

Surface and Bulk Analysis of Bleaching Soybean Fabric in the Presence of Protein Hydrolysate

D. Vynias, H. Owens, C. M. Carr

Textiles & Paper, School of Materials, University of Manchester, Manchester M13 9PL, United Kingdom

Correspondence to: C. M. Carr (E-mail: chris.carr@manchester.ac.uk)

ABSTRACT: The effect of oxidative and oxidative-reductive bleaching on the colorimetric, topographical, and mechanical properties of soybean fabric has been investigated by yellowness index, abrasion resistance, tensile strength, Kawabata evaluation system for fabrics, scanning electron microscopy, X-ray photoelectron spectroscopy, and time of flight secondary ion mass spectrometry in order to examine both the bulk and surface properties. Surface changes to the soybean fiber due to bleaching treatments have been evaluated and the protective effect of protein hydrolysates assessed. Improved tensile strength, flat abrasion performance, and handle maintenance of the soybean fabric was demonstrated with the incorporation of Byco C in both bleaching treatments.

© 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 4271–4276, 2013

KEYWORDS: fibers; textiles; surfaces and interfaces; degradation

Received 11 June 2012; accepted 22 September 2012; published online 22 October 2012

DOI: 10.1002/app.38631

INTRODUCTION

Although petroleum-based fibers have been widely used in the textile industry their long term production and sustainability is being reassessed due to increased oil costs and their relatively slow end of life biodegradability. Accordingly in the light of these environmental and commercial factors and the recent advances in the genetic modification of plant proteins there has been renewed interest into regenerated proteins fibers. Zhang et al.¹ investigated the processing of blended PVA/soybean fiber and demonstrated that the incorporation of polyvinyl alcohol (PVA) into the spinning process enhanced mechanical properties. PVA is a synthetic polymer with high tensile strength and modulus,² and has been used as reinforcement in keratin fibers.³ Large-scale production of soybean fibers and associated garment manufacture has now been established in China.⁴

Although the dyeing⁵ and flammability⁶ of soybean fibers has been studied, little has been reported on the effect of bleaching with regard to reducing yellowness and maintaining fiber strength. Nevertheless other soy protein products prior to industrial use are frequently treated with oxidative agents such as with hydrogen peroxide, sodium peroxide, barium peroxide, or oxidizing salts.⁷

In this study, we compare two bleaching treatments in order to establish the effect on whiteness and fiber damage. Soybean bleaching was performed using an oxidative alkaline treatment and a combination treatment that involved oxidative bleaching followed by a reductive bleaching (sodium hydrosulphite,

Blankit, IN). To fully characterize the effect of bleaching on the fiber properties both bulk (strength and “handle”) and surface (topographical and chemical) analyses were performed. Through this detailed information optimized bleaching treatments could be developed to improve performance and maintain properties during bleaching. The surface sensitive X-ray photoelectron spectroscopy (XPS) technique provides both qualitative and quantitative characterization of the chemical species present at the fiber surface to a depth of 3–10 nm.⁸ In particular the oxidation state and chemical environment of surface species can be established allowing the effect of oxidative processing and polymer modification to be effectively monitored.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a complementary technique for characterizing surface interface chemistry and in particular fiber surface adsorbates.^{9–12} ToF-SIMS has a sampling depth of 1–2 nm and provides elemental and molecular mass spectra data by bombarding the sample surface with a primary particle beam and analyzing the masses of the sputtered secondary ions emitted from the surface.

EXPERIMENTAL

Materials

A 1/2 twill, scoured, 100% soybean fabric (210 g/m²) was used throughout this study, supplied by Huakang, China. The Byco C protein hydrolysate and Blankit IN (stabilized sodium hydrosulphite) were kindly supplied by Croda Chemicals, Widnes, UK and BASF, Manchester, UK, respectively.

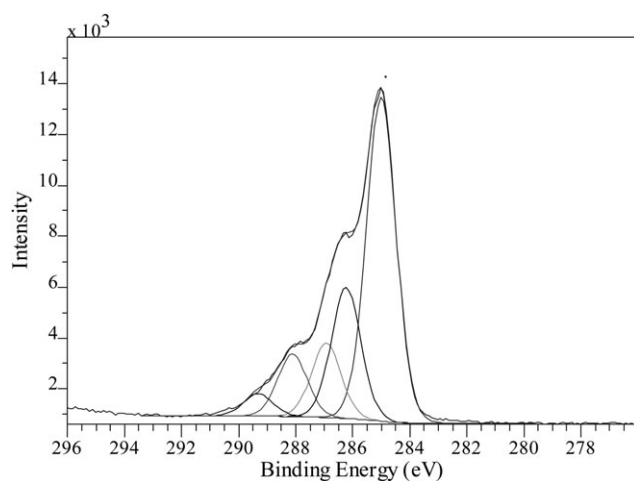


Figure 1. C(1s) XPS spectrum of untreated soybean fabric.

Bleaching Treatments

All bleaching treatments were performed in a John Jeffreys “open” laboratory bleaching and dyeing machine. Treatment conditions for the bleaching procedures were:

Oxidative Alkaline Bleaching. Oxidative bleaching was performed in a bath containing 30 ml/L hydrogen peroxide (50%), 5 g/L sodium silicate, 0.5 g/L nonionic wetting agent, for 60 min at pH 11, 90°C. The treated fabrics were then rinsed thoroughly in distilled water and dried at room temperature.

Oxidative-Reductive Bleaching. The first stage of the oxidative/reductive bleaching process was carried out with 30 ml/L hydrogen peroxide (50%), 5 g/L sodium silicate, 0.5 g/L nonionic wetting agent, for 60 min at pH 11 and 90°C. The second stage was performed with 6 g/L Blankit IN, 0.5 g/L nonionic wetting agent for 60 min at pH 7, 60°C. All bleaching treatments were performed at a materials : liquor ratio of 1 : 20. On completion of both bleaching treatments, the soybean fabric was rinsed thoroughly in distilled water and dried at room temperature.

Application of Protein Hydrolysate

Byco C was applied at 2–10% on mass of fabric (o.m.f.) in the bleaching bath at a materials : liquor ratio of 1 : 20. The bleached soybean fabrics were then hydroextracted and dried at room temperature.

Instrumental Analysis

Yellowness Index. The spectral reflectance of the soybean fabrics were measured using a Datacolor International Spectrophotometer (SpectraFlash 600) and the ASTM E313 Yellowness Index values were calculated under illuminant D65/10° observer. All fabric samples were folded and measured as four layers at 4–5 points over the fabric surface in order to obtain an average yellowness index (YID) value.

XPS Analysis. XPS analysis was performed with a Kratos Axis Ultra XPS instrument. The samples were analyzed with a monochromatic AlK α radiation source (1486.6 eV) operating at a base pressure of 3×10^{-9} Torr. Wide survey spectra were recorded at a pass energy of 100 eV in order to determine the surface chemical composition. High resolution spectra were

recorded with a pass energy of 20 eV and the binding energy (BE) values were calculated relative to the carbon (1s) photoelectron peak at 285.0 eV. Charge compensation for the samples was achieved using a 4–7 eV beam at a flood current of ~ 0.1 mA, with an electrically ground 90% transmission nickel mesh screen. All samples were analyzed in duplicate and the data was analyzed using CASA XPS software.¹³

ToF-SIMS Analysis. ToF-SIMS spectra were obtained under static conditions using a PHI 7000 instrument with a reflectron analyzer, a Cs⁺ ion source (8 KeV, pulse length 50 ns) and a pulsed electron flood source (50–70 eV) for charge compensation. The operating pressure was $< 5.33 \mu\text{Pa}$ (4×10^{-8} Torr). A total primary ion dose of $< 1 \times 10^{12}$ ions cm^{-2} was used for each sample, which lies below the threshold level of 1×10^{13} ions cm^{-2} for static SIMS.¹⁰ Soybean fabrics were mounted by fixing them to a metallic sample stub using a standard ring-clamping arrangement.

Bulk Analysis. Elemental analyses were performed by using a Carlo Erba instrument EA1108 Elemental Analyzer. The error associated to the measurement is $\pm 0.04\%$.

SEM Analysis. A Hitachi S3000N variable pressure scanning electron microscope (SEM) system was used throughout the study. A magnification of 2,000 : 1, a 5 kV accelerating voltage and a working distance of 10 mm were typically found to be the most appropriate analysis conditions and the samples were gold-coated prior to analysis. The cross-sections of the soybean fibers were obtained using a standard microtome.

Strength Measurements

The soybean fabrics were conditioned for 24 h at 20°C and 65% relative humidity (R.H.) prior to testing on an Instron 5564 testing system. The tensile strength data of untreated and bleached fabrics was an average of 10 measurements in the warp direction. The flat abrasion of the fabric was determined using a Martindale Flat Abrasion test system according to the British Standard BS 569091:1991.

Kawabata Evaluation System for Fabrics (KES-F) Analysis

The 20 \times 20 cm soybean fabrics were conditioned for 24 h at 20°C and 65% R.H. prior to testing. The selected KES-F shear and bending mechanical property values presented were the average of five measurements.¹⁴

RESULTS AND DISCUSSION

Soybean is composed of mainly 16 amino acids, with relatively high amounts of aspartic and glutamic acid but with relatively low cystine present.¹⁵ Huang¹⁶ suggested that the low wet strength properties of soybean reported in the literature^{17,18} could be attributed to the disruption of the interchain hydrogen bonding and ionic bonding through the polar amino acids glutamic and aspartic acid, which account for 30% of the amino acid content in the fiber, by water. Further the much lower proportion of cystine content of the soybean fiber as compared to that of wool fiber resulted in lower protein chain cross-linkages through disulphide groups and associated lower wet strength. Therefore, the importance of maintaining soybean fiber strength during potentially damaging wet processing is clear with the surface and bulk analyses allowing the effective characterization of the fiber’s mechanical performance.

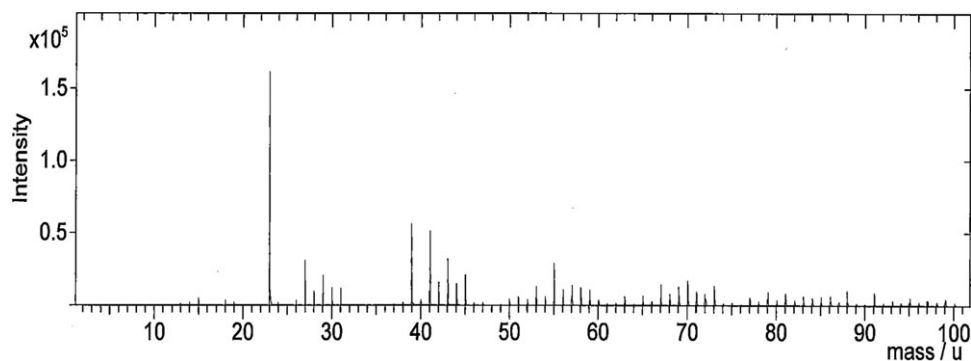


Figure 2. Positive ion ToF-SIMS spectrum of untreated soybean fabric.

XPS and To F-SIMS Analysis

The XP spectrum of soybean fiber shows the major photoelectron peaks located at BE values of 531.0, 400.0, 285.0, and 164.0 eV. These BE values correspond to the photoemissions from the O(1s), N(1s), C(1s), and S(2p) atomic orbitals, respectively. A low intensity S(2p) signal (0.3% atomic) was also observed at 164 eV, indicating a low cystine content at the fiber surface and reflects a similarly low bulk sulfur content, less than 0.2%. The surface carbon, oxygen, and nitrogen atomic composition were 74.7, 19.8, and 3.2% atomic, respectively while the bulk elemental analysis shows a carbon, oxygen, and nitrogen content of 53.6, 34.2, and 3.4%, respectively, suggesting the fiber has a carbon enriched surface layer, the nature of which is uncertain at present. The carbon 1(s) XP spectrum indicates the major carbon surface species is located at 285.0 eV and is attributed to C–H and C–C species, Figure 1. The other spectral components in the C (1 s) XPS spectrum of untreated soybean are assigned to C–N, C–OH, O=C/N–C=O, O–C=O, with the binding energies values located at 286.2, 286.9, 288.0, and 289.5 eV, respectively.

While the XPS data can provide useful information about the atomic composition of the fiber surface, the complementary approach of using ToF-SIMS is beneficial in that the molecular nature of the surface species can be determined. The positive and negative ToF-SIMS spectra of untreated soybean indicated the presence of a complex mixture of chemical species at the fiber surface. The major amino acids of soybean fiber were detected in the positive ion spectrum of untreated soybean at $m/z = 30^+$ (CH_4N^+), $m/z = 44^+$ ($\text{C}_2\text{H}_6\text{N}^+$), $m/z = 84^+$

($\text{C}_4\text{H}_6\text{NO}^+$), 86^+ ($\text{C}_5\text{H}_{12}\text{N}^+$), and $m/z = 88^+$ ($\text{C}_3\text{H}_6\text{NO}_2^+$) and were assigned to glycine, alanine, glutamic acid, leucine, and/or isoleucine, and aspartic acid, respectively, Figure 2.¹⁹ The ion intensities at $m/z = 23^+$ and 39^+ can be attributed to Na^+ and K^+ , respectively and they remained spectrally significant and fiber substantive despite subsequent aqueous processing.

In the negative ion ToF-SIMS spectrum of untreated soybean the signals observed at $m/z = 26^-$ (CN^-) and $m/z = 42^-$ (CNO^-) were assigned to the protein backbone.¹⁹ In addition significant spectral peak intensity was indicated at $m/z = 43^-$, and is typically associated with the presence of PVA ($\text{C}_2\text{H}_3\text{O}^-$) at the fiber surface, Figure 3.²⁰ Examination of the higher mass region indicates signal intensity at $m/z = 265^-$, 279^- , and 293^- , which can be assigned to C_{12} to C_{14} alkyl sulfate surfactants, while the signal intensities at $m/z = 311^-$, 325^- , 339^- , 353^- were assigned to C_{11} to C_{14} alkyl benzene sulfonate surfactants.

The effect of oxidative bleaching of the soybean fabric was to increase the surface oxygen content to 23.5% and reduce the surface carbon concentration to 67.1%. The bulk analysis showed relatively smaller changes in the carbon and oxygen content, although both the surface and bulk nitrogen were reduced to 1.5% and 2.7%, respectively. Examination of the C(1s) XP spectrum of hydrogen peroxide bleached soybean fabric indicated a relative reduction in C–H/C–C surface species and in an increase in the intensities of the C–O, C=O and O–C=O spectral components, Figure 4, again reflecting the oxidative nature of the process. The ToF-SIMS negative ion spectra of the bleached soybean fibers (not presented) again clearly demonstrated the presence of the PVA at

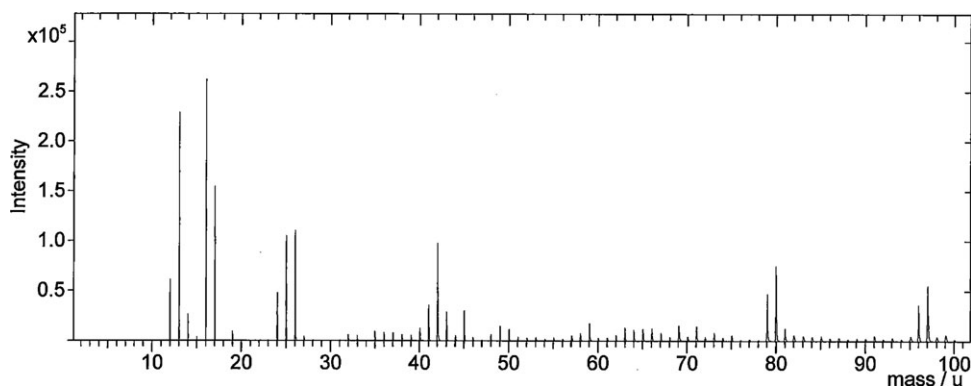


Figure 3. Negative ion ToF-SIMS spectrum of untreated soybean fabric.

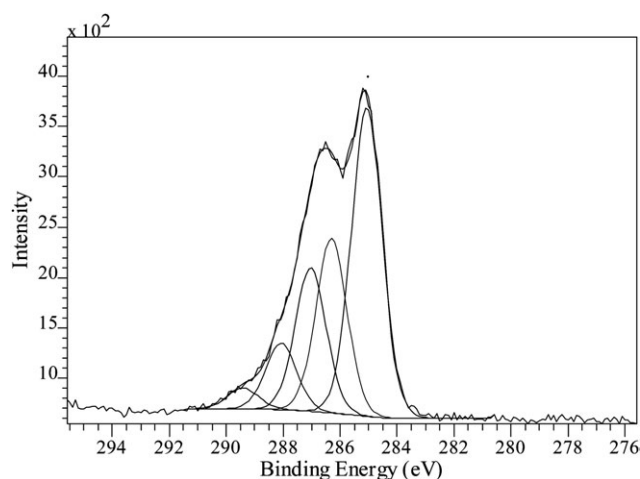


Figure 4. C(1s) XPS spectrum of oxidatively bleached soybean fabric.

the fiber surface and its durability to the bleaching processes. Similarly the effect of bleaching on the amino acids present at the fiber protein surface was relatively small with all the identified amino acids still present in the ToF-SIMS negative ion spectra after the bleaching processes.

SEM Analysis

SEM analysis of soybean fiber indicated parallel longitudinal striations on the surface, varying in length and depth, Figure 5. In addition SEM micrographs of the soybean fiber cross-section, Figure 6 showed a kidney bean-like cross-sectional shape. A previous study on the cross-sectional shapes of wet-spun fibers have associated the coagulation rate with the cross-section profile²¹ indicating that noncircular cross-sections occur due to a high coagulation rate in wet spinning.

In attempting to characterize the fiber damage the surface morphology of bleached samples was also examined by SEM but no obvious differences in the surface texture were observed. However, comparison of the cross-sections of the oxidative and oxidative/reductive bleached fibers showed significant differ-

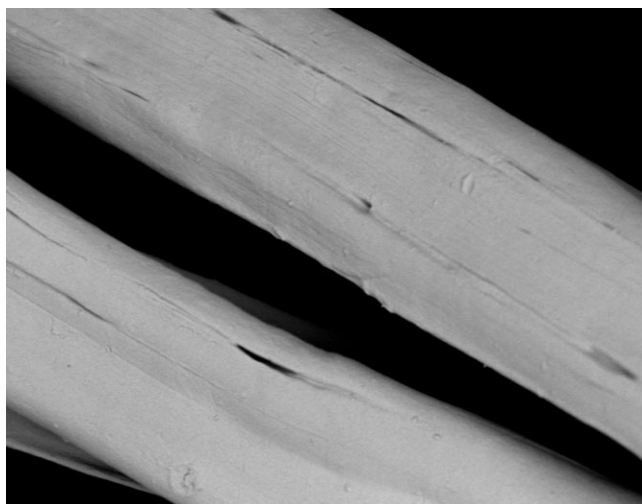


Figure 5. Scanning electron micrograph of untreated soybean fiber.

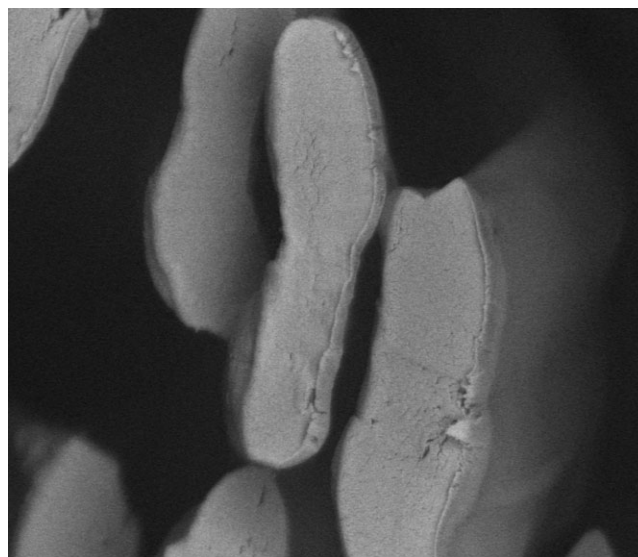


Figure 6. Scanning electron micrograph of cross-section of untreated soybean fiber.

ences. In particular, the oxidative bleached soybean showed evidence of degradation, Figure 7, with the fiber fracturing observed varying in size and depth. Further increased degradation following the combination oxidative/reductive treatment was also evident from the SEM micrographs as indicated by the increased depth and frequency of fiber fracturing, Figure 8.

Yellowness and Mechanical Properties

The effect of oxidative alkaline hydrogen peroxide bleaching of the soybean fabric was to clearly decrease the yellowness index, the tensile strength, and flat abrasion, Table I. However, the whitening effect was only marginally further improved by the combination oxidative-reductive bleaching treatment with the improved color being at the expense of increased strength loss, particularly with the flat abrasion test.

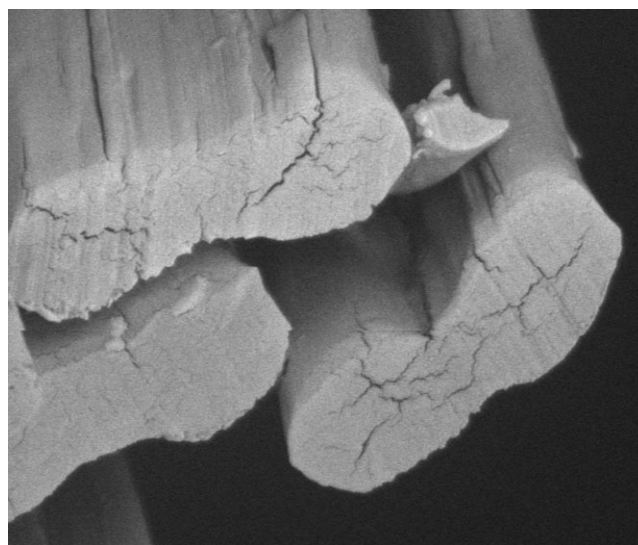


Figure 7. Scanning electron micrograph of the cross-section of oxidatively bleached soybean fiber.

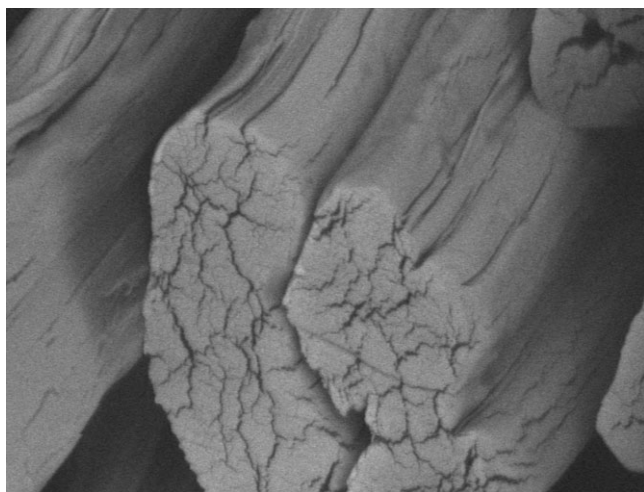


Figure 8. Scanning electron micrograph of the cross-section of oxidatively-reductively bleached soybean fiber.

It has previously been reported that bleaching can also lead to deterioration in protein-based fabric softness because of degradation of the protein and the probable loss of surface lipid.²² The Kawabata Evaluation System is considered to be an effective objective measurement system of textile fabric “handle,” determining the surface, bending, compressional, tensile, and shear properties of fabrics using forces similar to those applied by the consumer to the fabric during subjective evaluation. In this KES-F study both the oxidative bleached and oxidative-reductive bleached fabrics showed an increase in their shear hysteresis at 5°, 2HG5, values, Table II. This 2HG5 value is closely associated with interyarn friction and fabric softness and in this study the measured increased interyarn friction can be related to increased fiber damage and the subjective perception of harshening of the fabric handle. The shear and bending stiffness values also increased due to bleaching causing fiber damage and increasing fabric rigidity.

Table I. Effect of Bleaching and Protein Hydrolysates on the Yellowness Index, Tensile Strength, and Abrasion Resistance of Soybean Fabric

| Fabric treatment | Byco C % o.m.f. | Tensile strength (kN/m) | Abrasion resistance (cycles to break) | Yellowness index |
|------------------------|-----------------|-------------------------|---------------------------------------|------------------|
| Untreated | - | 17.6 ± 0.1 | 24,300 ± 200 | 41.9 |
| Oxidative ^a | 0 | 15.1 ± 0.1 | 14,100 ± 300 | 29.1 |
| | 2 | 16.7 ± 0.3 | 17,600 ± 400 | 29.3 |
| | 5 | 16.9 ± 0.2 | 22,700 ± 300 | 29.4 |
| | 10 | 16.8 ± 0.1 | 21,500 ± 200 | 29.7 |
| Oxid/Red ^b | 0 | 14.6 ± 0.3 | 8,300 ± 400 | 26.9 |
| | 2 | 15.8 ± 0.3 | 9,300 ± 100 | 26.9 |
| | 5 | 16.1 ± 0.1 | 11,500 ± 400 | 27.0 |
| | 10 | 15.9 ± 0.1 | 11,800 ± 300 | 27.3 |

^aOxidative—30 mL/L hydrogen peroxide (50%), 5 g/L sodium silicate, 0.5 g/L nonionic wetting agent, for 60 min at pH 11, 90°C, ^bOxid/Red—Oxidative first stage as above, 6 g/L Blankit IN, 0.5 g/L nonionic wetting agent, for 60 min at pH 7, 60°C.

Table II. Effect of Bleaching and Protein Hydrolysates on the Shear and Bending Properties of Bleached Soybean Fabrics as Determined by KES-F Analysis

| Fabric treatment | Byco C % o.m.f. | KES-F parameter | | |
|-------------------------------|-----------------|-----------------|--------------|-----------------------------|
| | | G (gf/cm. deg) | 2HG5 (gf/cm) | B (gf. cm ² /cm) |
| Untreated | - | 1.9 | 9.7 | 0.26 |
| Oxidative Bleach ^a | 0 | 2.1 | 11.1 | 0.28 |
| | 2 | 2.1 | 10.9 | 0.27 |
| | 5 | 1.9 | 9.9 | 0.25 |
| | 10 | 1.9 | 10.1 | 0.26 |
| Oxid/Red. Bleach ^b | 0 | 2.9 | 13.6 | 0.37 |
| | 2 | 2.8 | 13.5 | 0.36 |
| | 5 | 2.6 | 11.5 | 0.29 |
| | 10 | 2.7 | 11.8 | 0.30 |

^aOxidative—30 mL/L hydrogen peroxide (50%), 5 g/L sodium silicate, 0.5 g/L nonionic wetting agent, for 60 min at pH 11, 90°C, ^bOxid/Red—Oxidative first stage as above, 6 g/L Blankit IN, 0.5 g/L nonionic wetting agent, for 60 min at pH 7, 60°C.

Protein Hydrolysates

Protein hydrolysates and protein derivatives have previously been used as softeners/conditioners, wetting, shrink-resist, and fiber protective agents in wool keratin processing.^{23–26} In this study, the application of Byco C as a protective agent during the bleaching of soybean fabric was investigated. It was clear that the effect of incorporating the Byco C in both bleaching processes was beneficial with the loss of tensile strength and flat abrasion durability being reduced while still maintaining the bleaching effect, Table I. In minimizing the changes to the fiber’s physical structure the “handle” modification, as



Figure 9. Scanning electron micrograph of the cross-section of oxidatively bleached soybean fiber treated with 5% Byco C.

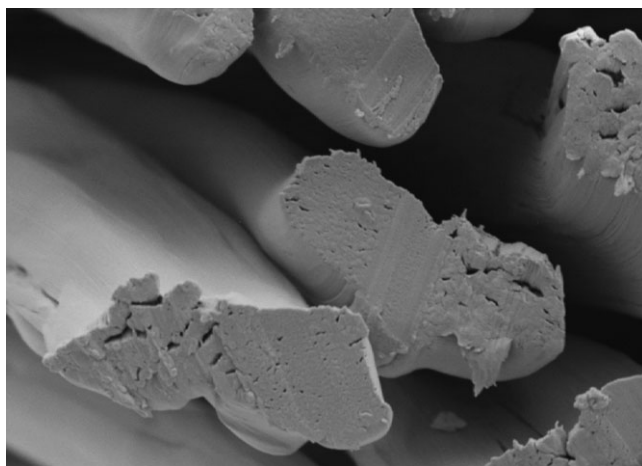


Figure 10. Scanning electron micrograph of the cross-section of oxidative-reductively bleached soybean fiber treated with 5% o.m.f Byco C.

determined by the KES-F system, due to the bleaching processes was also minimized, Table II.

Reflecting the observed strength retention benefit was the SEM analysis, which showed less fiber fracturing of the cross-sections for both the oxidative and oxidative/reductive bleaching treatments, Figures 9 and 10, again reflecting the hydrolysate's protective effect. Similarly the C(1s) XP spectrum showing less oxidation at the fiber surface with the higher BE oxidized species at 288.0 and 289.0 eV not increasing in intensity to the same extent as observed for the "unprotected" fiber.

CONCLUSIONS

The effect of oxidative and oxidative-reductive bleaching treatments on soybean fabric was to reduce the yellowness and impart fiber damage. SEM analysis revealed internal fiber fracturing caused by the bleaching treatments with the extent of fiber modification being more obvious with the oxidative-reductive treatment. The protein hydrolysate Byco C was demonstrated to function as an effective fiber protective agent when incorporated into the bleaching formulations, reducing both the tensile strength and flat abrasion strength losses, while still maintaining the fabric handle as indicated by the KES-F shear and bending properties. In achieving these mechanical property benefits the improvement in the observed color was unaffected.

Surface and bulk analysis indicated the presence of an enriched carbon layer at the soybean fiber surface with the subsequent bleaching reducing the concentration of the surface C—C/C—H species while increasing the oxidized carbon species. The increased oxidation of the surface interface reflects the deterioration of the fiber's mechanical properties, in particular the increase in surface friction and fabric harshening. The complementary ToF-SIMS positive ion analysis indicated the presence of characteristic amino acid species and PVA at the fiber surface but was less informative in terms of identifying fiber surface chemical modification.

ACKNOWLEDGMENTS

The authors thank the State Scholarship Foundation of Greece (I.K.Y.) for the award of a research scholarship to D. Vynias. In

addition the authors thank Alison Harvey and John Walton for their help in the KES-F and XPS analysis.

REFERENCES

- Zhang, X.; Min, B.; Kumar, S. *J. Appl. Polym. Sci.* **2003**, *90*, 716.
- Sakurada, I. *Polyvinyl Alcohol Fibers*; Marcel Dekker: New York, **1985**.
- Katoh K.; Shibayama M.; Tanabe T.; Yamauchi K. *J. Appl. Polym. Sci.* **2004**, *91*, 756.
- Huakang Ltd., www.soybeanfibre.com **2005**.
- Choi, J.; Kang, M.; Yoon, C. *Color. Technol.* **2005**, *121*, 81.
- Vynias, D.; Carr, C. M. *J. Appl. Polym. Sci.* **2008**, *109*, 3590.
- Meyer, E.; Williams, L. D. *Food Proteins*; American Chemical Society: Washington D. C., **1977**.
- Ratner, B. D.; Castner, D. G. *Surface Analysis: The Principal Techniques*; Vickerman, J. C., Ed.; Wiley: Chichester, **1997**.
- Swift, A.; Vickerman, J. *Surface Analysis: the Principal Techniques*; Vickerman, J. C., Ed.; Wiley: Chichester, **1997**.
- Voolooj, S.; Carr, C. M.; Mitchell, R.; Vickerman, J. C. *Surf. Interface Anal.* **2000**, *29*, 422.
- Mitchell, R.; Carr, C. M.; Parfitt, M.; Vickerman, J.C.; Jones, C. *Cellulose* **2005**, *12*, 629.
- Howell, D.; Mitchell, R.; Carr, C. M. *J. Mater. Sci.* **2007**, *42*, 5452.
- Walton, J.; Wincott, P.; Fairley, N.; Carrick, A. *Peak Fitting with Casa XPS, a Casa Pocket Book*. Acolyte Science: Cheshire, **2010**.
- Kawabata, S. *The Standardization and Analysis of Hand Evaluation*; Textile Machinery Society of Japan: Osaka, **1980**.
- Vynias, D. *Soybean Fibre: A Novel Fibre in the Textile Industry, Soybean, Chemistry and Physiology*; Ng, T.-B., Ed.; ISBN: 978-953-307-219-7, InTech, **2011**. Available from: <http://www.intechopen.com/books/soybean-biochemistry-chemistry-and-physiology/soybean-fibre-a-novel-fibre-in-the-textile-industry>.
- Huang, H. C. PhD Thesis, Iowa State University, Iowa, Ames, **1994**.
- Moncrieff, R. W. *Man-Made Fibres*; Butterworth: London, **1975**.
- Saltzberg, H. P. *Encyclopedia of Polymer Science and Engineering*, Vol. 2; Wiley: New York, **1969**.
- Wagner, M. S.; Castner, D. G. *Langmuir* **2001**, *17*, 4649.
- Vickerman, J. C.; Briggs, D.; Henderson, A. *The Static SIMS Library*; SurfaceSpectra: Manchester, **1997**; pp 294–295.
- Tsai, J. C.; Su, W. C. *J. Mater. Sci. Lett.* **1991**, *10*, 1253.
- Finnimore, E.; Bereck, A. *Melliand Textilber.* **1987**, *68*, E253.
- Schafer, K.; Dechesne, J. C.; Hocker, H. M. *Proc. Int. Wool Text. Res. Conf.* **1995**, *9*, 280.
- Harvey, A.; Carr, C. M.; Pereira, A. *J. Cosmet. Sci.* **2004**, *55*, 265.
- Cegarra, J.; Gacen, J.; Cayuela, D.; Riva, M. C. *J. Soc. Dyers Col.* **1994**, *110*, 308.
- Schafer, K.; Hocker, H. *Melliand Textilber.* **1996**, *77*, E87.