CHEMICAL FINISHING OF COTTON FABRIC WITH SILK FIBROIN AND ITS PROPERTIES

SIRIPON KOSAWATNAKUL,[*] MONTHON NAKPATHOM,[**] THOMAS BECHTOLD[***] and ARUNEE K. ALDRED[*]

[*]*Faculty of Science, Maejo University, ChiangMai, Thailand*
[**]*Textiles Laboratory, Polymer Research Unit, National Metal and Materials Technology Center, Pathum Thani, Thailand*
[***]*Institute of Textile Chemistry and Textile Physics, University of Innsbruck, Hoechsterstrasse 73, A6850 Dornbirn, Austria*
✉ *Corresponding author: Arunee K. Aldred, arkongdee@gmail.com*

Received March 4, 2017

Silk fibroin was extracted from silk waste and formulated as finish for cotton fabric, utilizing dimethyloldihydroxyethylene urea (DMDHEU) as crosslinker. The treated cotton fabrics were analyzed using scanning electron microscopy (SEM), attenuated total reflectance Fourier transform infrared spectrophotometry (ATR-FTIR), and with regard to their nitrogen content. The presence of the extracted silk fibroin on the cotton fabric surface was confirmed by SEM images, nitrogen content and *K/S* values. The SEM images of treated cotton fabrics showed deposition of silk fibroin from silk waste on the fabric surface. The treated cotton fabrics were dyed with acid dye. The dyed cotton fabric demonstrated high color strength with increasing silk fibroin concentration. The physical properties of treated cotton fabrics, *i.e.* water uptake, wrinkle recovery angle and breaking strength, were determined. The test results showed significant increments in water uptake and wrinkle recovery angle values, as well as a slight decrease in breaking strength, with increasing concentration of silk fibroin.

Keywords: silk fibroin, cotton, dimethyloldihydroxyethylene urea, attenuated total reflectance Fourier transform infrared spectrophotometry, scanning electron microscopy

INTRODUCTION

Silk fibroin is derived from silk cocoons during the reeling process. Currently, 300-400 tons of silk fibroin per year is discarded as silk waste from Thai silk factories. Silk fibroin, a form of beta-pleated sheet consisting of glycine, alanine and serine as dominant residues, is a strong and tough fibrous protein material.[1] Silk blended/crosslinked cellulose-based materials are widely prepared for numerous technological applications.[2-6]

Cellulose and cellulose-based fabrics are generally subjected to a crosslinking process using finishes to impart easy-care properties. Different types of finishes, including urea/formaldehyde, melamine/formaldehyde and dimethylolethylene urea, have been investigated.[7] The uses of glyoxal, glutaraldehyde and epichlorohydrin as crosslinking agents for cellulosic fabric have been also reported.[8-13] Polycarboxylic acids, such as 1,2,3,4-butanetetracarboxylic acid, citric acid and maleic acid, combined with sodium hypophosphite, have been widely used with a view to minimizing the environmental impact.[14-21] However, despite the effectiveness of polycarboxylic acids for achieving easy-care properties and durability, they are not practical to use on an industrial scale because of their high cost and because their use causes shade changes in sulfur and reactive dyed materials.[8]

In this investigation, a long chain protein, *i.e.* silk fibroin extracted from silk waste, in combination with a small amount of commercial crosslinker, *i.e.* DMDHEU, was used in order to achieve easy-care cotton fabric. Such an approach in developing novel cotton fabrics would diminish the environmental impact of the textiles industry, by valorizing silk factory wastes, making them commercially recyclable. In the present work, the fixation of silk fibroin onto the surface of cotton fabric has been demonstrated and the physical properties of the cotton fabric chemically treated with silk fibroin have been tested.

EXPERIMENTAL

Materials

Scoured, bleached twill weave cotton fabric of 137.5 g/m^2 was selected in this study. Silk waste was purchased from Chul Thai Silk Co. Ltd., Thailand. Sodium carbonate used for degumming silk fibroin was supplied by Merck. DMDHEU used as crosslinker, with the commercial name of Fixapret F-Eco, was supplied by BASF; magnesium chloride used as catalyst was purchased from Univar, the co-catalyst, *i.e.* acetic acid, was supplied by RCI Labscan. Calcium chloride for dissolution of silk fibroin was supplied by Sigma-Aldrich, an acid dye, with the commercial name of Telon Red M-3B01, was supplied by DyStar.

Finishing of cotton fabrics with silk fibroin solutions

A solution of silk fibroin was first prepared from silk waste as follows. Silk waste was first cut into small pieces and degummed in a 0.5% w/v sodium carbonate solution at 90 °C for 30 min with a material to liqour ratio of 1:30. The obtained silk fibroin was then dissolved in a 50% w/v calcium chloride solution at 85 °C for 3 h, at a material to liquor ratio of 1:100, under stirring, by using a Daelim Starlet II infrared dyeing machine. After filtration, the silk fibroin solution extracted from silk waste was obtained.

A series of 100 ml finishing solutions for cotton fabric were subsequently prepared, by a similar procedure to the one used in our previous work for finishing cotton fabric with silk sericin.[22] Volumes of 2.5, 5.0, 7.5 and 10.0 ml of silk fibroin solution were added into four 100 ml volumetric flasks respectively, containing 2 g DMDHEU, 0.7 g magnesium chloride, 0.2 ml of 20% acetic acid, and 80 ml water. Each flask was then diluted with water to 100 ml. Scoured and bleached twill weave cotton fabric samples (15 x 20 cm) were immersed into each finishing solution and squeezed using a laboratory padding mangle at a speed of 2.5 rpm and a pressure of 0.125 kg/cm^2 (80% wet pick-up). The samples were labelled as SF-2.5, SF-5.0, SF-7.5 and SF-10.0 corresponding the concentrations of 2.5, 5.0, 7.5 and 10.0% v/v silk fibroin, respectively. A sample was treated in the same manner, but without silk fibroin in the finishing solution, and was labelled as SF-0. The padded fabrics were then dried at 105 °C for 2 min, cured at 160 °C for 2 min and thoroughly rinsed with water at 60 °C for 30 min.

Evidence of silk fibroin fixation on cotton fabrics

The untreated and fibroin treated cotton fabrics were anlayzed by attenuated total reflectance Fourier transform infrared spectrophotometry (ATR-FTIR) using an FT-IR/FT-Raman Perkin Elmer System 2000 over the range of 600-4000 cm^{-1}. The morphology of the fabrics was examined under a JEOL 5401LV scanning electron microscope at a working potential of 5 kV. The nitrogen content (%N) was determined according to the Kjeldahl method, using a KJELTEC 8400.[23]

The untreated and treated samples were also dyed with a 0.05% w/v aqueous solution of acid dye Telon Red 51 under acidic conditions (pH 4) at a fabric to liquor ratio of 1:30, for 30 min at 60 °C, in an infrared dyeing machine. The reflectance of the dyed samples was measured on a Datacolor 650 spectrophotometer over the range of 400-700 nm. Color strength, in terms of *K/S* values, was calculated using the Kubelka-Munk equation, as shown in Equation 1:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \qquad (1)$$

where $\frac{K}{S}$ is color srtength and R is reflectance of the cotton fabrics.

Physical property tests of cotton fabric samples

The %water uptake of the cotton fabric samples was determined. The fabric samples (4 x 4 cm) were immersed into distilled water for 4 h, after which the excess water was wiped off. The moist fabrics were then weighed, dried at 105 °C for 4 h in a laboratory oven, and finally reweighed. The %water uptake value was calculated from Equation 2:

$$\%\,Water\ uptake = \frac{Weight\ of\ moist\ fabric - Weight\ of\ dried\ fabric}{Weight\ of\ dried\ fabric} \times 100 \qquad (2)$$

The %wrinkle recovery angle of the fabrics was evaluated according to AATCC 128, using a wrinkle recovery tester (Daiei Kagaku Seiki Mfg.) and calculated from Equation 3:

$$\%\,Wrinkle\ recovery\ angle = \frac{Opening\ angle}{180} \times 100 \qquad (3)$$

The breaking strength of the cotton fabrics was tested in warp and weft directions, according to ASTM 5034-2001, using a Tinius Olsen H5KT universal testing machine with a 75 mm gauge length at an extension rate of 300 mm/min.

RESULTS AND DISCUSSION

Evidence of silk fibroin fixation on cotton fabric

As illustrated in Figure 1, the ATR-FTIR spectrum of untreated cotton shows absorption bands at 3342, 2902, 1433 and 1161 cm^{-1}, which are associated with OH stretching, CH_2 stretching, CH_2 scissoring and C–O–C stretching, respectively.[24] A strong absorption band is observed in the fabric treated with DMDHEU alone and in the one treated with DMDHEU plus silk fibroin at 1640 cm^{-1}. It indicates C=O stretching of the carbonyl group in DMDHEU and silk fibroin.[3] In contrast, the weak absorption band at 1640 cm^{-1} present in the spectrum of untreated cotton is associated with adsorbed H–O–H.[24]

The spectra of cotton fabrics treated with DMDHEU alone and with DMDHEU plus silk fibroin are similar due to the similar chemical bonds of the nitrogen atom in the composition of DMDHEU and silk fibroin. However, as shown in Figure 2, in the spectrum of cotton fabric treated with DMDHEU plus 10.0% v/v silk fibroin (SF-10.0), the absorption band at 1165 cm^{-1} corresponding to C–N stretching[25] splits into two small absorption bands at 1165 cm^{-1} and 1146 cm^{-1}. This indicates there is chemical linking between silk fibroin and cotton fabric with the assistance of DMDHEU, which results in a different ATR-FTIR pattern.

Figure 3 presents the SEM micrographs of untreated and treated fabrics. As may be noted in Figure 3b, the particles of silk fibroin were deposited on the surface of cotton fabric. Also, the higher the concentration of silk fibroin, the more numerous particles are found on the surface of treated cotton fabrics, as may be seen in Figure 3c to 3f.

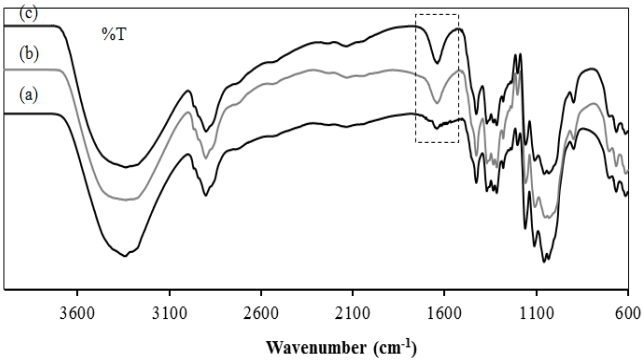

Figure 1: ATR-FTIR spectra of cotton fabric samples (a) untreated (UT), (b) treated with DMDHEU alone (SF-0), and (c) treated with DMDHEU and 2.5% v/v silk fibroin (SF-2.5)

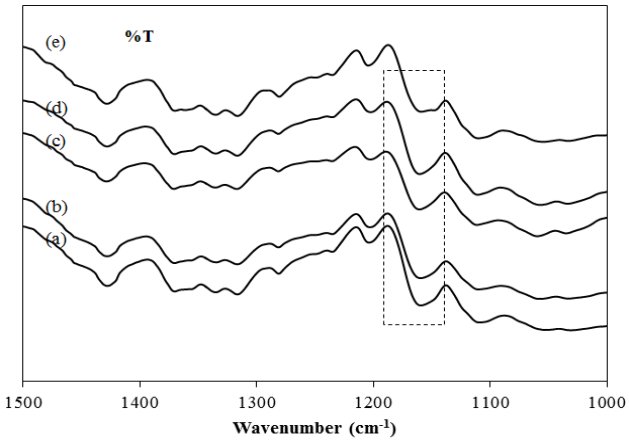

Figure 2: ATR-FTIR spectra of cotton fabric samples treated with (a) DMDHEU alone (SF-0), (b) DMDHEU and 2.5% v/v silk fibroin solution (SF-2.5), (c) DMDHEU and 5.0% v/v silk fibroin solution (SF-5.0), (d) DMDHEU and 7.5% v/v silk fibroin solution (SF-7.5), and (e) DMDHEU and 10.0% v/v silk fibroin (SF-10.0)

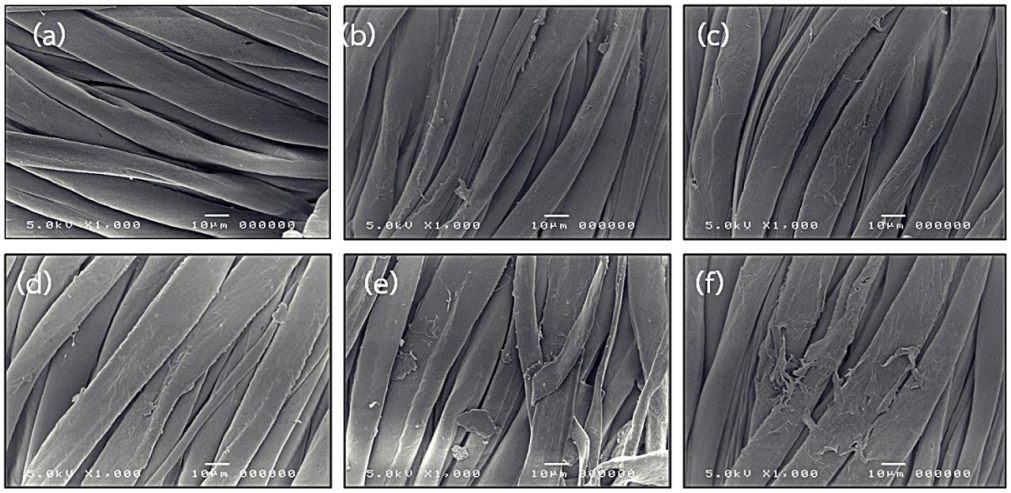

Figure 3: SEM micrographs of cotton fabric samples (a) untreated (UT), (b) treated with DMDHEU alone (SF-0), and treated with a combination of DMDHEU and (c) 2.5% v/v (SF-2.5), (d) 5.0% v/v (SF-5.0), (e) 7.5% v/v (SF-7.5) and (f) 10.0% v/v (SF-10.0) silk fibroin solution

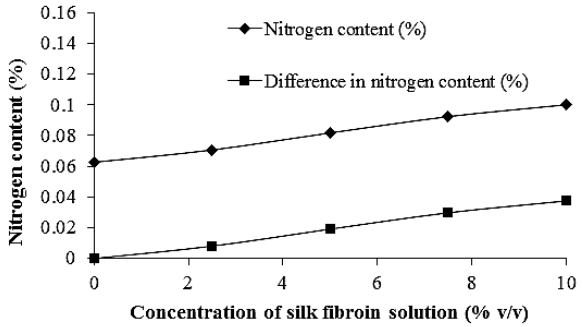

Figure 4: Nitrogen content of treated cotton fabrics as a function of silk fibroin concentration in the finishing solution

The effect of the silk fibroin concentration on the nitrogen content of the obtained treated cotton fabric was studied. A trace of 0.018% nitrogen was found in untreated cotton fabric, while a higher value, of 0.0706%, was found in the cotton fabric treated with DMDHEU alone (SF-0). In addition, the nitrogen content was substantially higher after the cotton fabrics were treated with the combination of DMDHEU and silk fibroin, as seen in Figure 4. The nitrogen content of the cotton fabric continuously increased from 0.008 to 0.0191, 0.0297 and 0.0374% when the concentration of silk fibroin was varied from 2.5 to 5.0, 7.5 and 10.0% v/v (SF-2.5 to SF-10.0). Therefore, it is clear that as the concentration of silk fibroin increases, it is able to crosslink more easily with the cotton fabric with the assistance of DMDHEU.

After dyeing with an acid dye, the reflectance of the cotton fabric samples was determined and color strength expressed in terms of *K/S* was calculated. As seen in Figure 5, the *K/S* value of the sample treated with DMDHEU alone (SF-0) is 7.32, compared to 0.65 for the untreated (UT) sample. The treatment of fabric samples with a combination of DMDHEU and silk fibroin gradually increases *K/S* values with increasing silk fibroin concentration. The result indicates that more amino groups from silk fibroin are present on the surface of cotton fabric. The amino groups turned to a positive charge under acidic conditions during dyeing, which increased the potential of ionic attraction and thus led to increased acid dye uptake. This result was confirmed by staining of the dyed regenerated fibroin on a polyamide surface. The suggested binding forces are postulated as being the result of a mixture of ionic interactions and hydrogen bonding.[26]

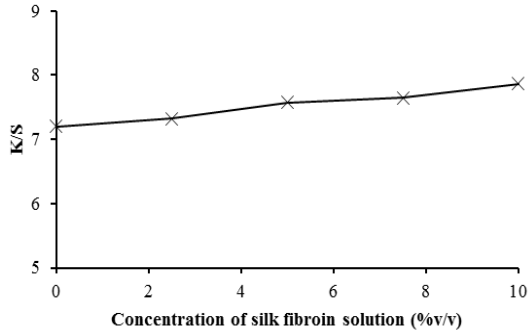

Figure 5: Color strength of treated dyed cotton fabrics as a function of silk fibroin concentration in the finishing solution

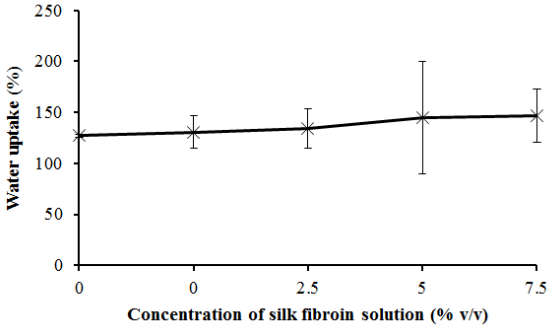

Figure 6: Water uptake of treated cotton fabrics as a function of silk fibroin concentration in the finishing solution

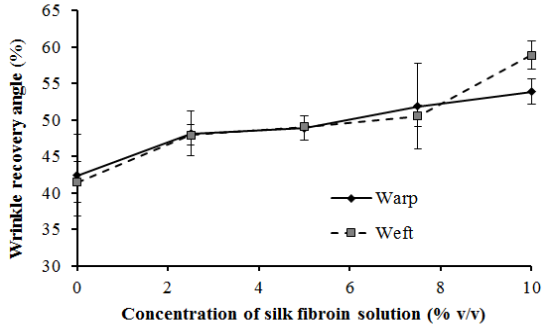

Figure 7: Wrinkle recovery angle of treated cotton fabrics as a function of silk fibroin concentration in the finishing solution

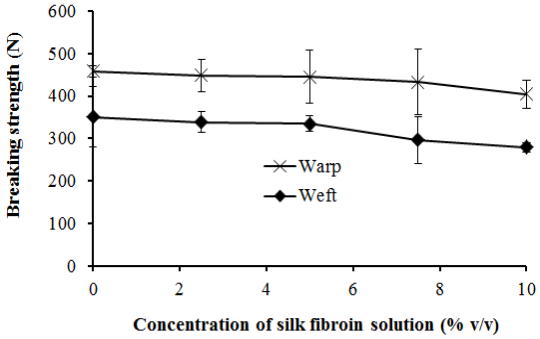

Figure 8: Breaking strength of treated cotton fabrics as a function of silk fibroin concentration in the finishing solution

Physical properties of cotton fabric treated with silk fibroin

The water uptake of untreated cotton fabric (UT) is 130.3%, which is greater than the value of 126.8% for the sample treated with DMDHEU alone (SF-0), as shown in Figure 6. A lower value of water uptake/moisture regain of resin-finished cellulosic fabric has been also observed in earlier studies and it has been suggested that this value is directly related to the degree of crosslinking, while the introduction of crosslinkers reduces the degree of substrate accessibility.[27-28] However, the value (130%) of the sample treated with the finishing solution containing 2.5% v/v silk fibroin (SF-2.5) is comparable to that of the untreated sample. In addition, an increase in water uptake from 130% to 144% is observed in the samples treated with increasing concentrations of silk fibroin from 2.5 to 10.0% v/v (SF-2.5 to SF-10.0). This indicates that the hydrophilic groups of silk fibroin contribute to greater adsorption of water on the surface of cotton fabric, resulting in higher water uptake of the silk fibroin treated fabric. This observation has been also made in our previous study, where cotton fabric was treated with silk sericin.[22]

The wrinkle recovery angle of treated cotton fabrics in warp and weft directions is shown in Figure 7. Compared to the wrinkle recovery angle value of the untreated sample (UT) (32.9% in warp and 35.2% in weft), an increase by approximately 17% and 11% in warp and weft directions, respectively, is noticed in the sample treated with DMDHEU alone (SF-0). The introduction of silk fibroin in the finishing solutions additionally enhances the wrinkle recovery angle up to 37% (warp) and 42% (weft), as the amount of silk fibroin increases to 10.0 % v/v (SF-10.0).

The breaking strength of the treated cotton fabrics is shown in Figure 8. The breaking strength of the untreated cotton in warp and weft directions is 646.0 and 505.6 N, respectively. After treating with DMDHEU, a significantly lower breaking strength, by about 30%, is observed in both directions. Although the concentration of magnesium chloride was lower than that used in our previous work on cotton fabric treated with sericin,[22] there is a further slight decrease in breaking strength when the silk fibroin content is raised. A fibroin concentration of 10.0% v/v in the finishing solution gives lower breaking strength by 37% and 44% in warp and weft directions, respectively. It is known that a loss in breaking strength is accompanied with a high level of durable press performance.[29-30] This can be

attributed to the stiffening of cellulose chains by chemical linkages of DMDHEU and silk fibroin. In addition, a reduction of tensile strength is caused by the use of magnesium chloride as a catalyst, as reported in previous studies.[22,31]

CONCLUSION

Cotton fabric was chemically finished with fibroin extracted from silk waste, in combination with DMDHEU crosslinking agent, using the pad-dry-cure technique. The presence of silk fibroin on the finished fabric was confirmed by SEM, nitrogen content analysis and acid dyeing. The concentration of silk fibroin in the finishing solutions affected the physical properties of cotton fabric to varying degrees. Higher silk fibroin concentration clearly improved wrinkle recovery and water uptake values, but had a slightly negative influence on the tensile strength property of the treated fabric samples.

ACKNOWLEDGEMENTS: This research was supported by National Science and Technology Development Agency (NSTDA), Thailand, through Young Scientist and Technologist Project (YSTP).

REFERENCES

1 E. Marsano, P. Corsini, M. Canetti and G. Freddi, *Int. J. Biol. Macromol*., **43**, 106 (2008).
2 S. Çalamak, C. Erdoğdu, M. Özalp and K. Ulubayram, *Mater. Sci. Eng., C*, **43**, 11 (2014).
3 P. Moonsri, R. Watanesk, S. Watanesk, H. Niamsup and R. L. Deming, *J. Appl. Polym. Sci*., **108**, 1402 (2008).
4 M. A. Moraes, M. F. Silva, R. F. Weska and M. M. Beppu, *Mater. Sci. Eng., C*, **40**, 85 (2014).
5 S. Shang, L. Zhu and J. Fan, *Carbohyd. Polym*., **86**, 462 (2011).
6 S. Shang, L. Zhu and J. Fan, *Carbohyd. Polym*., **93**, 561 (2013).
7 P. Bajaj, *J. Appl. Polym. Sci*., **83**, 631 (2002).
8 T. Harifi and M. Montazer, *Carbohyd. Polym*., **88**, 1125 (2012).
9 M. G. Fouda and H. M. Fahmy, *Carbohyd. Polym*., **86**, 625 (2011).
10 N. A. Ibrahim, M. H. Abo-Shosha, H. M. Fahmy, Z. M. El-sayed and A. A. Hebeish, *Mat. Proc. Technol*., **200**, 385 (2008).
11 S. Kittinavarat, P. Kantuptim and T. Singhaboonponp, *J. Appl. Polym. Sci*., **100**, 1372 (2006).
12 R. Purwa and M. Joshi, *AATCC Rev*., **5**, 40 (2005).
13 C. Schramm and B. Rinderer, *Text. Res. J*., **72**, 357 (2002).
14 A. E. Shafei, S. Shaarawy and A. Hebeish, *Carbohyd. Polym*., **79**, 852 (2010).
15 K. F. El-tahlawy, M. A. El-bendary, A. G. Elhendawy and S. M. Hudson, *Carbohyd. Polym*., **60**, 421 (2005).
16 J.-Y. Kang, J. Deivasigamani and M. Sarmardi, *AATCC Rev*., **4**, 28 (2004).
17 W. Li, X. Xu, S. Chen, X. Zhou, L. Li *et al*., *Carbohyd. Polym*., **71**, 574 (2008).
18 H. Peng, C. Q. Yang and S. Wang, *Carbohyd. Polym*., **87**, 491 (2012).
19 C. Schramm, B. Rinderer and R. Tessadri, *Carbohyd. Polym*., **105**, 81 (2014).
20 W. Sricharussin, W. Ryo-Aree, W. Intasen and S. Poungraksakirt, *Text. Res. J*., **74**, 475 (2004).
21 C. Q. Yang and D. Wang, *Text. Res. J*., **70**, 615 (2000).
22 A. Kongdee, T. Bechtold and L. Teufel, *J. Appl. Polym. Sci*., **96**, 1421 (2005).
23 AOAC official method 2001.11 in Protein (crude) in animal feed, forage (plant tissue), grain, and oilseeds (2002).
24 N. Abidi, L. Cabrales and C. H. Haigler, *Carbohyd. Polym*., **100**, 9 (2014).
25 M. A. Koperska, D. Pawcenis, J. Bagniuk, M. M. Zaitz, M. Missori *et al*., *J. Polym. Degrad. Stabil*., **105**, 185 (2014).
26 H.-T. Ngo and T. Bechtold, *J. Appl. Polym. Sci*., (2016), doi: 10.1002/APP.43880.
27 N. R. Bertoniere, W. D. King and C. M. Welch, *Text. Res. J*., **64**, 247 (1994).
28 A. Kongdee, A. P. Manian, M. Lenninger, J. Schlangen and T. Bechtold, *J. Appl. Polym. Sci*., **115**, 2898 (2010).
29 I. Kang, C. Q. Yang, W. Wei and G. C. Lickfield, *Text. Res. J*., **68**, 865 (1998).
30 H. Peng, C. Q. Yang and S. Wang, *Carbohyd. Polym*., **87**, 491 (2012).
31 C. Q. Yang, W. Wei and G. C. Lickfield, *Text. Res. J*., **70**, 910 (2000).