Biodeterioration of Coated Nylon Fabric

D. K. SETUA, G. D. PANDEY, R. INDUSEKHAR, G. N. MATHUR

Defence Materials & Stores Research & Development Establishment, P. O. DMSRDE, G. T. Road, Kanpur 208013, India

Received 9 September 1998; accepted 22 October 1998

ABSTRACT: Biodegradation characteristics of nylon fabric coated with fluorocarbon polymer (oil and water repellent) and thiourea-formaldehyde (fire retardant) were studied. The fabric was exposed to soil burial, air exposure, and standard culture media for various intervals of time and evaluated for changes in physicomechanical properties, oil and water repellency, air permeability, as well as flame-retardant properties. Significant falls in these properties were observed, the extent of which was found to be maximum in the case of soil burial followed by air medium and standard culture. Themogravimetric analysis showed enhanced heat stability of the unexposed fabric compared with base nylon. Exposure of the coated fabric to various biomedia caused extensive damage of the fire retardant material and also resulted in a significant reduction in the flame-resistant properties. Fluorocarbon material, on the other hand, did not degrade on bioexposure and its presence improved the thermal stability of the coated fabric. Fourier transform infrared spectroscopy showed remarkable changes, e.g., peak shifts, intensity variations, as well as elimination of peaks in the case of soil burial compared with the unexposed sample. Scanning electron microscopy was used to investigate the changes in the surface topography associated with the degradation of the coated fabric vis-à-vis those of the controlled one. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 685–691, 2000

Key words: biodegradation; coated fabric; thermogravimetric analysis; infrared spectroscopy; scanning electron microscopy

INTRODUCTION

A wide range of textile materials are used as substrates for coated fabrics. Common types of fiber used are cotton, rayon, nylon, polyester, and blends of polyester with cotton or rayon. Coated nylon fabric finds extensive usage in the development of various types of clothing outfits for extraordinary service conditions. Strategic applications require specialized coating materials and techniques to modify the base fabric and to impart flame retardancy, oil and water repellency, as well as sufficient air permeability. To date efforts have been centered mainly on the studies of various types of coating materials, nature of coating-substrate adhesion, and physical property evaluations for various coated fabrics based on nylon, polyester, cotton, etc.[1–10] However, thus far no study has been made on the biodeterioration of these fabrics, which is of paramount importance especially for such critical applications.

Studies on the weathering and degradation behavior of both natural and synthetic fibers and fabrics have been reported by Ross.[11] However, attempts to correlate outdoor exposure to weather-o-meter tests have not been very successful. The degradation of fabric was also reported to be prevented by application of a protective coating.[5,12] The critical parameters that control degradation were observed to be coating thickness (the thicker the coating, the larger is the protec-

Correspondence to: D. K. Setua.

Journal of Applied Polymer Science, Vol. 75, 685–691 (2000)
 CCC 0021-8995/00/050685-07

tion), presence of ultraviolet stabilizer and fungicides in the coating composition, different climatic conditions, and presence of pollutants. Discoloration because of microbiological attack on polyvinyl chloride coated fabric has been studied by Eichert.[13] The organisms for study were *Aspergillus niger, Penicillium funiculosum, Paecilomyces varioti, Trichoderma longibrachiatum,* and *Chaetomium globosum*. Profuse growth was observed on coated fabric without fungicide but no growth was seen on uncoated fabric and coated fabric with fungicide. The mechanical properties (tensile strength and tear strength) of the infected fabric, however, did not show any change despite discoloration. Eichert[14] has also studied the yellowing of polyvinyl on chloride coated fabric caused by weathering by measurement of the light transmission properties of different coating formulations.

A vast amount of literature exists on the degradation characteristics of archeological textiles, e.g., cotton, linen, wool, flex, and hemp fiber. Jakes and Angel,[15] Jakes and Mitchell,[16] and Schweger and Kerr[17] have described the methods of determination of elemental composition and crystalline contaminants in cotton. Batzer and colleagues,[18] and Janaway[19] have reported on chemical and physical analysis of recovered cotton after laboratory soil burial test. Studies have also been reported on wear and damage in modern textiles using a differential staining technique in light microscopy[20] and scanning electron microscopy.[21,22] However, these studies are focused mainly on the fiber fracture patterns. More systematic study on the changes in the physicomechanical, morphology, and functional properties associated with the decay of the coated fabrics in various bioexposures, e.g., soil burial, aerial exposure, and standard culture media is lacking. This is partly because of the inability of traditional methods to analyze property changes at the micro-level as well as the inherent limitation of the samples which are translucent and often contaminated in these bioexposures.

In this article we report on our studies on the biodegradation characteristics of coated nylon fabric currently being used in protective clothing for services. The microbial degradation of nylon is accomplished through the action of enzymes, highly specific in nature, and their ability to catalyze biochemical processes rapidly under physiological conditions.

EXPERIMENTAL

Coated nylon fabric (95 g/sq m; Kusumgar Corporates, Mumbai, India) containing 10–14% of fire retardant (FR; LN Chemicals, Mumbai, India) material (thiourea-formaldehyde, molar ratio 1:2) and 1% fluorocarbon (FC) polymer (Scotchgard FC-232 of 3M, St. Paul, MN) was obtained from the trade.

Strips of the fabric were exposed to a soil bed (prepared in the laboratory and highly rich with degrading bacteria and fungi), aerial exposure, and standard culture medium (containing *Aspergillus niger, Aspergillus terrus, Aureobasidium pullulans, Paecilomyces varioti, Penicillium funiculosum, Penicillium ochrochloron, Scopulariopsis vicaulis,* and *Trichoderma veride*) for different intervals, e.g., 30, 60, and 90 days in the temperature range between 30 and 40°C and relative humidity of 60 to 90%. To distinguish between the deterioration caused by microorganism or chemical processes involved during exposure of the fabric, especially in the soil burial case, a control soil test was also designed for similar duration, pH, water content, etc. The heat sterilization of the soil was performed by heating the soil at 600°C in an oven for 1 h followed by keeping it in a laboratory autoclave operated at a steam pressure of 15 psi. Above atmospheric pressure, which corresponds to a temperature of 120°C, even bacterial spores that survive several hours of boiling are rapidly killed at 120°C.[23]

After exposure, the samples were taken out, cleaned with water, dried, and weight losses in each case were recorded. The samples were then tested for their physical properties, e.g., breaking strength (as per the ASTM D 1682-64) and tear strength (as per ASTM D 2261-83), water repellency (as per IS 5914, 1970), and air permeability (as per IS 11056, 1984) along with the control (unexposed) specimens. All the specimens were subjected to the vertical flammability test as per BS 3119, 1959. The specimen of size (50.8 mm $\times$ 300 mm) and thickness up to 0.2 mm was exposed to an open flame for 10 s; the flame was then removed and flammability characteristics of the material were determined as follows:

1. After flame: The length of time for which the material continued to flame after the ignition source was removed.
2. Afterglow: Afterglow was the time for which the material continued to glow, i.e.,

Table I Physicomechanical Properties of the Fabric

		Control Soil (No. of Days)	Soil Burial (No. of Days)			Aerial Exposure (No. of Days)			Standard Culture (No. of Days)
Property	Unexposed	90	30	60	90	30	60	90	30
Breaking strength (Kgf)									
Warp	89.3	88.7 (99.3)	84.3 (94.4)	80.3 (89.9)	78.3 (87.6)	87.0 (97.4)	85.0 (95.1)	83.0 (92.9)	89.0 (99.6)
Weft	54.7	53.4 (97.6)	50.3 (92.0)	47.7 (87.2)	46.0 (84.1)	52.6 (96.2)	50.3 (92.0)	47.0 (85.9)	52.0 (95.1)
Tear strength (Kgf)									
Warp	1.6	1.5	1.4	1.2	1.1	1.5	1.5	1.3	1.6
Weft	1.3	1.2	1.1	0.8	0.7	0.8	0.8	0.8	1.0
Weight (g/sq m)	96.0	94.0	92.0	92.4	93.2	91.0	91.0	91.2	91.9

Values in the parenthesis indicate percent retention of properties after bioexposure.

absence of flaming but with the emission of light from the combustion zone.

3. Char Length: This provided the maximum extent of damage or charring of the material measured in the vertical direction, ignoring any surface effect such as scorching or smoke deposition.

The oil repellency was determined as follows. A test specimen 25 mm wide and 250 mm in length with the major axis parallel to the machine direction was placed over a Whatman no. 1 filter paper covering a 28-mm diameter cylindrical mandrel and a load of 50 ± 5 g attached to each end of the specimen. A drop weighing 4 ± 1 mg of diethyl phthalate colored with CI dispersed red 11 (e.g., serisol brilliant red X 3 B), was allowed to fall through 5 mm onto the upper surface of the specimen. At the end of 6 h, the specimen was carefully removed and the filter paper was examined for penetration of dyed liquid.

The themogravimetric analysis (TGA) analyses were performed in a TA Instruments Inc., (USA) 2950 model thermogravimetric analyser from room temperature (30 ± 2°C) to 800°C at a heating rate of 50°C/min in nitrogen atmosphere (flow rate 60 mL/min).

A JEOL JSM-35 CF scanning electron microscope was used to analyze the changes in the surface topography and extent of biodegradation of the protective coating in different samples. Before scanning electron microscopy (SEM) observation, the surfaces were thoroughly vacuum cleaned and gold coated without touching the surface and stored in a desiccator. Details of the sample preparation technique have been reported elsewhere.[24,25]

Fourier transform infrared spectroscopy (FTIR) studies were conducted in a Nicolet Magna-750 IR spectrometer on the unexposed (FC/FR treated) and soil buried fabrics using the variable attenuated total reflectance technique often used for opaque samples.

RESULTS AND DISCUSSIONS

Physicomechanical properties of the coated fabric both before and after exposure to different biomedias are appended in Table I. The primary factors responsible for biodegradation were the bioagencies (fungi and bacteria), temperature, and humidity. Microorganisms caused degradation of the coating chemically by catalytic hydrolysis in the presence of enzymes which also penetrated into the threads of the fabric and caused mechanical damage. Strength properties, therefore, were reduced and maximum extent of fall was observed in the case of soil burial, which was then followed by aerial exposure and standard culture. The percentage of retention of breaking strength was also decreased with the increase in exposure duration and in the warp direction the values were always more than in the weft direction. This might be attributed to the higher warp texture and crimp in this weaving direction. Tear strength greatly depends on the extent to which fabric structure allows yarn bunching during tearing, the individ-

Table II Functional Properties of the Fabric

Property	Unexposed	Control Soil (No. of Days)	Soil Burial (No. of Days)			Aerial Exposure (No. of Days)			Standard Culture (No. of Days)
		90	30	60	90	30	60	90	30
Oil repellency rating[a]	9	9	0	—	—	0	—	—	4
Water repellency (spary rating no.)	90	80	50	—	—	50	—	—	50
Air permeability (cc/cm^2/s) at 1 cm water head (test area 5.07 sq cm)	43.0	42.5	40.19	36.49	34.02	42.08	40.43	38.36	40.24
Flammability characteristics: after flame, s, afterglow, s, char length, cm	NIL	NIL	Support flame vigorously and char length reduced to less than 50% in 3 s			Support flame vigorously and char length reduced to less than 50% in 4.5 s			Support flame vigorously and char length reduced to less than 50% in 5 s

[a] Minimum number out of 10 specimens showed no penetration.

ual yarn strength, and type of coating. Likewise, the breaking strength, tear strength also reduced with an increase in the exposure time.

The effect of bioexposures on functional properties, e.g., flame retardancy, water and oil repellency, and air permeability are shown in Table II. The oil repellency of the coated fabric was abruptly reduced within 30 days of bioexposures and the effect was more pronounced in the cases of soil burial and aerial exposure than in standard culture. This was attributed to less severity of the standard culture test. The water repellency of the

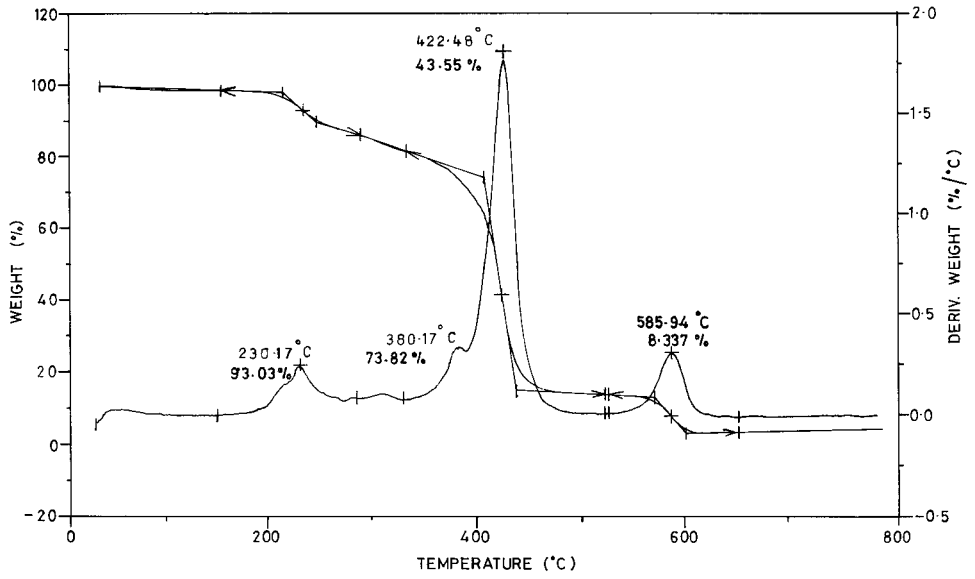

Figure 1 TGA plots of the unexposed fabric.

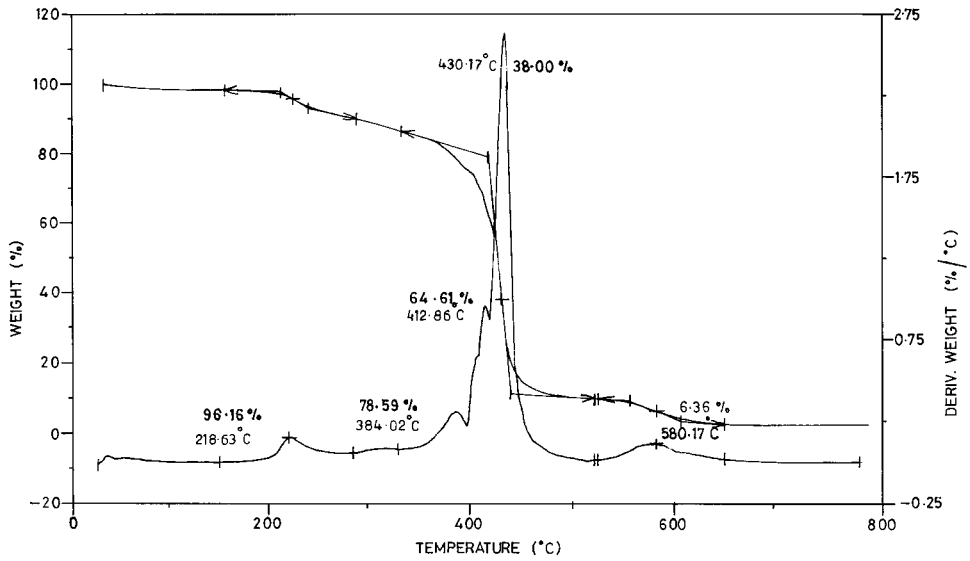

Figure 2 TGA plots of the soil buried fabric.

samples, assessed by a spray-rating test, which simulated slight rainfall, was also not satisfactory because practically complete wetting of the whole of the face occurred within the time frame as above. Air permeability, a parameter that is purely dependent on yarn structure as well as fabric structure and cloth cover also reduced with the extent of biodeterioration of the protective coating under varied test conditions. As expected, because of fragmentation of the flame-proof coating on bioexposures, the exposed fabric always experienced a severe fall in flame retardancy.

Marginal fall in both physicomechanical properties (Table I) as well as functional properties (Table II) of the fabric caused by exposure in control sterile soil indicates preponderance of biological deterioration over chemical deterioration.

TGA plots of the unexposed fabric (Fig. 1) showed characteristic decomposition peaks, one at 230°C and another at 380°C due to FR and at 586°C due to FC in addition to the peak at 422°C for the base nylon. It was apparent that thiourea-formaldehyde (FR) degraded much earlier compared with nylon and probably caused an increase in the heat stability of the coated fabric because of formation of an inflammable and infusible mass on top of the fabric that acted as a barrier to heat damage. Presence of fluorocarbon polymer, which

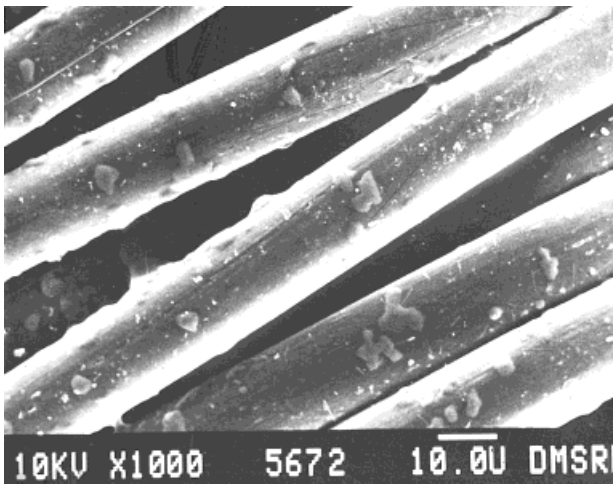

Figure 3 SEM photograph of the surface of the unexposed fabric.

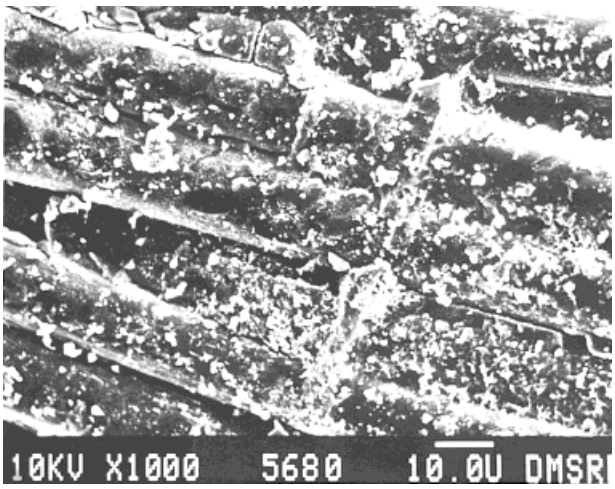

Figure 4 SEM photograph of the surface of the fabric after soil burial test.

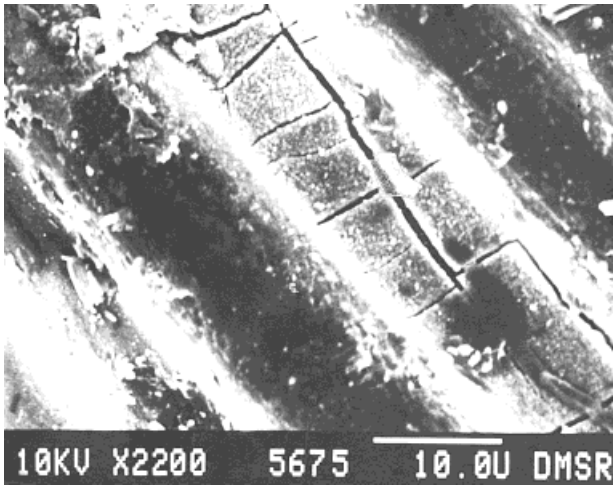

Figure 5 SEM photograph of the surface of the fabric after aerial exposure.

was much more heat stable, further enhanced the heat-resistance properties but marginally because its concentration (1%) was comparatively less than FR (14%). Bioexposures of the fabric caused extensive damage of the surface coating and resulted in a substantial decrease in the flame-retardant properties. Figure 2 shows the TGA plots of the sample exposed to soil burial. The initial decomposition temperature of FR was reduced from 230 to 218°C. The base fabric also underwent biodegradation which resulted in formation of an additional peak at 412°C. The degradation pattern was changed altogether and a higher weight loss was recorded in the decomposition range between 384 to 430°C.

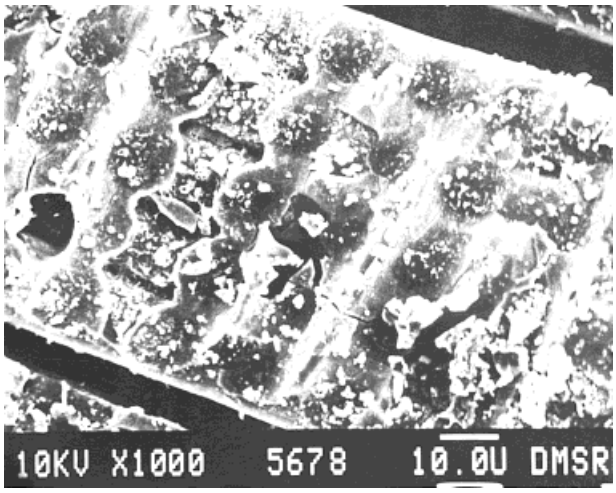

Figure 6 SEM photograph of the surface of the fabric after standard culture test.

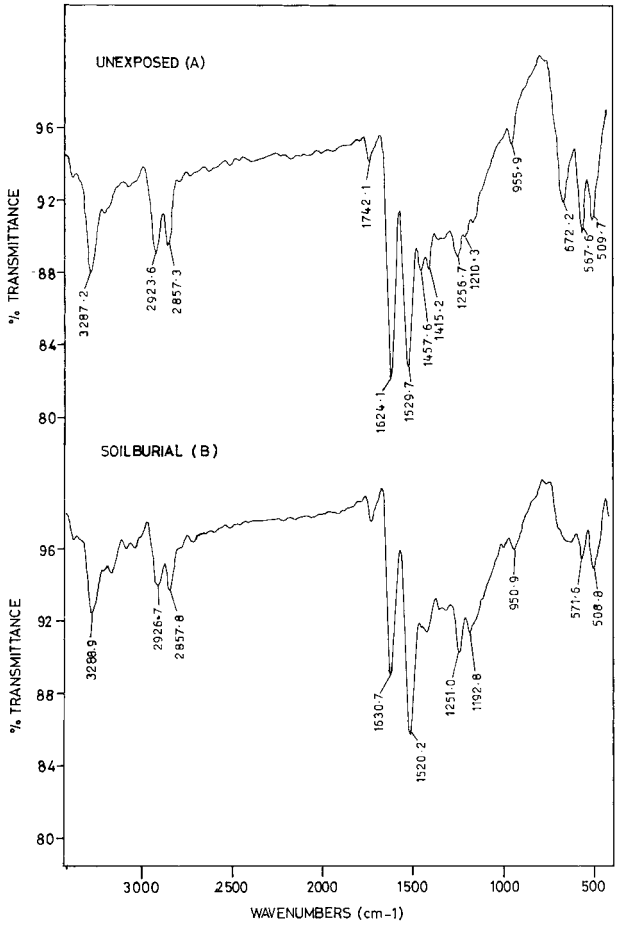

Figure 7 FTIR spectra of the unexposed (A), and soil buried fabrics (B).

Figure 3 is the SEM photograph of the surface topography of the unexposed fabric. Fabric yarns were found to be coated with a film of FC/FR chemicals bearing small inhomogeneities at a few places where some scattered blisters were observed because of preferential coagulation of the crosslinked polymers. Figures 4 to 6 are the SEM photographs of the surface of the bioexposed samples. The samples that underwent the soil burial test for 30 days showed complete deterioration of the coating material and formation of debris (Fig. 4). An aerial exposed sample showed brittle failure with branching of the cracks in channels (Fig. 5). The extent of damage was, however, less in the case of the standard culture where the surface showed formation of agglomerates of the fragmented products (Fig. 6).

Figure 7(A and B) are the FTIR spectra of the surface of the unexposed and soil burial (30 days) samples respectively obtained by using the attenuated total reflectance technique. Decomposition

of FR materials during bioexposure and removal of small fragmented products along with polymeric FC during cleaning of the fabric with water after exposure resulted in marked changes in the spectra. Elimination of several peaks, e.g., at 672, 1415, and 1457 cm^{-1} as well as intensity alterations for the pair of peaks at 509 and 567 cm^{-1}, and also at 1529 and 1624 cm^{-1} [compare Figs. 7(A,B)] were clearly evident. Besides the above, Figure 7B also showed peak shifts in almost all the cases in the region between 1630 to 500 cm^{-1}.

CONCLUSIONS

1. Protective nylon clothing containing fluorocarbon and fire-retardant additives is susceptible to biodegradation.
2. Exposure to soil burial has been found to be the most damaging, which is then followed by aerial exposure and standard culture.
3. The combination of thermogravimetric analysis, FTIR, and SEM techniques have been demonstrated to be reliable methods for characterization of biodeterioration of coated textiles.

REFERENCES

1. Smith, W. C. J Coated Fabrics 1986, 15, 180.
2. Haddad, R. H.; Black, J. D. J Coated Fabrics 1986, 16, 123.
3. Wypych, J. Polymer Modified Textile Materials; Wiley Interscience: New York, 1988.
4. Dartman, T.; Shishoo, R. J Coated Fabrics 1993, 22, 317.
5. Eichert, U. J Coated Fabrics 1994, 23, 311.
6. Eichert, U. J Coated Fabrics 1994, 24, 20.
7. Wilkinson, C. L. J Coated Fabrics 1996, 26, 45.
8. Lukas, D.; Glazyrina, E.; Pan, N. J Text Inst 1997, 88, 149.
9. Bourbigot, S.; Richardcampisi, L.; Le Bras, M.; Delobel, R. J Text Inst 1997, 88, 64.
10. Horrocks, R.; Kandola, K. J Coated Fabrics 1997, 27, 27.
11. Ross, J. H. In Environmental Effects on Polymeric Materials; Rosa, D. V.; Schwarz, R. T., Eds.; Interscience: New York, 1968; Vol. I & II.
12. Drummheuer, W. J Coated Fabrics 1983, 13, 108.
13. Eichert, U. J Coated Fabrics 1994, 24, 77.
14. Eichert, U. J Coated Fabrics 1994, 24, 107.
15. Jakes, K. A.; Angel, A. In Determination of Elemental Distribution in Ancient Fibers, Archeological Chemistry IV; Allen, R. O., Ed.; ACS Symposium Series 220; American Chemical Society: Washington, DC, 1998; pp. 451–464.
16. Jakes, K. A.; Mitchell, J. C. JAIC 1992, 31, 343–353.
17. Schweger, B. F.; Kerr, N. Textiles collected during the temporary exhumation of a crew member from the Third Franklin Expedition: Findings and analysis 1987; J IIC-CG, 12, 9–19.
18. Batzer, A.; Dokkedal, L.; Jensen, E. S. Moseforsog med nature plantefarvede stofprover, Tekstillhistorisk Forsograpport; J.nr. 10/72; Historisk-Arkaeologisk Forsogscenter Lejre, 1983.
19. Janaway, R. C. In Evidence Preserved in Corrosion Products: New Field in Artifact Studies; Janaway, R. C.; Scott, B., Eds.; Occasional Papers 8. UKIC: London, 1989; 8; pp. 21–29.
20. Clegg, G. G. J Text Inst 1949, 40, T449–480.
21. Hearle, J. W. S.; Lomas, B.; Cooke, W. D.; Duerden, I. J. Fiber Failure and Wear of Materials; Ellis Horwood: Chichester, 1989.
22. Zeronian, S. H.; Alger, K. W.; Ellison, M. S.; Alkhayatt, S. M. Studying the Cause and Type of Fiber Damage in Textile Materials by Scanning Electron Microscopy, Historic Textile and Paper Materials; Needles, H. L.; Zeronian, S. H., Eds.; ACS Symposium Series 212; American Chemical Society: Washington DC, 1989; pp. 95–109.
23. Stanier, R.Y.; Adelberg, E. A.; Ingraham, J. L.; Wheelis, M. L. In Introduction to the Microbial World; Stanier, R. Y., Ed.; Prentice-Hall: New York, 1979.
24. Setua, D. K.; De, S. K.; Dhindaw, B. K. J Scanning Electron Microscopy, Part III, 1982, 973.
25. Setua, D. K.; De, S. K. J Mater Sci 1983, 18, 847.