were calculated according to eqs. (1.1) and (1.2).

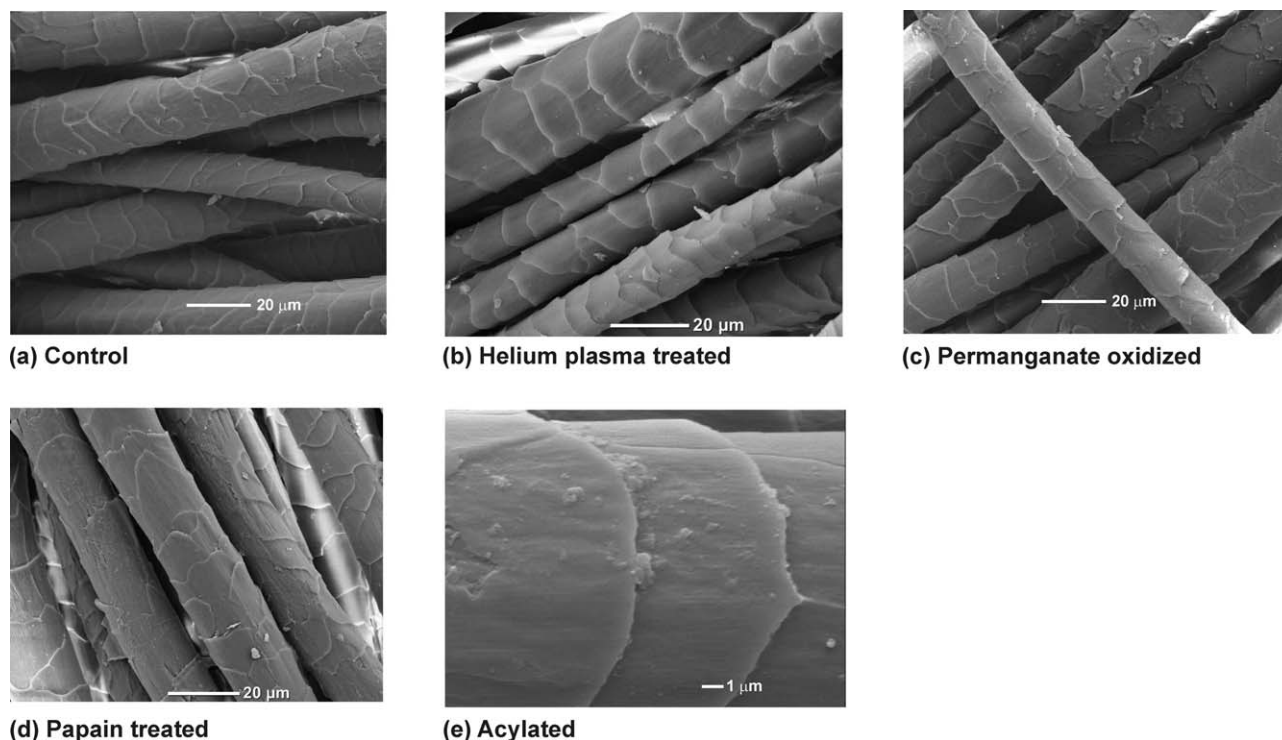
$$\text{D1925 Yellowness} = 100(1.3013X - 1.1498Z)/Y \quad (1.1)$$

$$\text{CLE Whiteness} = Y + 800(0.3138 - x) + 1700(0.3309 - y) \quad (1.2)$$

## RESULTS AND DISCUSSION

### Surface Morphological Evaluation

The effect of the various representative physical and chemical treatments on the morphological features of the wool fibers in the fabric squares is illustrated in Figure 1. From Figure 1(a) it is evident that largely intact scales still cover most of the surface of control wool fibers, except for some damage that has likely occurred during textile processing. The application of helium plasma treatment for 60 s [Figure 1(b)] did not noticeably affect the surface morphology of the fibers. Partial removal of scales was observed to a less significant extent on permanganate-oxidized wool [Figure 1(c)] but to a more significant extent on papain-treated wool [Figure 1(d)]. Treatment with succinic anhydride [Figure 1(e)] resulted in an uneven deposition of foreign materials on the fiber surface due to the effect of acylation,



**Figure 1.** SEM images of control and modified wool fabrics.

which is in line with a similar study on the morphological features of acylated wool.<sup>24</sup> Damage on the cuticle scales was also evident on the surface of acylated wool (image not shown).

#### Contact Angle Measurement

The effects of our physical and chemical modifications on the fabric wettability were evaluated using contact angle goniometry, which measures the angle of contact that the test liquid makes on the fabric surface. The results are shown in Table I.

With the exception of acylation, the modification techniques adopted in this study increased wool wettability. It should be noted that with the helium plasma-treated wool, extreme hydrophilicity was observed after 60 s helium plasma treatment so that the fabric sample absorbed the water droplet completely as soon as the droplet reached its surface.

Surface wettability is an important property for textiles. The hydrophobicity of natural wool is largely attributable to the presence of covalently bound lipids on the outermost layer. The dramatic hydrophilicity exhibited on plasma-treated wool is consistent with removal of the outer lipid layer of wool.<sup>32</sup> The increased hydrophobicity observed for acylated wool is consistent with the successful introduction of acyl groups onto the wool surface. Arai et al.<sup>24</sup> once reported that acylation of silk and wool with acid anhydrides could produce water-repellent fibers.

#### FTIR-ATR Spectrometric Evaluation

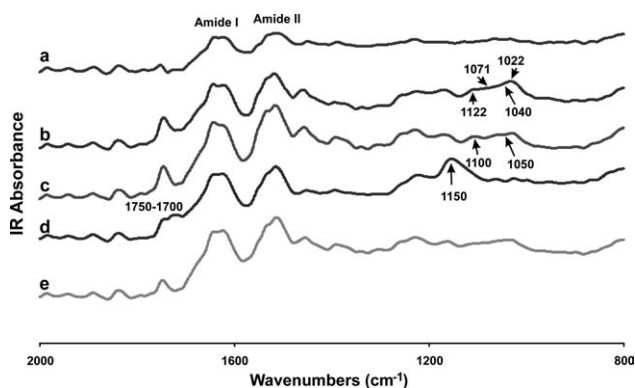
To study the surface chemical structure changes of wool after modification, control wool fabric along with those after four

different treatments were examined by IR spectroscopy, using the ATR technique. The results are shown in Figure 2.

From Figure 2(a), it is apparent that the intensities of characteristic amide I and II bands of wool decreased markedly after the plasma treatment. Interestingly, decreases in the absorbance intensities of these two amide bands have also been reported with argon plasma treated collagen films and oxygen plasma treated wool.<sup>13,33</sup> Furthermore, no new absorbance peaks in the region of S=O stretching vibration ( $1200\text{ cm}^{-1}$ – $1000\text{ cm}^{-1}$ ) were detected in the IR spectrum of plasma-treated wool, which indicated that the helium gas plasma used in this study did not cause significant oxidation of wool cystine. This differs from what was observed in a previous study that reported significant oxidation of cystine had occurred on helium plasma treated wool when high voltages in the range 1.8–2.2 kV were used<sup>34</sup> (as opposed to the 90 V used in this study).

**Table I.** The Average and Standard Deviation of 20 Contact Angle Measurements from Control and Modified Wool Fabrics

	Average contact angle (°)	STDEV
Control wool	117.12	8.24
Acylated wool	124.18	7.85
Helium plasma-treated wool	n/a	n/a
Papain-treated wool	98.07	11.77
Permanganate-oxidized wool	110.98	8.12



**Figure 2.** FTIR-ATR spectra of (a) helium plasma treated, (b) permanganate oxidized wool, (c) papain treated, (d) acylated, and (e) control wool fabrics.

When the fabric was treated with permanganate in a concentrated salt solution [Figure 2(b)], there was an increase in absorbance at  $1022\text{ cm}^{-1}$  which may have been the result of the formation of *s*-sulfonate. No change was observed at  $1040$ ,  $1122$ , and  $1071\text{ cm}^{-1}$  which has been attributed, respectively, to cysteic acid, cystine dioxide and cystine monoxide moieties. This would support the view that using a concentrated salt solution in association with permanganate treatment helps to mitigate cystine oxidative damage.<sup>17</sup>

The IR spectrum of papain treated wool [Figure 2(c)] looked almost identical to that of control wool. There were some very small new absorbance peaks at  $1100$  and  $1051\text{ cm}^{-1}$  which may be due to the exposure of functional hydroxyl or carboxyl groups on the surface of papain-treated wool. However, it would seem that papain treatment had little effect on the disulphide bonds of wool, which is in agreement with a recent finding that little oxidation of cystine was detected in protease treated wool.<sup>35</sup>

In the case of wool acylated with succinic anhydride [Figure 2(d)], the shoulder at  $1750\text{--}1700\text{ cm}^{-1}$  could be due to the free carboxyl groups formed as a result of the opening of the anhydride ring, whereas the absorbance peak at  $1150\text{ cm}^{-1}$  can be attributed to the formation of ester moieties by the acylation of hydroxyl groups of amino acid residues. Daoud et al.<sup>36</sup> and Arai et al.<sup>24</sup> reported similar IR spectra for wool acylated with acid anhydrides.

### Tryptophan-Type Fluorescence

Tryptophan-type fluorescence provides a convenient method to examine the photoreactions of this primary amino acid in wool proteins. The fluorescence maximum shown in the UV region at  $\lambda_{\text{ex}} = 295\text{ nm}$ ,  $\lambda_{\text{em}} = 340\text{ nm}$  is entirely attributed to the relaxation of the singlet state of tryptophan.<sup>25,37</sup>

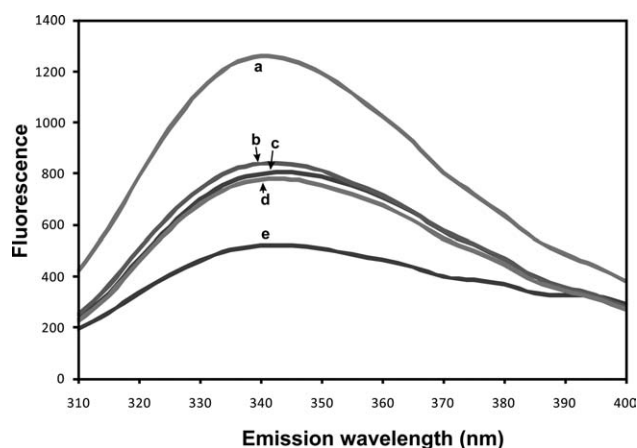
Figure 3 demonstrates the Trp-type fluorescence emission from both control and treated wool fabric samples. From Figure 3 it is apparent that the papain and plasma treatments applied in this study had little influence on the Trp-type fluorescence intensity of wool between  $340$  and  $350\text{ nm}$ , whereas there was a considerable reduction in fluorescence when the wool was acylated and a significant increase when oxidized with permanga-

nate. One likely cause for the increase observed in the permanganate oxidized wool is the partial oxidation of cystine as demonstrated in its IR spectroscopic evaluation [Figure 2(b)]. Cystine is regarded as the inherent quencher of natural blue fluorescence and photoexcited tryptophan or tyrosine,<sup>38–40</sup> so it is likely that this increase in fluorescence intensity correlates to oxidation of wool proteins.<sup>25,41</sup> In the case of the acylated wool, the decreased fluorescence is in agreement with the study of Bhatnagar and Gruen<sup>42</sup> who reported that alkylating or acylating agents exert a quenching effect on the fluorescence of wool.

Despite of the complexity of wool photochemistry, tyrosine (Tyr) and especially tryptophan (Trp) have been regarded as the most likely candidates for producing yellow chromophores in irradiated wool.<sup>43,44</sup> Lennox and Rowlands<sup>45</sup> have found a good correlation between Trp content and the rate of wool photoyellowing. Through the use of flash photolysis at  $265\text{ nm}$  in the absence of oxygen, Smith<sup>46</sup> noted a species with an absorption maximum of  $520\text{ nm}$  in their irradiated keratin that they suggested could be a tryptophan free radical. Triplet-excited Trp and Tyr residues can undergo photoexcited electron transfer to electron acceptors in wool keratin to form free radical cations.<sup>46</sup> Using an HPLC technique combined with mass spectrometry (MS), Dyer et al.<sup>47,48</sup> identified photo-oxidation products directly within the proteins of photoyellowed wool and photoyellowed bleached wool and concluded that tryptophan- and tyrosine-derived chromophores were major colored photoproducts.

### Tensile Strength

The breaking loads of five types of wool fabrics in the warp direction are shown in Table II. The breaking load of helium plasma-treated wool fabric was comparatively larger than that of untreated control. This was perhaps due to the increased interyarn and interfiber friction of plasma treated wool. For permanganate oxidized and papain-treated wool, the considerably reduced breaking loads could result from weakened disulphide bonds of permanganate oxidized wool and those surface damages on papain-treated wool. As to acylated wool, the breaking load was slightly lower than that of untreated control, which



**Figure 3.** Tryptophan-type fluorescence intensities ( $\lambda_{\text{ex}} = 295\text{ nm}$ ,  $\lambda_{\text{em}} = 345\text{ nm}$ ) of (a) permanganate oxidized, (b) helium plasma-treated, (c) control, (d) papain-treated, and (e) acylated wool fabrics.

**Table II.** The Tensile Properties of Control and Modified Wool Fabrics

	Breaking load in warp direction (kgf)
Control wool	4.414
Acylated wool	4.184
Helium plasma-treated wool	4.725
Papain-treated wool	3.769
Permanganate-oxidized wool	3.80

indicates that acylation does not induce adverse effect on the intrinsic tensile property of wool.

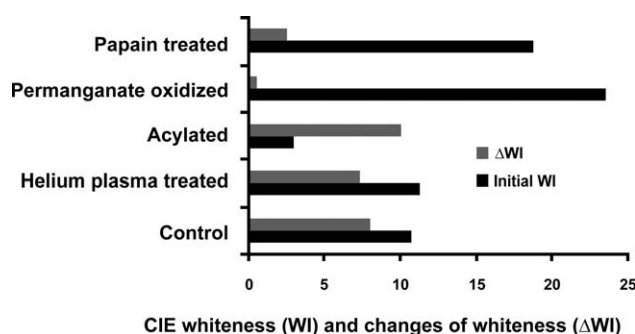
### Color and Photostability Evaluation

The color of textile products is vital to its aesthetic appeal to consumers. The color and maintenance of color in textile products is thus of extremely high importance. In this study, the subsequent photostability of wool after surface and interior modification was fully assessed with color measurements on wool fabric samples before and after light irradiation.

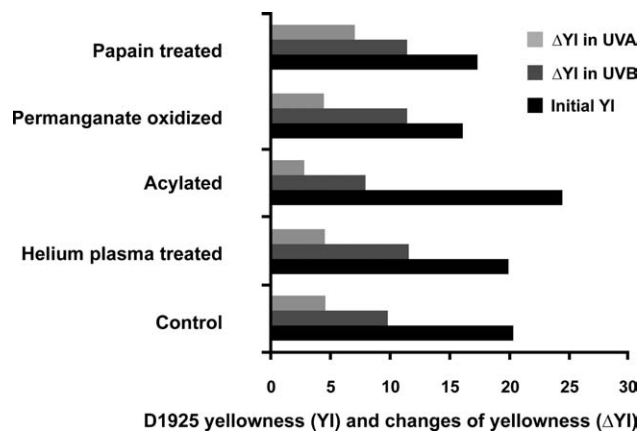
According to the initial color measurements of wool fabric samples after different treatments, Figure 4 shows that both papain and permanganate oxidization treatments increased the initial whiteness of wool whereas acylation did the opposite. Plasma treatment did not affect the color of wool after treatment for 60 s. No effect on color was observed on plasma-treated wool fabric sample even with a 10 min treatment (data not shown).

Irradiation tests were conducted under UVA, UVB, and blue light respectively, varying irradiation times utilized for each irradiation light source relative to the amount of color change induced. Consistent results were obtained from repeated irradiation tests.

The photobleaching rates of different types of wool fabric samples under blue light irradiation are also shown in Figure 4. From this, it would seem that the photobleaching rates of wool using different treatments were dependent on their initial whiteness. Helium plasma treated wool and control wool had similar initial whiteness and photobleached at a similar rate. Acyated wool was the least white before irradiation, and photobleached at the fastest rate. Permanganate oxidized and papain-treated



**Figure 4.** Initial CIE Whiteness (WI) of control and modified wool fabrics and changes of CIE Whiteness ( $\Delta$  WI) under 55 h blue light irradiation in dry state.



**Figure 5.** Initial D 1925 Yellowness (YI) of control and modified wool fabrics and changes of D 1925 Yellowness ( $\Delta$ YI) under 55 h UVA and 6 h UVB irradiation in dry state.

wool that appeared much paler after the modification, photobleached at a slower rate relative to the others. This observation appears to be supported by Lennox and King<sup>49</sup> who found that photobleaching is more pronounced with deeply yellow wool whereas UV yellowing is more apparent with whiter wool. From an application viewpoint, the observation that permanganate-treated wool has both greater initial whiteness and good color stability to blue light indicates promise for utilization with interior textile applications, where photobleaching can be a significant problem.

On the basis of the initial D 1925 yellowness and changes of D1925 yellowness before and after 6 h UVB and 55 h UVA irradiation, it would seem that changes in yellowness under UV irradiation were more dependent on the modification type rather than the initial wool yellowness (Figure 5). Under exposure to UVB, acyated wool yellowed at a slightly slower rate than control wool, whereas the other three types of treated wool yellowed at a similar rate, faster than the control, regardless of their initial yellowness values.

Likewise, under UVA irradiation, acyated wool yellowed at a slower rate than the other types of wool. Permanganate treatment was not observed to accelerate the photoyellowing of wool after 55 h of irradiation in these conditions. Interestingly, in a previously reported study examining the effects of sunlight exposure, a permanganate-salt process was found to appreciably increase the degree of yellowing.<sup>28</sup> Papain-treated wool, on the other hand, was found to yellow at the fastest rate under UVA, possibly as a result of the enzymatic removal of surface located UVA-absorbing chromophores, the same process to which the greater initial whiteness can be attributed.

### CONCLUSIONS

Surface and interior modification techniques including enzymatic treatment, plasma treatment, permanganate oxidation, and acylation were applied to wool in this study. The morphological surface features, IR spectra, tryptophan-type fluorescence, tensile strength, and wettability properties of modified wool were examined along with their subsequent color and

photostability under UVA, UVB, and blue light irradiation. We found that tryptophan-type fluorescence emission was largely quenched in the acylated wool but exacerbated on permanganate oxidized wool. The degree of subsequent photobleaching of modified wool correlated inversely to the initial whiteness imparted by the modification, whereas subsequent photoyellowing of modified wool in UV appeared to be more dependent on the means of modification rather than the initial color. Evaluation of the effect of wool surface and interior modification on subsequent photostability was shown to be an important practical consideration in the development and application of new functional wool treatments.

#### ACKNOWLEDGMENTS

The authors wish to thank Wool Research Organisation of New Zealand Inc. and the New Zealand Wool Industry Charitable Trust for funding this research. The authors also thank Dr. Stefan Clerens for his critical review on this manuscript, Dr. Duane Harland for obtaining the SEM images, and Mr. Peter Brorens for his assistance with the tensile strength test.

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