Biodegradability of Cellulose Fabrics

Chung Hee Park,[1] Yun Kyung Kang,[1] Seung Soon Im[2]

[1]*Department of Clothing and Textiles, Seoul National University, Seoul, Korea*
[2]*Department of Textile Engineering, Hanyang University, Seoul, Korea*

Received 30 December 2003; accepted 27 April 2004
DOI 10.1002/app.20879
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Biodegradability of cellulose fabrics was evaluated by use of a soil burial test, an activated sewage sludge test, and an enzyme hydrolysis. Surface changes after biodegradation were observed by optical microscopy. From X-ray diffraction analysis (XRD), changes in the crystallinities and the internal structures as a result of degradation were also investigated. It was shown that biodegradability decreased in the following order: rayon > cotton ≫ acetate. Rayon fibers, which have a low crystallinity and a low degree of orientation, showed the highest biodegradability in most cases. However, in spite of its low crystallinity, acetate fibers exhibited very low biodegradability, probably because of the presence of hydrophobic groups in its structure. On the other hand, linen showed an inconsistent behavior in that it had the highest biodegradability in the soil burial test, but a lower biodegradability than that of cotton in the activated sewage sludge test. XRD analysis revealed that there was a slight increase in the crystallinity of linen, cotton, and rayon fabrics at the initial stage, but a continuous decrease thereafter. From the correlation analysis, it was revealed that the biodegradability of cellulose fabrics was closely related to the moisture regain of the fibers, which reflects the hydrophilicity and internal structure of the fibers at the same time. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 248–253, 2004

Key words: biodegradable; enzymes; fibers; strength; X-ray

INTRODUCTION

When textiles are buried in soil, soil-resident microorganisms take part in the degradation of textile materials, which is called biodegradation, and the biodegradability is often used as a standard measurement for the environmental friendliness of textile products.

The biodegradability of textiles is expected to be influenced by such factors as crystallinity, degree of orientation, the degree of polymerization, hydrophilicity/hydrophobicity of textile materials, condition of soils where materials are buried, and the species of microorganisms. Previous studies[1–4] about the biodegradability of polymers have shown greater biodegradability in polymers of lower molecular weight, lower crystallinity or orientation, and higher hydrophilicity.

Cotton and linen fibers have three hydroxyl groups (–OH) in repeating groups of the molecules, and also are known to have relatively high crystallinity and orientation. On the other hand, regenerated cellulose fibers such as rayon and acetate have lower crystallinity and a more amorphous region. Rayon is also highly hydrophilic, like most of the cellulose fibers, but acetate is less hydrophilic than other cellulose fibers because of the substitution of acetyl groups (–$COCH_3$) for some of the hydroxyl groups in the molecules.[5,6]

Cellulose fibers, widely used as various textile products, have been thought to be environmentally friendly fibers in the sense that they are known to be readily degraded by soil microorganisms when they are buried. However, all cellulose fibers are not characterized by the same biodegradable behavior because of the differences in chemical and physical characteristics. Cotton, linen, rayon, and acetate all contain celluloses but differ in chemical compositions, crystallinity, the degree of polymerization, and manufacturing processes. In addition, each fibrous material has different noncellulose content and composition.[5] All these differences would influence the degradation behavior of cellulose fibers, resulting in different biodegradabilities.

Biodegradability of cellulose fibers, as in other textile materials, could be measured by soil burial test, activated sludge test, and enzymatic hydrolysis test. In 1960–1970, a number of studies were conducted on textile biodegradation, using various microorganisms, by Bati and Bloch,[16] Meyers and Scott,[17] and Langvad.[18] Charpentier[19] used the soil burial test in a study of textile biodegradation. However, little study was done on the evaluation of cellulose biodegradability as an overall evaluation method for the environmental friendliness of textile products.

Correspondence to: C. Park.
Contract grant sponsor: Korea Science and Engineering Foundation; contract grant number: R01-1999-00194.

Journal of Applied Polymer Science, Vol. 94, 248–253 (2004)

TABLE I
Specification of Specimens

Fiber	Yarn type	Yarn number		Yarn count (5×5 cm^2)		Weight (g/m^2)	Thickness (mm)	Weave construction
		Weft	Warp	Weft	Warp			
Linen	Staple	25Lea (66tex)	25Lea (66tex)	180	172	250 ± 5	0.63	Plain
Cotton	Staple	20tex	20tex	141	135	100 ± 5	0.29	Plain
Rayon	Filament	13tex	13tex	175	109	75 ± 5	0.19	Plain
Acetate	Filament	11tex	11tex	228	151	83 ± 5	0.13	Plain

The biodegradation process of textiles is profoundly affected by the environment where microorganisms exist, which makes it difficult to standardize the test method. Therefore, we will need an overall investigation of biodegradation data resulting from various test methods to determine the environmental friendliness of textile products.[20] Moreover, we lack the information regarding the structural changes of cellulose fibers occurring in the degradation process, where the changes in chemical composition or physical characteristics are expected to take place.

Therefore, the biodegradability of cellulose fibers was measured by various test methods such as the soil burial test, activated sludge test, and enzymatic hydrolysis test, after which the degradation behaviors based on these test methods were compared. Changes in the internal structure of samples were examined by X-ray diffraction (XRD) according to the biodegradation time. In addition, this study is expected to provide basic information for the research about the environmental friendliness of cellulose-made textile products.

EXPERIMENTAL

Specimens

The specimens were cotton, rayon, and acetate standard test fabrics prescribed in KS K 0905 (Korean Standards Association, Seoul, Korea). Linen was obtained at the market (Table I).

Chemicals

The enzyme used for hydrolysis test was cellulase from *Trichodema viride*. The chemicals used for the tests were extra pure or premium grades.

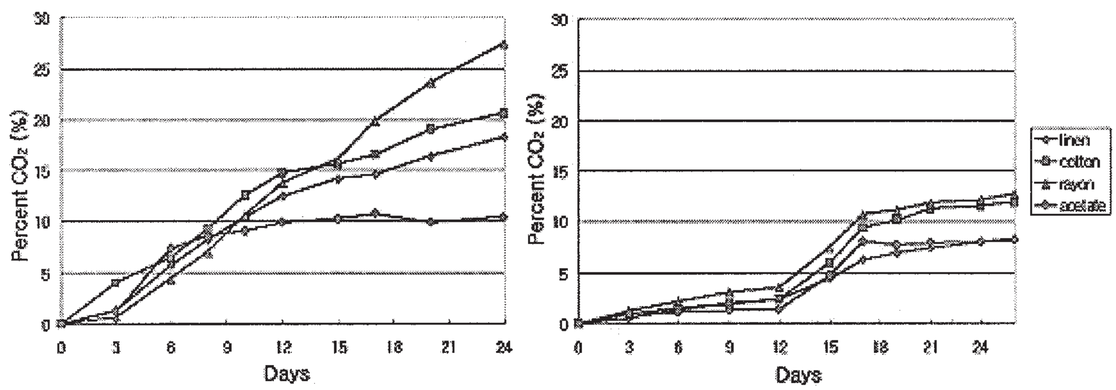
Methods

Evaluation of biodegradability

Activated sludge test[15]. Relative biodegradability in the activated sludge test was estimated from the ratio of the actual amount of carbon dioxide evolved to the theoretical amount of carbon dioxide to be evolved, according to ASTM D 5209-92. Carbon dioxide evolved (in mg) was obtained by titration with 0.05N HCl. Percentage carbon dioxide evolved is calculated as follows:

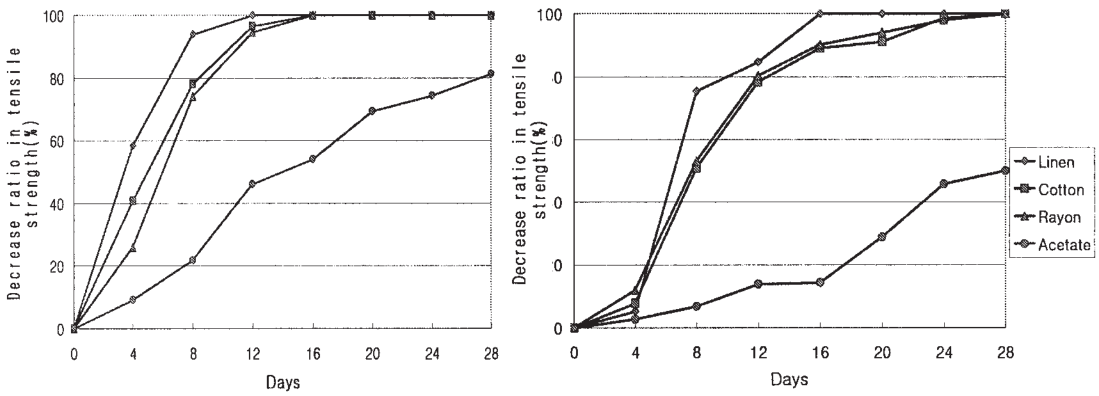
$$\text{Precentage } CO_2 = \frac{\text{mg } CO_2 \text{ produced}}{\text{mg } CO_2 \text{ theoretical}} \times 100$$

$$= \frac{1.1 \times \text{mL HCl} \times 12}{44 \times \text{total carbon of specimen}} \times 100$$



(A) (B)

Figure 1 Biodegradability by percentage CO_2 from activated sludge test. [Experimental period: (A) August 17 to September 10; (B) November 2–28.]



(A) (B)

Figure 2 Biodegradability from decrease ratio in tensile strength of soil burial test. [Experimental period: (A) August 8 to September 5 (average temperature: 26.5–22.5°C); (B) September 20 to October 23 (average temperature: 7.0°C).]

Soil burial test[14]. According to AATCC Soil Burial Method 30-1993, natural soil was used to fill a box to a depth of 11 cm. Each sample was cut into 2.5 × 15 cm pieces, after which the tensile strength of samples was measured; samples were then buried in the soil at 3 cm depth and allowed to degrade for 28 days. During the degradation period, water was supplied at a regular interval to maintain the moisture regain of soil at 25 ± 5%. After degradation, samples were rinsed with distilled water and dried, and the tensile strength of samples was measured. Biodegradability was evaluated from the decreasing rate of tensile strength.

Enzymatic hydrolysis. Specimens (25 mg) and acetate buffer (2 mL; acetic acid/sodium acetate, pH 5.00) were placed in a test tube and 1000 CU (cellulase unit) of cellulase was added. After degradation was allowed to proceed in the mixture in an incubator at 37°C for a specified time, the mixture was filtered through a membrane (0.2 μm thick) and the amount of total organic carbon (TOC) dissolved in the filtrate was measured. Remaining specimens after membrane filtering were passed through a glass filter (No. 3) and dried. The weight loss ratio was calculated using the weight of specimen before enzyme hydrolysis and weight of the remains.

$$\text{Weight loss} = \frac{A - R_s}{A} \times 100$$

where A is the weight of the specimen before enzyme hydrolysis and R_s is the weight of remains after enzyme hydrolysis.

Observation of surface change. After soil burial tests, the surface changes after biodegradation were observed by optical microscopy (magnification ×100; Model EHS204752, Olympus, Osaka, Japan).

Changes of internal structure[13]

The changes in the specimen crystallinity and internal structure as a result of degradation were also investigated by using an X-ray diffractometer (M18XHF-SRA, Mac Science Co., Roswell, GA).

RESULTS AND DISCUSSION

Biodegradability of cellulosic fibers

Biodegradability from activated sludge test

Figure 1(A) and (B) represent percentage CO_2 of cellulose fabrics measured in two different periods by the activated sludge test. Here the percentage CO_2 from the activated sludge test is an index of biodegradability. Rayon showed the highest percentage CO_2, and the amount of CO_2 evaluation decreased in the order of rayon > cotton > linen > acetate. Cotton, despite its great hydrophilicity, showed lower biodegradability than that of rayon because of its higher crystallinity than that of rayon. Linen has a highly crystalline and very well orientated structure, by which microorganisms were hindered from gaining access to the internal region

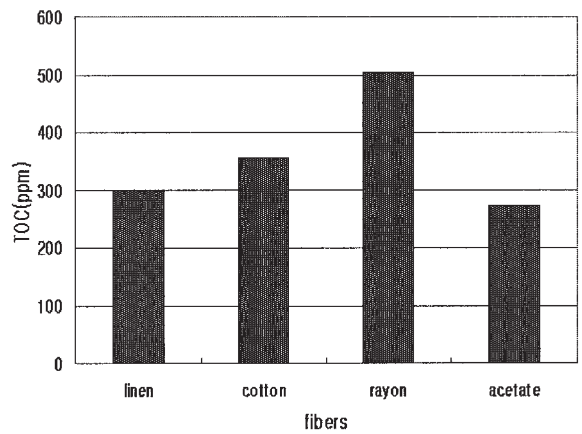


Figure 3 TOC (total organic carbon) of water-soluble compounds produced by enzymatic hydrolysis for 8.5 h (37°C, pH = 5.00).

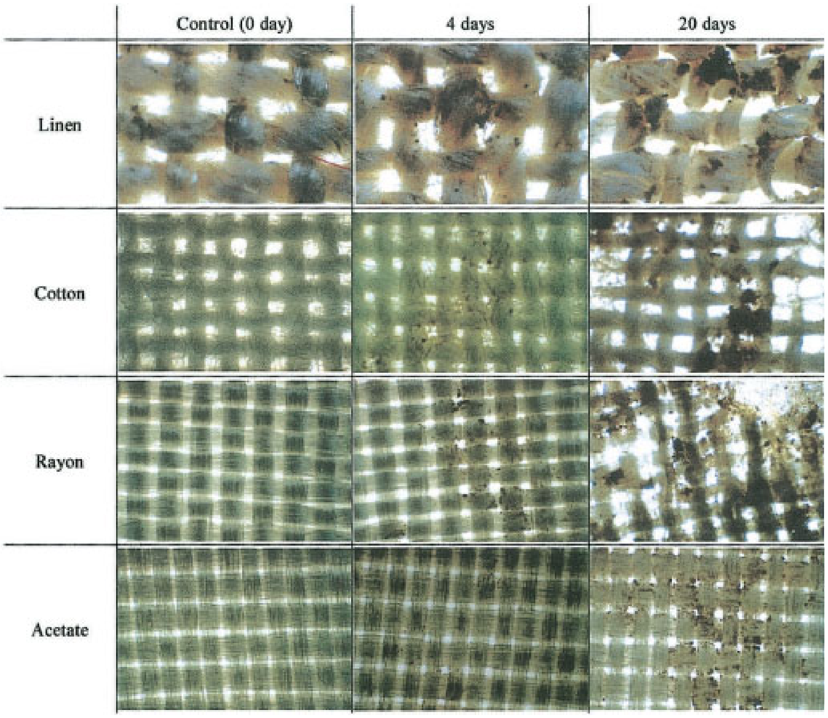


Figure 4 Microscopic photographs of specimens from soil burial test.

of fibers, thus resulting in low biodegradability. Acetate showed the lowest biodegradability, regardless of its low crystallinity, and this could be explained by the fact that quite a few hydroxyl groups in acetate molecules were replaced by hydrophobic acetyl groups.

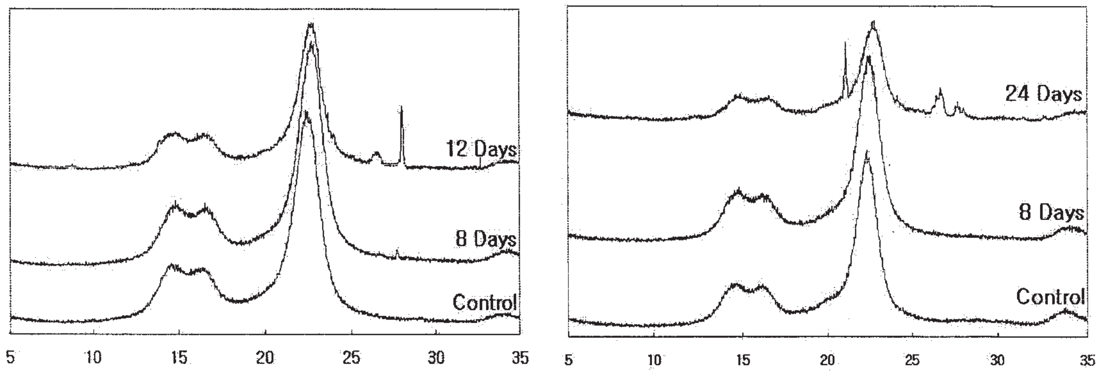
The result from the second experiment [Fig. 1(B)] showed the lower amount of CO_2 evaluation and smaller deviations, even though both experiments were performed at the same temperature (30 ± 2°C). This phenomenon could be explained by the variance in strains and number of microorganisms exiting in sludge, attributed to the difference in the collecting period.

Biodegradability from soil burial test

Decreasing ratio (%) in tensile strength of degraded samples was measured by soil burial test and the results are presented in Figure 2 as an index of biodegradability. In the two sets of repeated experiments, linen showed the highest biodegradability. Acetate, in particular, kept the original shape even after the other sample fabrics were too degraded and dissociated to measure the tensile strengths of fabrics.

The decreasing ratio in tensile strength of samples (except linen), tested by this method, showed a similar trend as that of samples in the activated sludge test. Linen, however, obtained different results from those in sludge test methods, showing the highest biodegradability. Linen became too degraded and damaged to measure tensile strength after 12 days in the first experiment, and after 16 days in the second experiment. This may probably be because linen has the largest portion of noncellulose ingredient, including lignin, which provides a favorable place to break into the internal structure for annelids, arthropods, as well as microorganisms resident in soil. Small animals like earthworms were actually found only from the buried linen.

Results from the first and second experiments showed a similar tendency except in the biodegradation rate, which could be caused by the changes of laboratory conditions, such as temperature and humidity, as the season changes while the experiments were being performed. Microorganisms in soil are generally more active in higher temperature and humidity; therefore the result from the first experiment conducted in summer obtained a higher degradation rate and biodegradability than those from the second experiment performed in winter, during which the temperature and humidity are lower. Of particular interest from the second experiment is that we observed the induction period where biodegradation barely occurred at the initial stage, and a few days later biodegradation started to occur. This induction period was also observed in the activated sludge test. From this phenomenon, we infer that it would take some time for an environment, especially at low temperature, to become prepared for biodegradation favorable to biodegradation.



(A) (B)

Figure 5 X-ray diffraction pattern of specimens: (A) linen; (B) cotton.

Degradability from enzymatic hydrolysis

Total organic carbon (TOC) was measured for the enzymatic solution filtered from the sample residue after being degraded by cellulase for a fixed time. TOC represents the dissolved amount of aqueous organic carbon in a solution; that is, organic materials in water are oxidized to carbon dioxides, and the concentration of carbon dioxides is quantified for the analysis of total carbon concentration. In the enzymatic degradation, insoluble cellulose is degraded into aqueous glucose by cellulase, and this glucose solution can be quantified by TOC. Total organic carbon is determined by the difference between the total carbon (TC) and inorganic carbon (IC) of the measured solution.[20]

TOC values of cellulose samples degraded for 8.5 h by cellulase are illustrated in Figure 3. TOC was the greatest in rayon and the TOC values decreased in the order of rayon > cotton > linen > acetate as in the activated sludge test. Generally, enzyme gains access more easily into the amorphous region than into the crystalline region. Rayon has a relatively greater noncrystalline region than that of other cellulose fibers, and that would be the main reason for the highest degradability of rayon fibers. Cotton and linen, which have almost twice the crystallinity of rayon, showed lower TOC values. Acetate, however, in spite of the lowest crystallinity, showed the lowest enzymatic hydrolysis rate among all of the tested cellulose fibers. This would be attributed to the hydrophobic nature of acetate, in which cellulase has greater difficulty in reaching acetate molecules than in other samples.

Appearance change

Figure 4 shows the microscopic photographs (magnification ×100) of biodegraded specimens by the soil burial test. We were able to observe that microorganisms including fungi appeared on the surface of the fibers with the passing of time.

Linen developed more fungi than other samples and exhibited the most serious shape deformation caused by fiber damage. Cotton and rayon samples also formed quite a few fungi and their shape was changed and damaged as burial time developed. Acetate showed the least amount of fungi formed and the least shape deformation as time passed because of its slowest rate of degradation.

Changes of internal structures with degradation time

Figure 5 represents the XRD curves according to soil burial time lapse, and Table II shows the crystallinities calculated from the quantitative analysis[11] through simple indices. It was observed for linen and cotton that the major crystalline peak, which appeared around $2\theta = 22.8$ by cellulose crystalline plane 002, went higher as degradation time developed and then became lower again after a certain period of time (Fig. 5); that is, crystallinity increased at the initial stage and then decreased again as time elapsed (Table II). When biodegradation progresses, disordered noncrystalline region in the internal cellulose fiber would be the first target for soil microorganisms, thus increasing the crystallinity. Af-

TABLE II
Crystallinity of Specimens from Soil Burial Test

Specimen	Control	4 days	8 days	12 days	16 days	20 days	24 days
Linen	73.7	77.8	76.4	77.6	—[a]	—[a]	—[a]
Cotton	71.8	75.8	72.8	70.1	70.0	68.6	65.9

[a] X-ray diffraction curve for crystallinity could not be produced because of severe damage in shape and degradation.

TABLE III
Correlation Coefficients Between Biodegradabilities and Properties of Specimens

		Crystallinity	Moisture regain	Cellulose content
Biodegradability by activated sewage sludge test (1st)	Pearson's coefficient of correlation	0.038	0.879	−0.131
	Level of significance (both sides)	0.962	0.121	0.869
Biodegradability by activated sewage sludge test (2nd)	Pearson's coefficient of correlation	−0.100	0.704	−0.412
	Level of significance (both sides)	0.900	0.296	0.588
TOC by enzyme hydrolysis	Pearson's coefficient of correlation	−0.344	0.956[a]	0.054
	Level of significance (both sides)	0.656	0.044	0.946

[a] The coefficient of correlation is meaningful at the 0.05 level (both sides).

ter the amorphous region has been decomposed, microorganisms will attack the crystalline part. That can explain why the crystallinity increased relatively at first, and then decreased as degradation progressed.

Factors influencing biodegradabilities

The correlation was examined between actual biodegradability data and properties of specimens that were presumed to affect biodegradability. The correlation analysis was performed using SPSS statistical analysis program and the results are presented in Table III. Based on the results from correlation analysis, moisture regain—as the property inclusive of crystallinity and hydrophilicity—appeared as the most influential factor on the biodegradabilities in this study. Crystallinity was exhibited to be negatively correlated, especially in the enzyme hydrolysis.

CONCLUSIONS

In this study, we investigated the boidegradabilities of cellulose fabrics by various test methods such as activated sewage sludge test, soil burial test, and enzyme hydrolysis. The external appearance of samples was observed by microscope with the progress of degradation time. We also analyzed the changes of internal structure from X-ray diffraction patterns.

1. The biodegradability (activated sewage sludge test, soil burial test, and enzyme hydrolysis) was greatest in rayon, which was followed by cotton $>$ acetate, in decreasing order. Linen, however, showed inconsistent behavior. Although showing the greatest biodegradability in the soil burial test, linen exhibited lower biodegradability than that of rayon and cotton in other tests.
2. From the microscopic observations, we observed that the colors of the specimen surface turned brown and black as a result of the action of microorganisms.
3. Results from X-ray analysis revealed that crystallinities of linen and cotton increased slightly at the beginning, but decreased continuously thereafter.
4. From the correlation analysis between the properties of cellulose fibers and the biodegradabilites, moisture regains and biodegradabilities were represented to be most closely correlated.

This work was supported by Grant R01-1999-00194 from the interdisciplinary research program of the Korea Science and Engineering Foundation.

References

1. Park, Y. H. J Korean Fiber Soc 1991, 28, 9.
2. Kim, I. B.; Lee, M. C.; Seo, I. S.; Shin, P. K. Polymer (Korea) 1995, 19, 727.
3. Doi, Y.; Fukuda, K. Biodegradable Plastics and Polymers; Elsevier: Amsetrdam, 1994.
4. Park, T. K. Lucky Polym Tech 1994, 31, 7.
5. Young, R. A.; Rowell, R. M. Cellulose—Structure, Modification, and Hydrolysis; Wiley–Interscience: New York, 1986.
6. Kennedy, J. F.; Philips, G. O.; Wedlock, D. J.; Williams, P. A. Cellulose: Its Derivatives, Chemistry, Biochemistry and Applications; Ellis Horwood: Chichester, UK, 1985.
7. Park, H. S.; Kim, Y. H. J Korean Fiber Soc 1991, 28, 102.
8. Jo, G. J.; Bae, S. Y.; Lee, M. C.; Kim, H. W.; Park, P. K.; Wakida, T. J Korean Fiber Soc 1998, 35, 362.
9. Kim, S. R. J Korean Fiber Soc 1979, 16, 53.
10. Bae, S. Y.; Lee, M. C.; Shin, I. K.; Kim, M. H. J Korean Fiber Soc 1996, 33, 403.
11. Patil, N. B.; Dweltz, N. E.; Radhakrishnan, T. Text Res J 1962, 32, 460.
12. Chidambareswaran, P. K.; Sreenivasan, S.; Patil, N. B. Text Res J 1979, 49, 493.
13. Chidambareswaran, P. K.; Sreenivasan, S.; Patil, N. B. Text Res J 1987, 57, 219.
14. AATCC Technical Method 30-1993. American Association of Textile Chemists and Colorists: Research Triangle Park, NC.
15. ASTM D 5209-91. Annu Book ASTM Stand 1991, Part D12, Annex 10.
16. Bati, M.; Bloch, M. Chem Abstr 1970, 72, 131115a.
17. Meyers, P.; Scott, E. Chem Abstr 1969, 70, 103903w.
18. Langvad, F. Chem Abstr 1970, 72, 106974x.
19. Charpentier, M. Chem Abstr 1969, 70, 19215r.
20. Kim, E. Y.; Park, C. H. J Korean Soc Clothing Text 2001, 25, 1270.