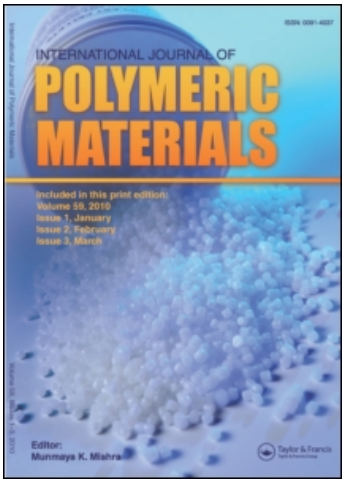

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Structure of Naturally Coloured Cottons

A. F. Richards[a]; T. Rowe[a]; U. Stankovič Elesini[b]
[a] Faculty of Technology, Bolton Institute, Bolton, UK [b] Department of Textiles, University of Ljubljana, Ljubljana, Slovenia

To cite this Article Richards, A. F. , Rowe, T. and Elesini, U. Stankovič(2000) 'Structure of Naturally Coloured Cottons', International Journal of Polymeric Materials, 47: 4, 549 — 557
To link to this Article: DOI: 10.1080/00914030008031311
URL: http://dx.doi.org/10.1080/00914030008031311

Intern. J. Polymeric Mater., 2000, Vol. 47, pp. 549–557
Reprints available directly from the publisher
Photocopying permitted by license only

Structure of Naturally Coloured Cottons

A. F. RICHARDS[a], T. ROWE[a] and U. STANKOVIČ ELESINI[b,*]

[a] *Bolton Institute, Faculty of Technology, Bolton, UK;*
[b] *University of Ljubljana, Department of Textiles, Snežniška 5, S1-1000 Ljubljana, Slovenia*

(Received 15 December 1998)

Previous work on the morphology of naturally coloured green suggested than that the secondary wall of the fibres consists of alternate layers of cellulose and a waxy organic substance called suberin. The work described in this paper has shown that modern varieties of green cotton do contain a large proportion of suberin. Data from fibre swelling is consistent with alternate layers of suberin and cellulose in the secondary wall. The naturally coloured fibres have a lower tenacity and work of rupture than conventional white fibres although they have an acceptable level of textile properties. The crystallinity of the coloured fibres is lower than for white cotton, but the cellulose has the cellulose I structure, normally found in cotton.

Keywords: Naturally coloured cotton; suberin; physical properties; layers; wide angle X-ray diffraction; cuoxam

1. INTRODUCTION

In the twentieth the major objective in breeding cotton has been to produce heavier yields of finer cotton with a good whiteness. Consequently naturally coloured cotton had almost disappeared over the last 50 years due to the availability of inexpensive dyes and the need to maximise output of cotton from the available land. In the last few years however there has been interest in producing naturally coloured cotton. In theory the potentially polluting dyeing processes can be avoided and such fibres can be regarded as environmentally friendly. Commercially, naturally coloured cotton production in the USA

*Corresponding author.

began in 1988. In 1994 approximately 32.400 hectares of naturally coloured cotton were harvested. Available colours include tan, green, reddish brown, and ivory. Claims have been made that, compared to white cotton, naturally coloured cotton has higher insect and disease resistance and natural wool–like elasticity.

The objective of this research has been to evaluate quantitatively the structural and mechanical characteristics of some American varieties of naturally coloured cottons. Previous workers have described some important differences, which are outlined below, between the structure of naturally green cotton and that of brown or white cottons. One aspect has been to investigate the morphology of new varieties, which are produced by crossing green cotton with a white variety.

Investigations into the structure of naturally coloured cottons are not new. In 1983, Yatsu *et al.* [1] and Smutz *et al.* [2] investigated the structure of green cotton. They found that although brown cottons had a similar structure to white varieties, the green varieties were significantly different. Yatsu *et al.*, suggested that green cotton fibres had a smoother texture and found that they contained 14 to 17% organic solvent extractable material compared to 0.6% for white cotton. When the fibres were stained with the osmium tetroxide (a stain for lipid or fat like materials), the white cotton fibre shows a very thin (0.02 μm) primary wall, while green cotton fibre has a series of concentric rings in the secondary cell wall (Fig. 1). Observing the stained green cotton at higher magnification, they found that each ring consisted of a lamella pattern which was characteristic of a substance termed, suberin (Fig. 1C).

The composition of the aliphatic components of the extracted material from the white and green cottons was determined. The material from white cotton was a normal wax from an esterification reaction of a fatty alcohol and a fatty acid. The material from the green cotton however was formed from the esterification mainly of *w*-hydroxyalcohols with 20 or more carbon atoms. The wax was therefore aliphatic polyester, which was likely to be more resistant to hydrolysis during scouring than a normal cotton wax. The wax in green cotton is termed suberin and contains also some phenolic components, which can link directly to cellulose.

Later in 1993, Schmutz *et al.* [2] identified trans-caffeic acid as the only phenolic component in the wax extracted from the green cotton.

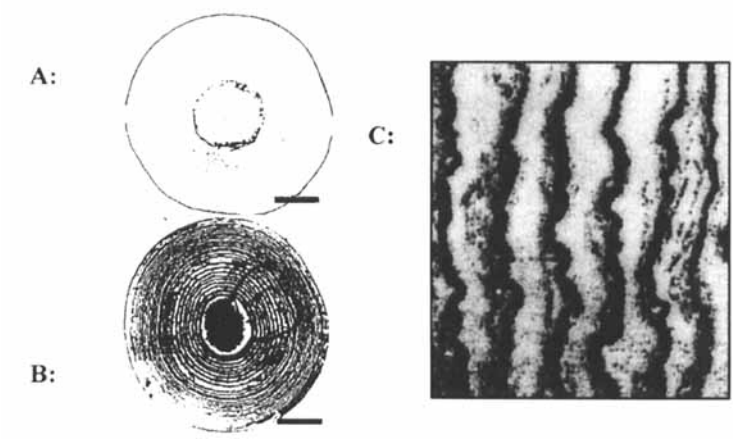

FIGURE 1 Electron micrograph of a transverse section through **A**: an ordinary never-dried white upland cotton fibre, **B**: a never-dried green coloured upland cotton fibre and **C**: electron micrograph of the secondary wall of the green cotton showing the cellulose and the suberin layers [1].

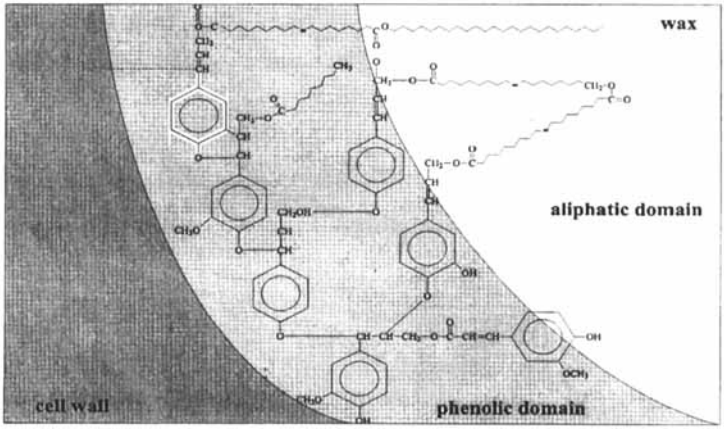

FIGURE 2 Model proposed for the structure of suberin [6].

They suggested that trans-caffeate linked to fatty acids (mainly ω–hydroxy fatty acids) with the ester bonds is involved in anchoring the suberin to the cellulosic secondary wall. Suberin containing mainly bifunctional fatty acids can theoretically form a three-dimensional network in the presence of glycerol. Since glycerol was, found in green cotton but not in white, it was suggested, that the glycerol was

associated mainly to the suberin. As the result, suberin could form a network of polymer molecules. An important conclusion, was that cinnamic-acids derivatives were important for the development of green colour; cinnamic acid derivatives were absent from white fibres. The suggested model for the structure of suberin is shown in Figure 2.

2. RESULTS AND DISCUSSION

2.1. General Fibre Characteristics

Before considering the structure of naturally coloured cottons it is necessary to look at the general characteristics of the fibres themselves. Table I shows the physical characteristics of the fibres as measured by an IIC-Shirley Fineness Maturity Tester. The tensile properties of the fibre samples were measured on an Instron Type 6022; for each cotton sample 25 single fibre measurements were carried out. The results are shown in Table II.

The results show that this sample of green cotton is not only less mature but as a result rather finer than the brown and white cottons. The values for tenacity for all three cotton fibres are low compared with values listed in the literature [3, 4]. One reason may be that a

TABLE I General properties of the cotton samples

	American white cotton	*American brown cotton*	*American green cotton*
Micronaire index	3.7	3.8	2.6
Maturity ratio	0.86	0.84	0.59
Percentage maturity [%]	76.8	74.4	50.8
Fineness [dtex]	1.57	1.65	1.38

TABLE II Tensile properties of the cotton fibre samples; the numbers in brackets represent the coefficient of variation (CV in %)

	White cotton	*Brown cotton*	*Green cotton*
Tenacity [cN.tex^{-1}]	14.33 (34.8)	9.78 (36.9)	9.12 (41.6)
Extension [%]	5.78 (26.6)	4.96 (23.3)	6.18 (25.3)
Specific work of rupture [cN.tex^{-1}]	0.39	0.20	0.25

specimen length of 22 mm was used. According to Meredith [3] the tenacity for cotton fibres increases by 54% when the specimen length is reduced from 10 mm to 1 mm and is doubled when the specimen length is reduced to 0.2 mm. The results show that the green and brown cottons although weaker and having a reduced work of rupture compared with the white cotton, are still adequate for most textile purposes.

2.2. Wax Content

Table III shows the percentage of wax in the cottons as determined by Soxhlet ethanol extraction. After 6 and 24 hours extraction with ethanol, the white and the brown cotton samples have percentages of wax which correlate well with the values quoted in the literature for mature cotton. The percentage of wax is very high for green cotton but it is still lower than that found by Yatsu *et al.* [1]. According to Conrad [4] the wax content of green cotton drops after this cotton is crossed with white cotton. Since the green cotton used in this research has been already crossed with the white cotton with the intention of producing longer, stronger and more mature fibres, this could be the reason for the lower wax content. A significant proportion of the wax in green cotton is only removed from the fibre after extracting with ethanol for 24 hours. This suggests that the wax has a different chemical nature to normal cotton wax.

2.3. Iodine Absorption

The iodine absorption test measures the accessibility of the fibre to the iodine. Thus a totally amorphous fibre would be expected to show a large iodine absorption. In a totally crystalline fibre absorption of the iodine can only take place on the outer surfaces of the crystallites within the fibre. The results are shown in Table IV.

TABLE III Percentage of wax

	Percentage of wax [% by weight]	
Sample	*After 6 hours*	*After 24 hours*
White cotton	0.76	1.24
Brown cotton	0.60	0.82
Green cotton	4.66	5.28

TABLE IV Fibre accessibility (ISV – iodine sorption value)

Sample	*ISV* [*mg* $I_2 \cdot g^{-1}$ *sample*]		*Degree crystallinity* [%]	
	Raw	*Ethanol extracted*	*Raw*	*Ethanol extracted*
White Memphis	36.3	67.0	91.2	83.7
Brown Cotton	89.8	104.5	78.2	74.7
Green Cotton	81.2	71.3	80.3	82.7

Results show that the white raw cotton has a significantly lower ISV and hence a higher crystallinity than the brown and green cottons. After ethanol extraction, the ISV of the white and the brown cotton increases while in the case of the green cotton, ISV decreases. The raw green cotton has thus a more open and less crystalline structure with more interfibrillar surfaces. The removal of the suberin wax may facilitate the penetration of the iodine reagent into the fibre.

2.4. Fibre Swelling

Cotton fibres are susceptible to swelling agents such as sodium hydroxide and cuprammonium hydroxide (cuoxam). If prior to swelling, the samples are dyed with methylene blue; this gives better contrast between the different parts of fibres and enables the position of the impurities such as pectins and proteins to be seen. When a cotton fibre is swollen with a strong swelling agent, the pressure of the secondary wall causes the rupture of the primary wall and the fibre swells into a characteristic collar or spiral shape. The white fibres show the characteristic collar swelling with little visible internal structure (Fig. 3). However, the green fibres show an unusual swelling with alternate coloured layers which surround the lumen (Fig. 4). The uncoloured layers are undoubtedly attributed to the cellulose of the secondary wall, while the coloured layers are less easy to attribute. These layers considering the conclusions of Yatsu *et al.* [1] could be suberin since other impurities such as proteins and pectins are usually not present in the secondary wall.

2.5. X-Ray Diffraction

The most fundamental method of measuring the crystallinity of a fibre is by X-Ray diffraction. Wide angle X-ray diffraction of the

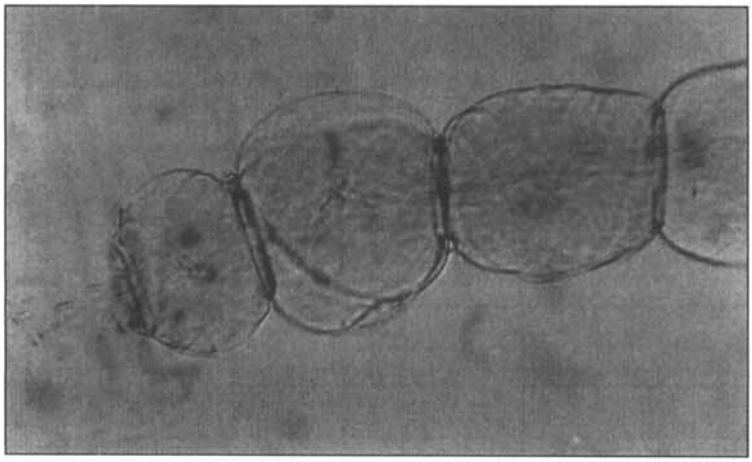

FIGURE 3 White cotton fibres swollen in Cuoxam; optical microscope, mag. 126x.

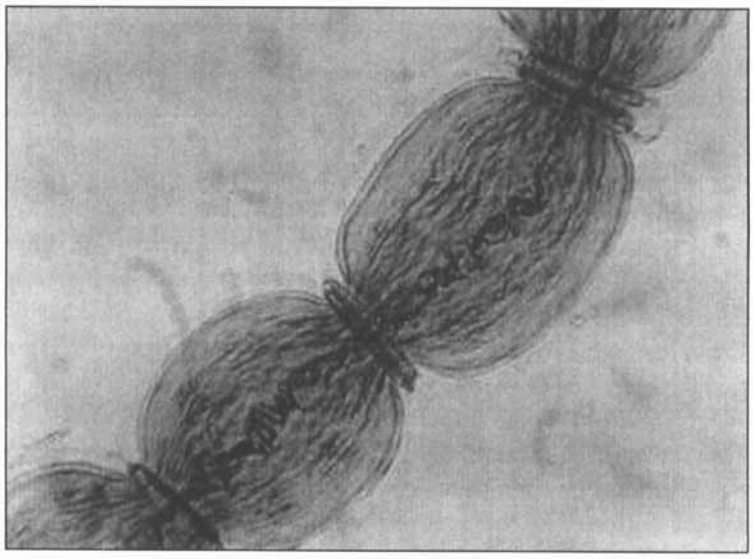

FIGURE 4 Green cotton fibres swollen in Cuoxam; optical microscope, mag. 126x.

samples was carried out by the Institute of Physical Chemistry at the University of Graz in Austria.

The results which are shown in Table V, are very similar for all of the cotton samples, and are consistent with the Cellulose I structure

TABLE V Unit cell dimensions

Sample	*a* [*nm*]	*b* [*nm*]	*c* [*nm*]	γ [°]	*V* [nm^3]	ρ [$g \cdot cm^{-3}$]
White Ethanol extracted	0.79	0.83	1.04	96.8	0.682	1.570
Brown Ethanol extracted	0.79	0.84	1.04	97.1	0.682	1.568
Green Ethanol extracted	0.79	0.84	1.04	97.0	0.687	1.558
Green raw	0.79	0.83	1.04	96.9	0.677	1.581

TABLE VI Crystallite dimensions

Sample	*a* [*nm*]	*b* [*nm*]	*c* [*nm*]	γ [°]	*V* [nm^3]
White Ethanol extracted	6.29	5.91	6.50	93.0	312.0
Brown Ethanol extracted	6.01	4.31	4.59	86.8	144.5
Green Ethanol extracted	6.23	3.89	3.79	89.8	150.8
Green raw	5.59	3.12	3.25	63.2	74.8

which is normally found in cotton. However, a difference among the samples can be found in the crystallite dimensions L_{khl} shown in Table VI. Assuming, that the crystallites in all four cottons have a monoclinic structure, the crystallite dimensions a, b, c and γ can be evaluated in the same way as the unit cell.

From the table it can be seen, that before extraction, the green cotton has smaller crystallites than the other types. After extraction these crystallites become larger with a volume similar to those of the brown cotton. The crystallinity index increases, which means that the crystallites may be able to coalesce during the ethanol extraction of the green cotton. The removal of the rings of suberin may release the strains in the structure. A similar trend is shown by the results of the iodine absorption test.

3. CONCLUSIONS

According to Yatsu *et al.* [1] and Schmutz *et al.* [2] green cotton fibres have a different morphology *i.e.*, the secondary cell wall in the green

cotton fibre is composed of alternate cellulose–suberin layers. In their work the suberin layers in green cotton fibres were visually identified by staining with osmium tetroxide, but a different method was used in this research. The green cotton fibres were stained with methylene blue and swollen with Cuoxam. The observed structure of the green fibres used in this work as revealed by swelling is consistent with the structure put forward previously.

Quantitatively, suberin was determined by ethanol extraction. Due to its polymeric nature suberin is more difficult to remove from the fibre than normal cotton wax. Thus, 24 hours extraction with ethanol was required for the complete removal of the suberin. The results of ethanol extraction show that the green cotton has a significantly higher suberin content than the wax content of the white or brown cotton.

The analysis of the fibre structures by X-ray diffraction show that the cellulose in all of the fibres is the cellulose I structure normally found in cotton. However, in the raw green fibres the crystallites are significantly smaller than in the brown or white fibres. This may be due to the alternate suberin and cellulose layers on the secondary wall inhibiting the development of the crystallites. When the green fibres are fully extracted with ethanol then the crystallite size increases to the level found in the other fibres.

References

[1] Yatsu, L. Y., Espelie, K. E. and Kolattukudy, P. E. (1983). *Plant Physiol.*, **73**, 521–524.
[2] Schmutz, Jenny, T., Amrhein, N. and Ryser, U. (1993). *Planta*, **189**, 453–460.
[3] Morton, W. E. and Hearle, J. W. S., Physical Properties of Textile Fibres, The Textile Institute, Manchester, 1993.
[4] Meredith, R., The Mechanical Properties of Textile Fibres, North Holland Publishing, Amsterdam, 1956.
[5] Conrad, C. M. (1943). *J. Agric. Res.*, **66**, 307–312.
[6] Kolattukudy, P. E. and Soliday, C. L. (1984). *ARCO Plant Cell Research Institute–UCLA Symposium*, pp. 381–400.