

Impregnation of Silk Sericin into Polyester Fibers Using Supercritical Carbon Dioxide

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ABSTRACT: Silk sericin was impregnated into polyester fabric using supercritical carbon dioxide (SCCO₂) to overcome polyester hydrophobicity. The effects of sericin molecular weight, pH of sericin, solution and cosolvent types on sericin impregnation were investigated. Enzyme-hydrolyzed, acid-, based-hydrolyzed sericin in SCCO₂, and a 30 kDa sericin in SCCO₂ modified with cosolvents such as water, methanol, 1-propanol, and acetone; and a modifier: sodium hydroxide solution were used in this work. Impregnation of sericin in polyester was indicated by Fourier transform infrared spectrophotometry (FTIR) and dyeing with acid dye. Degradation of polyester fibers during SCCO₂ process was indicated by scanning electron microscopy

(SEM). Methylene blue dyeing was used to realize carboxyl group in polyester. The results showed no impregnation of sericin into polyester by using SCCO₂ modified with cosolvents. However, sericin was impregnated into modified surface polyester since hydrophilic groups such as carboxyl and hydroxyl groups were regenerated by alkaline hydrolysis. Samples impregnated with hydrolyzed sericin showed high color strength of Supranolechtbordeaux B acid dye. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2091–2097, 2007

Key words: polyester; fiber modification; supercritical carbon dioxide; sericin

INTRODUCTION

Polyester is the king among synthetic textile fibers because of the combination of excellent bulk properties and production cost. However, polyester has its own limitations; hydrophobicity and related static propensity are great disadvantages. Physical and chemical modifications of polyester surface are of interest to achieve hydrophilic material. Plasma treatment is a common technique to modify polyester surfaces.^{1–4} Cold plasma at atmospheric pressure has been used to improve surface properties to meet ecological requirement.⁵ Chemical modification is another approach to improve polyester surfaces. Graft polymerization with acrylic acid onto Poly(ethylene terephthalate)/polyethylene blend treated with DC pulse plasma has been succeeded to increase hydrophilicity and water retention of the blend.⁶ Azo acrylates have been grafted onto PET by gamma irradiation.⁷

Supercritical carbon dioxide (SCCO₂) is a great potential method for different fields of applications. Extraction of natural products from fruits and vegeta-

bles is widely used.^{8–11} Productions of decaffeinated coffee and tea using SCCO₂ are the most common processes.^{12–15} In textile, the research activities are mostly directed to polyester dyeing.^{16–21} Modification of polyester surface with sericin using SCCO₂ has never been reported. This article describes chemical modification of polyester surface with a natural polymer i.e. sericin, using SCCO₂. Sericin produced by silk worm contains lots of hydrophilic moieties. The impregnation of sericin using SCCO₂ is a key of environmental friendly process to improve polyester hydrophilicity. Cosolvents such as water, methanol, ethanol, 1-propanol, and acetone, and a modifier i.e., sodium hydroxide, were used for SCCO₂ modifications. Impregnation of sericin in polyester was proved using FTIR and dyeing with acid dye. Methylene blue dyeing was used to realize the chemical changes of polyester surface.

EXPERIMENTAL

Chemical and materials

Sericin of a 30 kDa supplied by Seiren (Fuku, Japan), NaOH (AR grade) and Achromobacter Protease I supplied by Wako Pure chemical Industries (Osaka, Japan), HCl (AR grade) and methylene blue (GR, 98.5%) purchased by Nacalai Tesque (Kyoto, Japan),

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TABLE I
Preparations of Hydrolyzed and Alkaline Sericin Solutions

Sample	Preparation of sericin			Material for sericin distribution
	Hydrolysis	Dialysis	NaOH added	
MFHE	Enzyme (pH = 9)			Glass filter paper
MDHA	Acid	✓		PET
MFHA	Acid		✓ (pH = 10)	Glass filter paper
MPHA	Acid		✓ (pH = 9)	PET
WDHB	Base	✓ (pH = 8)		PET
WFS			✓ (pH = 8)	Glass filter paper
WFHAS	Acid		✓ (pH = 9)	Glass filter paper

99% acetic acid purchased by Merck (Darmstadt, Germany), and Supranolechtbordeaux B acid dye supplied by DyStar (Frankfurt, Germany) were used as received.

METHODS

Preparation of hydrolyzed sericin

Enzyme-hydrolysis

Sericin of 30 kDa was hydrolyzed using protease enzyme.^{22,23} A weight of 0.0703 g sericin was added in 23 mmol/mL *Achromobacter* Protease I in Tris-HCl solution and incubated at 37°C for 15 h. The solution was dropped on glass fiber filter. The filter was dried in an oven at 100°C (sample MFHE).

Acid hydrolysis

Sericin of 30 kDa was hydrolyzed using hydrochloric acid. A weight of 0.08 g sericin was subjected to 8 mL of 6M HCl. Hydrolysis reaction was carried out at 60°C for 2 h. The following procedures were used to remove acid.

Acid-hydrolyzed solution was neutralized with sodium hydroxide, 8 mL of 6M NaOH was added into hydrolyzed sericin solution, pH of the solution was checked using pH paper. Some of water was evaporated; the remained solution was dropped on glass filter paper (samples MFHA) and polyester fabric (sample MPHA). Water in filter paper and fabric was dried out in an oven at 100°C.

The acid-hydrolyzed sericin solution was dialyzed against distilled water for 3 h. Some of water was dried out. The remained solution was dropped on polyester fabric, the sample was dried in an oven at 100°C (sample MDHA).

Small amount of 6M sodium hydroxide solution was added into acid-hydrolyzed sericin solution until pH of the solution was 9. The solution was dropped on glass filter paper. Glass filter paper was then dried in an oven at 100°C (sample WFHAS).

Base hydrolysis

Sericin powder (0.16 g) was subjected to 8 mL of 6M NaOH. Hydrolysis reaction was carried out at 60°C

for 2 h. A volume of 4 mL of the hydrolyzed solution was dialyzed against distilled water until pH of solution was 8 (samples WDHB).

Preparation of alkaline sericin

Sericin (0.08 g) was dissolved in small amount of water. Several drops of 6M NaOH were added into the solution, pH of the solution was checked using pH paper. The solution was dropped on glass filter paper. The filter paper was dried in an oven at 100°C (samples WFS).

Preparations of hydrolyzed and alkaline sericin solutions for the impregnation are presented in Table I.

Impregnation of sericin using SCCO₂

Sericin impregnation in polyester using SCCO₂ was carried out at 120°C, 25 MPa for 1 h. Figure 1 shows simplified diagram of SCCO₂ equipment used in the investigation. A concentration of 0.5 wt % sericin (30 kDa) was used for the impregnation. There were several methods for sericin impregnation using SCCO₂ process. Sericin was added as powder into SCCO₂ column, mixed with cosolvents/dissolved in water and distributed on glass filter paper/polyester as described earlier. Cosolvents such as water, methanol, ethanol, 1-propanol, and acetone were used to modify polarity of SCCO₂; their concentration of 2.5% (on volume of SCCO₂) was used. Hydrolyzed sericin distributed on filter paper or polyester fabric was

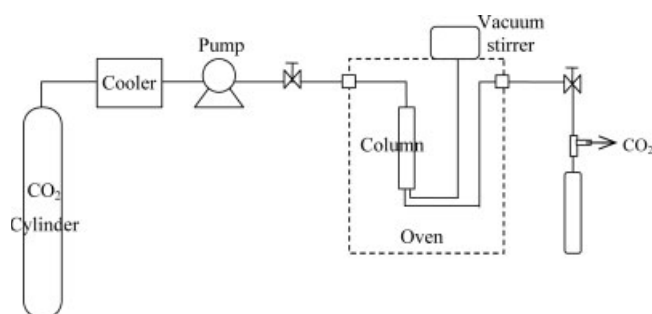


Figure 1 Simplified diagram of SCCO₂ equipment.

TABLE II
***L*-, *a*-, and *b*-Values of Unprocessed and Processed Polyester Dyed with Supranolechtbordeaux B**

Sample	<i>L</i>	<i>a</i>	<i>b</i>
UP	56.07	21.70	2.30
W-F	52.53	24.67	3.60
A-0	55.17	21.93	2.23
A	55.03	22.63	4.13
P	55.27	22.43	3.57
E	55.50	22.10	4.33
M-0	55.10	22.53	3.40
M	55.27	22.60	3.40
M-F	55.13	22.20	3.30
MFHE	55.33	21.60	3.37
MFHA	46.30	29.43	0.17
MDHA	54.63	21.90	2.60
WDHB	50.30	24.03	3.33
WFS	53.90	22.90	3.13
WFHAS	55.20	22.80	2.87

used for the impregnation without addition of cosolvents.

Characterization of polyester fibers

To verify sericin impregnated in polyester, samples were dyed with 2% Supranolechtbordeaux B at 60°C for 30 min at a liquor ratio of 1 : 100, in acidic environment. A concentration of 0.1% methylene blue was used to dye samples at 60°C for 2 h at a liquor ratio of 1 : 50, to realize hydrolysis degradation of polyester. *L*- and *b*-values of samples dyed with methylene blue and Supranolechtbordeaux B were measured by Minolta Color Reader CR-10.

Morphology of polyester fiber surfaces were observed by a scanning electron microscope (SEM), Jeol JSM-5410LV. The samples were sputter coated with gold. Fiber morphology was examined at different magnifications.

Chemical structure of polyester fibers was identified. The fibers were cut into small pieces and mixed with KBr and pressed under a pressure of 10 tons for 5 min. To remove water adsorbed on sample pellets, the sample pellets were kept in a desiccator over phosphorus pentoxide for 24 h, and analyzed using FTIR (Bruker Vector 22, Germany).

RESULTS

Effect of cosolvents on sericin impregnation

As sericin was hydrophilic substance, sericin could impregnate in hydrophobic polyester using nonpolar SCCO₂. With more polar SCCO₂ modified with some solvents, we expected impregnation of sericin in polyester. Table II shows *L*-values of samples dyed with Supranolechtbordeaux B; unprocessed sample (sample UP), samples subjected to water and sericin

distributed on glass filter paper (sample W-F), acetone only (sample A-0), acetone and sericin (sample A), 1-propanol and sericin (sample P), ethanol and sericin (sample E), methanol only (sample M-0), methanol and sericin (sample M), and methanol and sericin distributed on glass filter paper (sample M-F).

Among samples, *L*-value of unprocessed were highest as 65.07. The high *L*-value indicates bright object found in unprocessed sample. Samples subjected to cosolvents only, and cosolvents and sericin, showed small reduction of *L*-values which indicate darker samples as observed in samples W-F and M-F. *L*-values of W-F and M-F reduce by 6.3 and 1.7%, respectively, when compared with unprocessed. The results show that these samples might contain small amount of sericin. However, it can be concluded that although polarity of SCCO₂ was improved by addition of cosolvents, there was no sericin impregnation in polyester fibers.

Effect of molecular weight of sericin on the impregnation

Enzyme hydrolysis by protease provided sericin of low molecular weights (~ 3 kDa)^{22,23} which was further used for the impregnation. *L*-value of the sample (MFHE) (shown in Table II) is comparable to those of other samples mentioned earlier. This indicates no effect of molecular weight of sericin on the impregnation in polyester fibers using SCCO₂.

Effect of sodium hydroxide on sericin impregnation in polyester fibers using SCCO₂

Dyeing with Supranolechtbordeaux B, *L*-values of samples impregnated with sericin in the presence of NaOH, (samples MFHA, WDHB, WFS, and WFHAS) were shown in Table II. As compared with unprocessed, lower *L*-values of samples MDHA, WFS, and WFHAS indicate sericin impregnation. Deeply impregnation of sericin might be received by using SCCO₂ process at 120°C, 25 MPa. In sample WDHB, more reduced value is determined. The results indicate the role of NaOH in sericin impregnation as all mentioned samples were processed in alkaline sericin solutions, except sample MDHA which was processed in acidic solution. It seems that there was the effect of pH of sericin solution on amount of sericin in polyester as greatest color strength was received from the sample processed at pH 10 (sample MFHA). Reduced *L*-value by 17.42%, when compared with unprocessed, is observed in sample MFHA.

By observation of polyester fiber surfaces under SEM, changes of surface morphology of the fibers were investigated (see Figs. 2 and 3). Large particles are present on the fibers surfaces of samples processed with alkaline sericin solutions (samples MFHA,

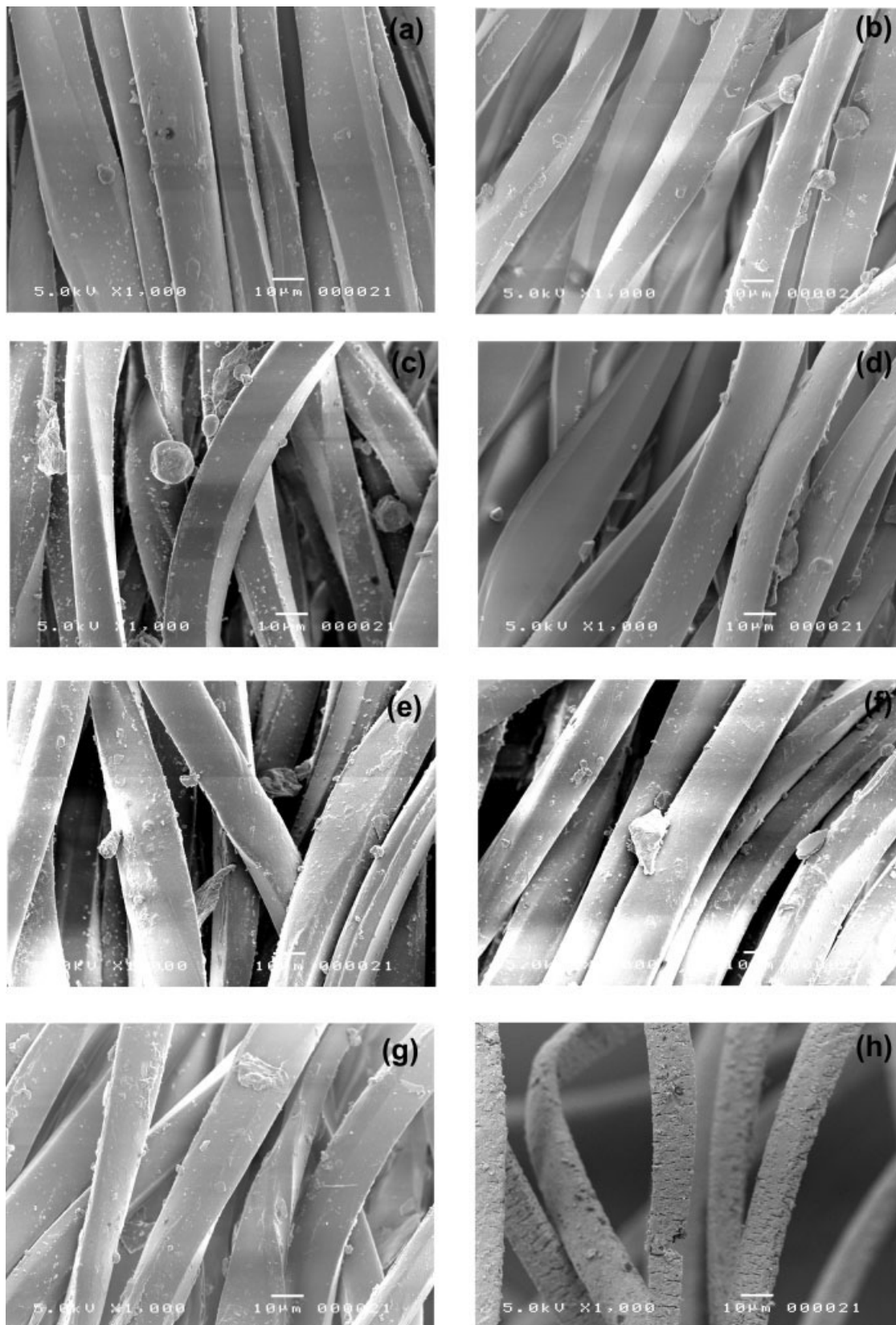


Figure 2 SEM images ($\times 1000$) of (a) unprocessed, (b) MFHA, (c) WFHAS, (d) MFHE, (e) WDHB, (f) WFS, (g) MDHA, and (h) MPFA.

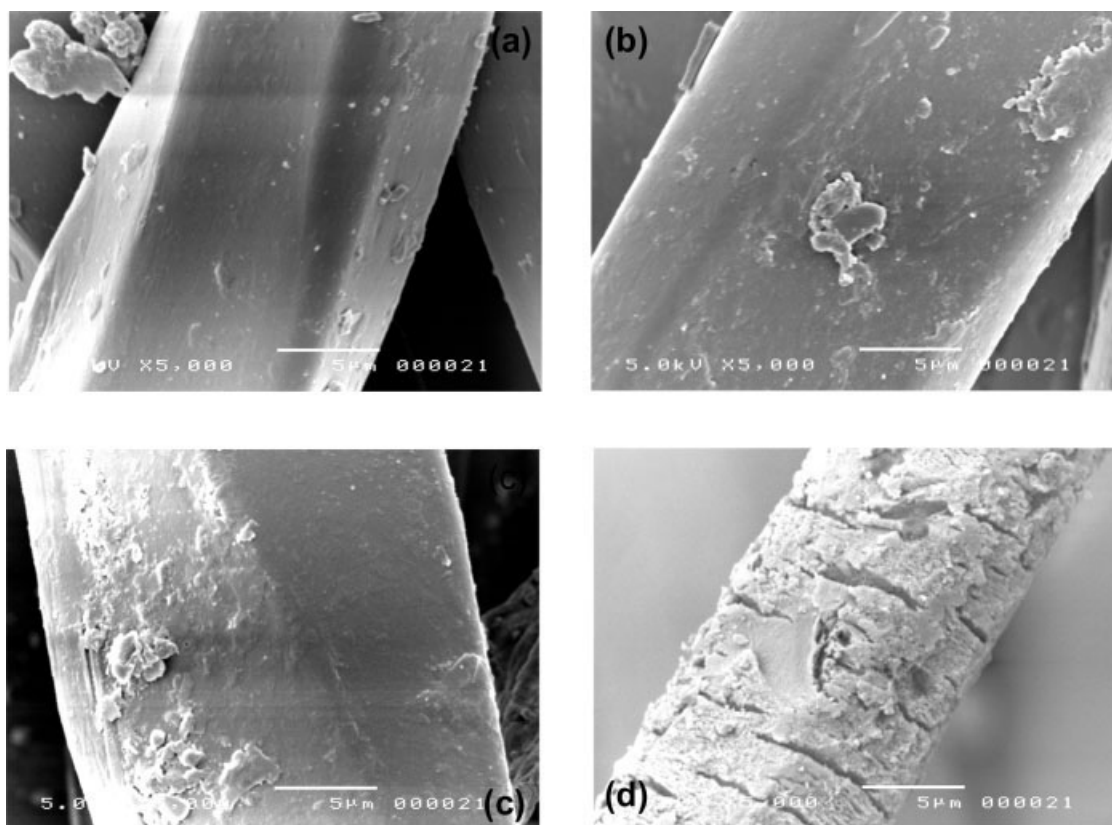


Figure 3 SEM images ($\times 5000$) of (a) unprocessed, (b) MFHA, (c) WDHB, and (d) MPHA.

WFHAS, WDHB, and WFS) which are not found in unprocessed and processed with enzymatic hydrolyzed sericin (sample MFHE). Impregnation of sericin in polyester fibers was confirmed by these images. Moreover, degradation of polyester fibers processed with SCCO₂ in strong alkali solution was observed. Broken fibers are seen clearly in sample MPHA [Fig. 3(d)] which was processed in strong alkaline solution at pH 10. As it has been reported, exposure of polyester to NaOH solution attributes to hydrolysis of ester groups, low molecular weight and water soluble fragments are produced and leading to weight loss of polyester fibers.^{24–26} We have tried to measure the molecular weight of processed samples, but the samples including MPHA were not dissolved in tetrahydrofuran. Thus, no molecular weight data are available after SCCO₂ process. However, 5000 \times magnification of SEM images of sample MPHA clearly supports the degradation of polyester fibers.

Carboxyl and hydroxyl compounds regenerated from alkaline hydrolysis resulted in more hydrophilic polyester, thus the samples were impregnated with sericin as investigated in samples WFS, WFHAS, and WDHB. Besides, the hydrolysis resulted in sample handling. Soft fabrics reflect structural changes of the fibers. Fine fibers were obtained from alkaline treatment as observed in previous investigation.²⁷ However, exposure to strong alkaline solution (at pH 10)

and subsequently process under severe condition, like SCCO₂ resulted in serious polyester degradation as investigated in sample MPHA. The sample was immediately separated out when it was washing in distilled water. Similarly, glass filter paper submerged in alkaline sericin (for sample MFHA) was broken into small pieces after SCCO₂ process as seen in Figure 4.

Dyeing sample with methylene blue to investigate carbonyl group was conducted as described by Klemp et al.²⁸ *L*- and *a*-values of samples are shown in Figures 5 and 6. *L*-values ranged as UP < MDHA < WFHAS < MFHA < WFS < WDHB < MPHA indicate the order of dark samples. Since *b*-values are considered for blue shade, lower value represents higher saturation of the blue. The order of bluer samples is ranged as UP < MDHA < WFHAS < MFHA < WDHB < WFS < MPHA. For sample MDHA, it was subjected to acidic sericin, carbonyl groups might be produced and also led to methylene blue adsorption.

Characterization of polyester fibers processed with SCCO₂ by means of FTIR

FTIR was subsequently used to characterize chemical structure of polyester before and after SCCO₂ process. Figure 7 shows spectrum of polyester samples which were processed by SCCO₂. Absorption band at 2800 cm⁻¹ is due to C—H stretching. High intensity

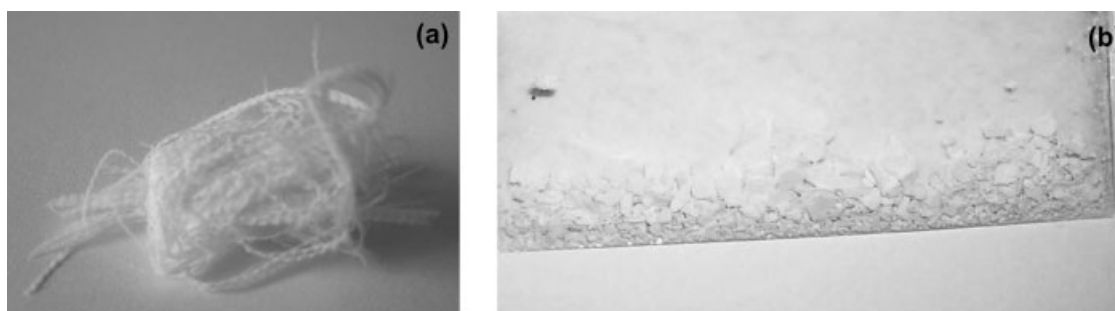


Figure 4 (a) Sample MPHA, (b) glass filter paper for sample MFHA processed in strong alkaline environment at pH 10.

absorption bands at 1720, ~ 1250 , ~ 1100 , and $\sim 750\text{ cm}^{-1}$ correspond to ester C=O, ester C—O, O—C—C, and C—H benzene ring, respectively.²⁹ Samples processed with sericin using SCCO₂ modified with acetone show similar spectra as unprocessed. The results indicate that there is neither polyester degradation nor sericin impregnation with cosolvents assistance as described earlier.

FTIR characterization of samples processed with alkaline sericin by SCCO₂ (samples MPHA, WDHB, and MFHA) provided spectra as also shown in Figure 7. Their spectra present an additional broad band at 3200–3600 cm^{-1} which corresponds to —OH stretching, when compared with unprocessed and processed with SCCO₂ modified with acetone. For sample MPHA, MPHA processed with strong alkaline sericin shows high intensity of —OH stretching band. This band refers to impregnation of sericin which constitutes $\sim 30\text{ mol } \%$ of —OH group.³⁰ The deeply impregnation of sericin was successful by using SCCO₂ as —OH stretching band was present very clearly in FTIR spectra. More apparent bands of ester C=O and ester C—O bands at 1720 and $\sim 1250\text{ cm}^{-1}$, respectively, are the evidences of carboxyl compounds produced from alkaline degradation which agree with results of methylene blue adsorption. By serious degradation, high amount of carboxyl compounds was produced, thus leads to great methylene blue adsorp-

tion (indicated by very low *L*- and *b*-values as observed for sample MPHA in Figs. 5 and 6).

CONCLUSIONS

Sericin was not impregnated into polyester by SCCO₂ modified with cosolvents, namely water, methanol, 1-propanol, and acetone. Interestingly, SCCO₂ provided great advantages of single step for sericin impregnation in polyester fibers. The impregnation was successful when processed by either SCCO₂ modified with NaOH or polyester surfaces modified with NaOH was used. Polyester with modified surfaces contained carboxyl and hydroxyl groups, thus, these groups adsorbed hydrophilic substance i.e., sericin during SCCO₂ process. Deeply impregnation was expected since high pressure at 25 MPa was used. With FTIR analysis and methylene blue adsorption, carboxyl groups in processed samples were investigated. Very high intensity of ester C=O at 1720 cm^{-1} and low *L*- and *b*-values of processed samples dyed with methylene blue were observed. Sericin impregnated in polyester fibers adsorbed Supranolechtbordeaux B, decrease in *L*-value was observed in processed samples. Sericin was penetrated into enlarge voids of polyester fibers during SCCO₂ process at high temperature (120°C). However, the impregnation of alkaline sericin must be compromised between pH

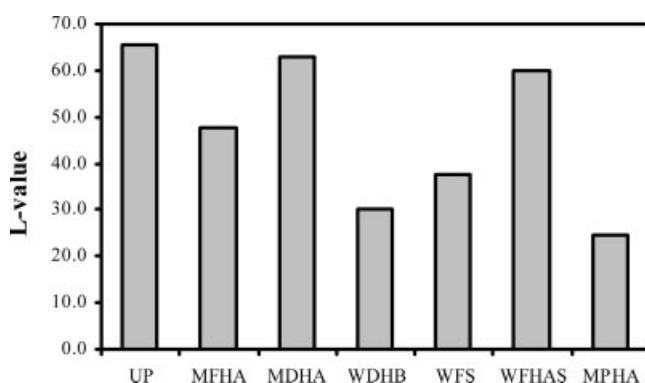


Figure 5 *L*-values of processed samples dyed with methylene blue.

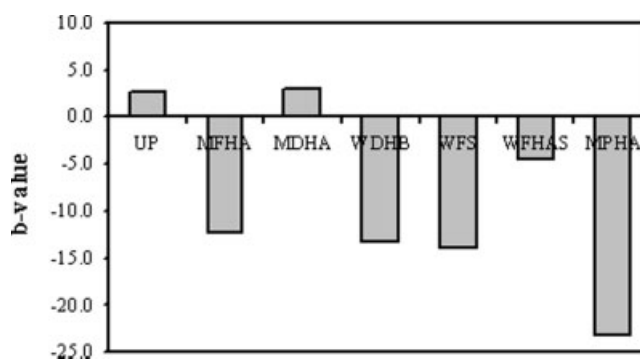


Figure 6 *b*-values of processed samples dyed with methylene blue.

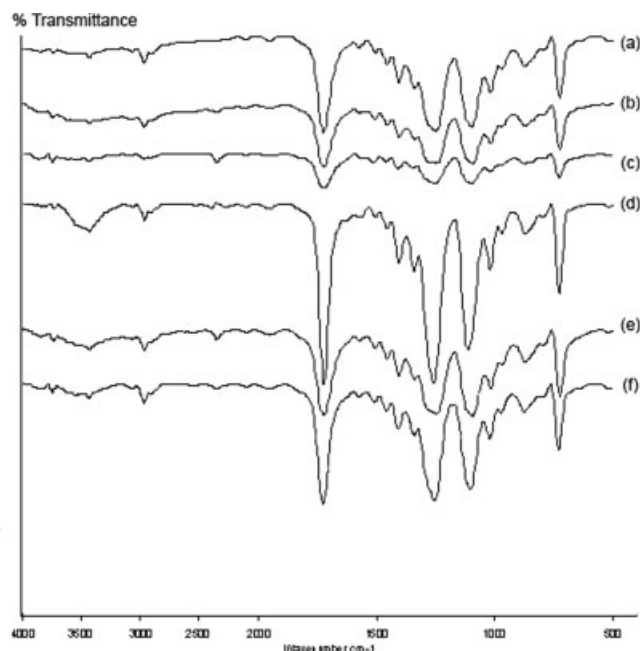


Figure 7 FTIR spectra of (a) unprocessed polyester, (b) polyester processed by SCCO₂ modified with acetone and (c) polyester treated with sericin using SCCO₂ modified with acetone (d) MPHA, (e) WDHB, and (f) MFHA.

of alkaline sericin and fiber degradation in such environment which could cause loss in fiber strength.

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References

- Amanatides, E.; Mataras, D.; Katsikogianni, M.; Missirlis, Y. F. *Surf Coat Technol* 2006, 200, 6331.
- Singh, N. L.; Qureshi, A.; Shah, N.; Rakshit, A. K.; Mukherjee, S.; Tripathi, A.; Avasthi, D. K. *Radiat Meas* 2005, 40, 746.
- Qiang, C. *J Phys D: Appl Phys* 2002, 35, 2939.
- Ueda, M.; Kostov, K. G.; Beloto, A. F.; Leite, N. F.; Grigorov, K. G. *Surf Coat Technol* 2004, 186, 295.
- Cheng, C.; Liye, Z.; Zhan, R.-J. *Surf Coat Technol* 2006, 200, 6659.
- Chen, J.-P.; Chiang, Y.-P. *J Membr Sci* 2006, 270, 212.
- Bucio, E.; Skewes, P.; Burillo, G. *Nucl Instrum Methods Phys Res Sect B* 2005, 236, 301.
- Copella, S. J.; Bartonin, P. in: Squires, T. G.; Paulaitis, M. E.; (Eds.), *ACS Symposium Series* 1985, 329, 202.
- Mathias, P. M.; Copeman, T. W.; Prausnitz, J. M. *Fluid Phase Equilib* 1986, 29, 545.
- Gironi, F.; Lamberti, L. In *Proceedings of the Third International Symposium on Supercritical Fluids*; Brunner, G.; Perrut, M., Eds.; Strasbourg, 1994; Vol. 2, p 459.
- Benvenuti, F.; Gironi, F. In *Proceedings of the Fourth Italian Conference on Supercritical Fluids and their Applications*; Capri, 1997; p 65.
- Subra, P.; Boissinot, P.; Benzaghrou, S. In *Proceedings of the Fifth Meeting on Supercritical Fluids: Materials and Natural Products Processing*; Perrut, M.; Subra, P., Eds.; Niece, 1998; p 307.
- Johannsen, M.; Brunner, G. In *Proceedings of the Third International Symposium on Supercritical Fluids*; Brunner, G.; Perrut, M., Eds.; Strasbourg, 1994; Vol. 1, p 83.
- Wang, S. In *Proceedings of the Fourth Meeting on Supercritical Fluids*; Barth, D.; Blanchard, J. M.; Cansell, F., Eds.; I.N.S.A: Villeurbanne; 1997, p 35.
- Lack, E.; Seidlitz, H. In *Extraction of Natural Products using Near-Critical Solvents*; King, M. B.; Bott, T. R., Eds.; Blackie: Glasgow, 1993; p 101.
- Oezcan, A. S.; Oezcan, A. *J Supercrit Fluids* 2005, 35, 133.
- Park, M.-W.; Bae, H.-K. L. *J Supercrit Fluids* 2002, 22, 65.
- Maeda, S.; Kunitou, K.; Hihara, T.; Mishima, K. *Text Res J* 2004, 74, 989.
- De Giorgi, M. R.; Cadoni, E.; Maricca, D.; Piras, A. *Dyes Pigments* 2000, 45, 75.
- Kawahara, Y. *Coloration Technol* 2001, 117, 266.
- Tabata, I.; Lyu, J.; Cho, S.; Tominaga, T.; Hori, T. *Coloration Technol* 2001, 117, 346.
- Tsunasawa, T.; Masaki, T.; Hirose, M.; Soejima, M.; Sakiyama, F. *J Biol Chem* 1989, 264, 3832.
- Masaki, T.; Fujihashi, T.; Nakamura, K.; Soejima, M.; *Biochem Biophys Acta* 1981, 660, 51.
- Gu, X.; Raghavan, D.; Nguyen, T.; VanLandingham, M. R.; Yebassa, D. *Polym Degrad Stab* 2001, 74, 139.
- Niu, S.; Wakida, T. *Textile Res J* 1995, 65, 771.
- East, G. C.; Rahman, M. *Polymer* 1999, 40, 2281.
- Grancaric, A. M.; Tarbuck, A.; Kallay, N.; Tomasic, V. 3rd Autex Conference 2003, Gdansk, Poland, 25–27, June, 2003.
- Klemp, D.; Phillipp, B.; Heinze, T.; Heinze, U.; Wagenknecht, W. *Comprehensive Cellulose Chemistry, Vol. 1*; Wiley-VCH: Darmstadt, 1998; p 236.
- Duarte, L. T.; Paulo e Silva, E. M.; Branco, J. R. T.; Lins, V. F. C. *Surf Coat Technol* 2004, 182, 261.
- Robson, R. M. *Handbook of Fiber Science and Technology*, 4th ed.; Marcel Dekker: New York, 1985; p 426.