

STRUCTURE AND THERMAL PROPERTIES OF NATURAL COLORED COTTONS AND BOMBAX COTTON

Li Zhang¹, Jianxin He^{1,2*} and S.-Y. Wang¹

¹College of Textiles, Dong Hua University, Shanghai 201620, People's Republic of China

²College of Textiles, Zhongyuan University of Technology, Zhengzhou 450007, People's Republic of China

Chemical compositions, crystalline structures and thermal properties of bombax cotton and natural colored cottons including laurel green, bottle green and brown cotton were investigated by chemical analysis, SEM, IR spectra and X-ray diffraction. The results showed that the crystallinity and crystallite sizes of laurel green cotton were lower than those of bottle green cotton because of the excess content of suberin in the former. The crystallinity of brown cotton was similar to that of white cotton, and bombax cotton had the lowest crystallinity but its crystallite orientation was the highest. Thermal property of bottle green cotton was the most stable, whose decomposition temperature was higher of 30°C than that of common white cotton because of its higher lignin content, and bombax cotton had the lowest thermal degradation temperature. But bottle green cotton reached the highest decomposition speed and made decomposition finish within a very short time, and bombax cotton was just the reverse.

Keywords: bombax cotton, crystalline structure, IR spectra, natural colored cotton, thermal properties

Introduction

Cellulose is the most abundant natural polymer, but only white cotton and some bast fibers such as ramie fiber and flax fiber can be used as textile materials. Usually, the environment is subject to be polluted by the dyeing process of these fibers and fabrics, and the dyed cottons tend to be discolored often after being washed. Nowadays natural color cotton fibers have been attracting significant attention owing to their characteristics and some unique properties such as natural inflaming retarding characteristic and the deepening of color after laundering [1, 2]. Besides, kapok, often called 'bombax cotton', has already been used in pillow stuffing, quilt stuffing and other stuffing widely because of its superiorities in luster and warmth aspects induced by unique thin cell wall and big hollow structure.

The unique characteristics of natural colored cottons and bombax cotton are closely related to their chemical composition and crystalline structures. Chen *et al.* compared the crystallite sizes of natural brown cotton, green cotton and white cotton [3], but the reason for the difference of crystallite sizes between the three cottons was not discussed. Elesini *et al.* discussed the chemical composition of natural green cotton with chemical analysis, and IR analysis and they believed that green cotton contained more suberin than white cotton, which resulted in the lack and disappearance of O6–H•••O bridge bond [4]. Hori *et al.* analyzed the chemical composition of bombax cotton, especially described the structure of lignin and drawn the

conclusion that bombax cotton had good lipophilicity [5]. Although more attention have been paid to the use of natural colored cotton and bombax cotton, generally speaking, there are still lacks of systematic studies about their structure and properties, especially, their thermal degradation behaviors have not been reported yet.

In this paper, chemical analysis, SEM, IR spectra and X-ray diffraction were used to investigate the differences about the chemical compositions, crystallite structures and thermal properties of natural colored cottons and bombax cotton and compared with those of white cotton.

Experimental

Materials

White cotton, natural brown cotton, natural laurel green and bottle green cottons came from Sinkiang of China. Bombax cotton was from Guangdong province of China. All chemicals used were purchased from local company as analytical reagents.

Methods

Chemical analysis

Compositions of carbohydrate components such as cellulose, lignin, xylan and solubility experiments were determined according to TAPPI 203 os-61, TAPPI 222 om-98, TAPPI 223 cm-84 and TAPPI 204, respectively.

* Author for correspondence: hejianxin771117@163.com

Morphological analysis

A JEOL JSM-5600LV electron microscopy with an accelerating voltage of 20 kV was used to study the cross section and surface morphology of samples. The Kajaani FS-200 fiber length determinator was used to measure the length of fibers.

FTIR spectroscopy

FTIR spectra of fiber samples were recorded with a Nicolet Nexus 670 FTIR spectrometer using the KBr disc technique (5 mg power of samples/300 mg KBr). 100 scans were taken with a resolution of 2 cm⁻¹.

X-ray diffractometry

X-ray diffractograms were recorded with a Rigaku-D/Max-2550PC diffractometer using Ni-filtered CuK_α radiation of wavelength 0.1542 nm. The X-ray unit operated at 40 kV and 30 mA. Angular scanning was conducted from 5 to 50° at 2° min⁻¹.

Crystallinities of fibers were calculated from diffraction intensity data using two different methods. The first one is deconvolution method. The diffraction profile was fitted by Gaussian function to find the contribution of each individual peak relative to the 101, 10-1, 002, 040 crystallographic planes and the amorphous background. Crystallinity X_d was calculated by [6]:

$$X_d = \left[1 - \frac{S_a}{S_a + S_{cr}} \right] \cdot 100\%$$

where S_a is the amorphous integrated area and S_{cr} is the sum of the area of the 101, 10-1, 002, 040 peaks.

The second method was the empirical method proposed by Segal for native cellulose [7]:

$$CrI = \frac{I_{002} - I_{amorph}}{I_{002}} \cdot 100\%$$

where CrI is the degree of crystallinity, I_{002} is the maximum intensity of the (002) lattice diffraction and I_{amorph} is the intensity diffraction at 18° 2θ degrees.

The average crystallite size of the direction perpendicular to 002 lattice plane was calculated from the Scherrer equation.

$$L = \frac{k\lambda}{\beta \cos\theta}$$

where L is the size of crystallite, k is the Scherrer constant (0.89), λ is the X-ray wavelength, β is the FWHM (Full width half maximum) of 002 reflection in radian and 2θ is the corresponding Bragg angle (reflection angle).

The degrees of crystallite orientation OG and OGI were calculated according to the description given by Bohn *et al.* [8].

$$OG = \frac{(180^\circ - HW/^\circ)}{180^\circ}$$

$$OGI = \frac{I_{ori}}{I_{total}}$$

where HW is the full width at half maximum; I_{ori} and I_{total} are the intensity integral of the oriented material and the total intensity of the resulting one-dimensional distributions, respectively.

Thermogravimetric analysis

Thermogravimetric analysis was carried out on Perkin Elmer TGA thermogravimetric analysis instrument. All the experiments were carried out with the same nitrogen flux. The heating-up speed was 10°C min⁻¹ and the degradation temperature was from 25 to 500°C.

Results and discussion

FTIR spectra analysis

Chemical compositions of the five cottons are shown in Table 1. The region from 2852 to 2920 cm⁻¹ in IR spectra is attributed to the C-H stretching (Fig. 1).

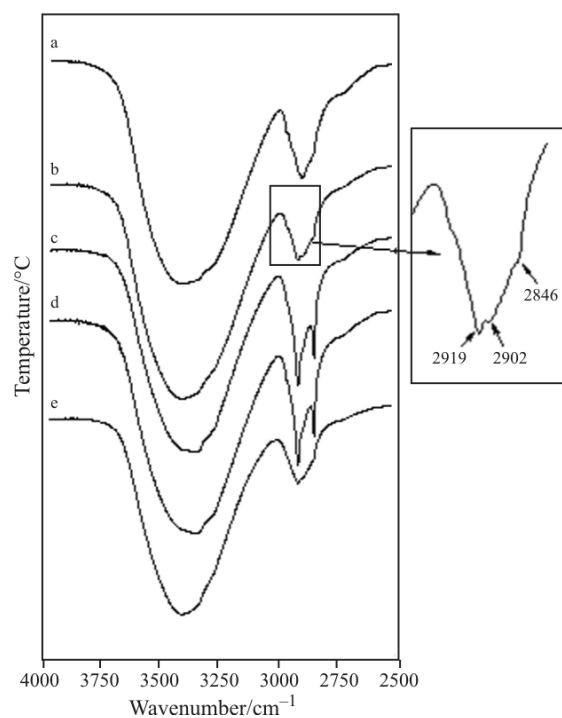


Fig. 1 FTIR spectra of natural colored cottons, bombax cotton and white cotton at 4000–2500 cm⁻¹; a – white cotton; b – brown cotton; c – bottle green cotton; d – laurel green cotton; e – bombax cotton

Table 1 Chemical composition of natural colored cottons, bombax cotton and white cotton

Chemical composition (%)	White	Brown	Bottle green	Laurel green	Bombax
Water	7.8	6.90	5.18	5.96	7.4
Hot-water extractive	1.88	2.54	1.52	1.78	1.90
Ethanol-benzene extractive	1.30	0.98	2.25	1.96	1.80
Acid-soluble lignin	–	4.38	9.34	8.40	16.4
Xylan	–	2.10	1.84	2.05	21.9
Cellulose	97	93.44	89.80	92.20	64.20
Waxiness	0.60	3.19	5.04	4.39	0.8
Pectin	1.2	0.43	0.51	0.40	0.41
Protein	1.34	2.35	2.90	2.18	–

In this region, white cotton shows a single peak at 2902 cm^{-1} and bombax cotton also shows a single peak at 2919 cm^{-1} . But the two green cottons show a doublet at 2919 and 2846 cm^{-1} , whereas brown cotton shows a triplet at 2919 , 2902 and 2846 cm^{-1} . Andreeva *et al.* attributed the absorbed peaks at 2919 and 2846 cm^{-1} to the antisymmetrical and symmetrical C–H stretching of noncellulose polysaccharides [9], but the studies of Stankovič *et al.* showed that the antisymmetrical and symmetrical C–H stretching of waxiness (fatty acid, fatty alcohol and fatty acid ester) also showed a doublet at 2919 and 2846 cm^{-1} [4]. From the chemical analysis results shown in Table 1, we can know that in the C–H stretching vibration region, the single peak at 2919 cm^{-1} of bombax cotton is attributed to hemicellulose (xylan). But the doublets of the two green cottons are mostly attributed to waxiness, which is proved by the stretching vibration region of acetyl group at $1700\text{--}1800\text{ cm}^{-1}$, because in the IR spectra of the two green cottons, despite of the absorption peak at 1737 cm^{-1} which is assigned to the absorption of the hemicellulose or fatty acid ester, there is an absorption peak at 1716 cm^{-1} attributed to the stretching vibration of the acetyl group of fatty acid (Fig. 2). The waxiness content of brown cotton is lower than that of green cotton because the C–H stretching vibration peak of cellulose in IR spectrum of brown cotton can be discriminated and the peak in the two green cottons is absent. Another need to explain was that the waxiness in brown cotton, which was similar to white cotton and difference from green cottons, was composed of fatty alcohol, because the absorption peaks at 1716 and 1737 cm^{-1} attributed to fatty acid and fatty acid ester was absent in the IR spectrum of the brown cotton.

Table 1 indicates that the content of hemicellulose (xylan) in bombax cotton is the highest, which is reflected in the IR spectrum because there is an obvious stretching vibration peak at 1456 cm^{-1} attributed to the CH_2 bend vibration of hemicellulose, but this peak is not shown in the IR spectra of white cotton and natural colored cottons (Fig. 2).

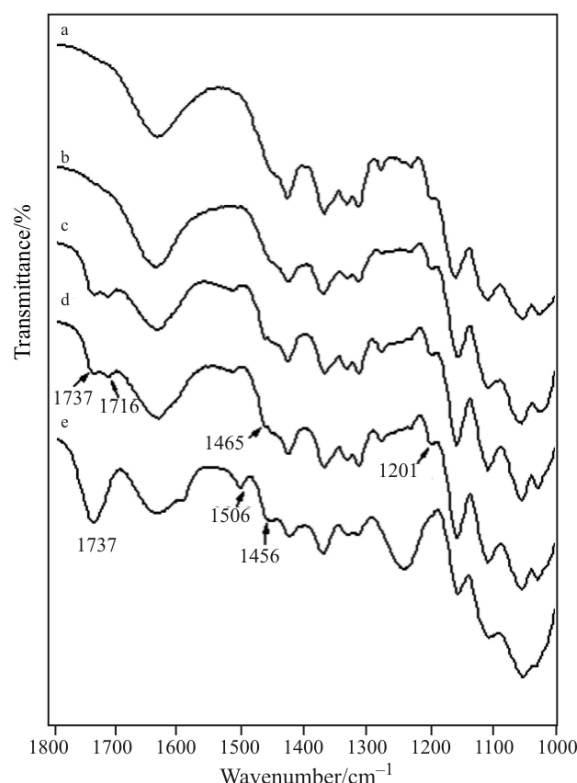


Fig. 2 IR spectra of natural colored cottons, bombax cotton and white cotton at $1000\text{--}1800\text{ cm}^{-1}$. a – white cotton; b – brown cotton; c – bottle green cotton; d – laurel green cotton; e – bombax cotton

In the IR spectra of two green cottons and bombax cotton, there has a band at 1506 cm^{-1} attributed to aromatic ring frame vibration, which shows the highest absorption in bombax cotton, indicating that bombax cotton has the greatest lignin content. But the lignin content of brown cotton should be very low because there is no obvious absorption peak in this region (Fig. 2). In the IR spectrum of bottle green cotton, the peak of 1465 cm^{-1} attributed to the C–H absorption peak of lignin can be seen clearly, but only a faint shoulder peak has been shown in the spectrum of laurel green cotton, which also indicates that the lignin content of

bottle green cotton is more than that of laurel green cotton. Obviously, the evidences given by IR spectra are consistent with our chemical analysis results.

And besides, it was worth while to note that in IR spectrum of bombax cotton, the absorption vibration of acetyl at 1737 cm^{-1} was more intense than our expected (Fig. 2). In general, noncellulosic polysaccharides, such as arabinoxylan from the walls of angiosperms and galactomannan from gymnosperms, are substituted by acetyl groups within a range of 2–4% of cell walls. In contrast, our chemical analysis indicated that the waxiness content and benzene ethanol extract in bombax cotton were very low; therefore, the xylan in bombax cotton was substituted with significantly high levels of acetyl groups. This was consistent with the report of Iiyama *et al.* and they considered that the DS of the acetyl group of xylan in bombax cotton was as high as 1.38–1.43 [10].

The structures and properties of cellulosic materials are intrinsically related to the interactions between the cellulose molecules. According to the model of hydrogen bond network in cellulose I given by Gardner and Blackwell [11], there are two kinds of hydrogen bonds, which are intra- and inter-molecular hydrogen bonds. 2-OH...O-6 and 3-OH...O-5 are intra-molecular hydrogen bonds and 6-OH...O-3' is intermolecular hydrogen bond. The broad band between 3600 and 3200 cm^{-1} assigned to OH-stretching vibrations hides several important bands concerning the hydrogen bonds.

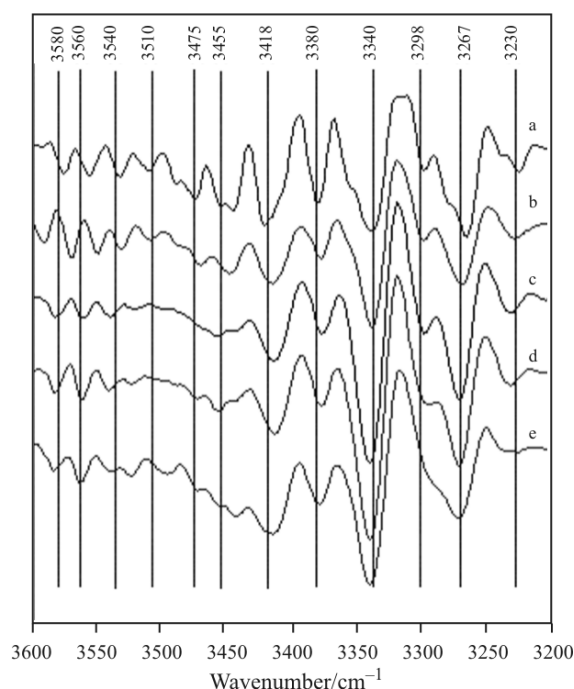


Fig. 3 Second derivative FTIR spectra in the range of OH group stretching vibration area; a – white cotton; b – brown cotton; c – bottle green cotton; d – laurel green cotton; e – bombax cotton

The second derivative FTIR spectra in the range of OH stretching vibration are shown in Fig. 3.

In the intra- and inter-molecular hydrogen stretching vibration region between 3600 and 3200 cm^{-1} [12, 13], white cotton has the highest resolution. For example, three shoulder peaks of white cotton at 3340–3380, 3267–3298 and $3220\text{--}3267\text{ cm}^{-1}$, respectively are not existent in other cottons [14, 15]. And in this region, the spectrum of brown cotton is much more closely to that of white cotton. For example, there have evident absorption peaks at 3510 and 3475 cm^{-1} in the spectra of white cotton and brown cotton but not exist in the two green cottons.

The differences between the two green cottons are not distinct, but for the peak at 3298 cm^{-1} attributed to the stretching vibration of O6–H...O bridge of 10l crystallographic plane [4], the intensity of bottle green cotton is more than that of laurel green cotton. In opposition to the vibration peak at 3298 cm^{-1} , for the peak at 1201 cm^{-1} attributed to bend vibration in hydroxyl plane, though relevant to CH₂OH group in cellulose, the absorption of laurel green cotton is stronger than that of bottle green cotton (Fig. 2).

Yatsu *et al.* believed that there was suberin in cotton, which was a kind of waxiness material, existed in the cellulose layer of fiber secondary cell wall [16]. The suberin is differ from the common waxiness because one of the compositions is ω -carboxylic acid, which contains aliphatic polyester that results in the lack of O6–H...O bridge in the fiber formation with warping the structure of cellulose I. And because of the warping of structure, the 1201 cm^{-1} attributed to OH bending presents in the IR spectrum. Therefore, despite a higher waxiness content in bottle green cotton compared with laurel green cotton, the suberin which have very deep influence on the hydrogen bond of cellulose I is less in bottle green cotton.

Fiber morphology

These fibers observed by SEM with 5000 magnification times are shown in Fig. 4. As we expected, there are obvious cellulose microfibrillars in white cotton fiber surface and the microfibrillar configuration also can be observed on the surface of brown cotton but these microfibrillars looks like wider (Fig. 4b). Obviously, the noncellulose components such as lignin and hemicellulose have influence on the surface morphology of fibers since cellulose microfibrillar configurations can not be observed in bombax cotton and bottle green cotton with low content of cellulose and laurel green cotton only has a few of cellulose microfibrillar on its surface (Fig. 4d).

Morphological character parameters of natural colored cottons, bombax cotton and white cotton are

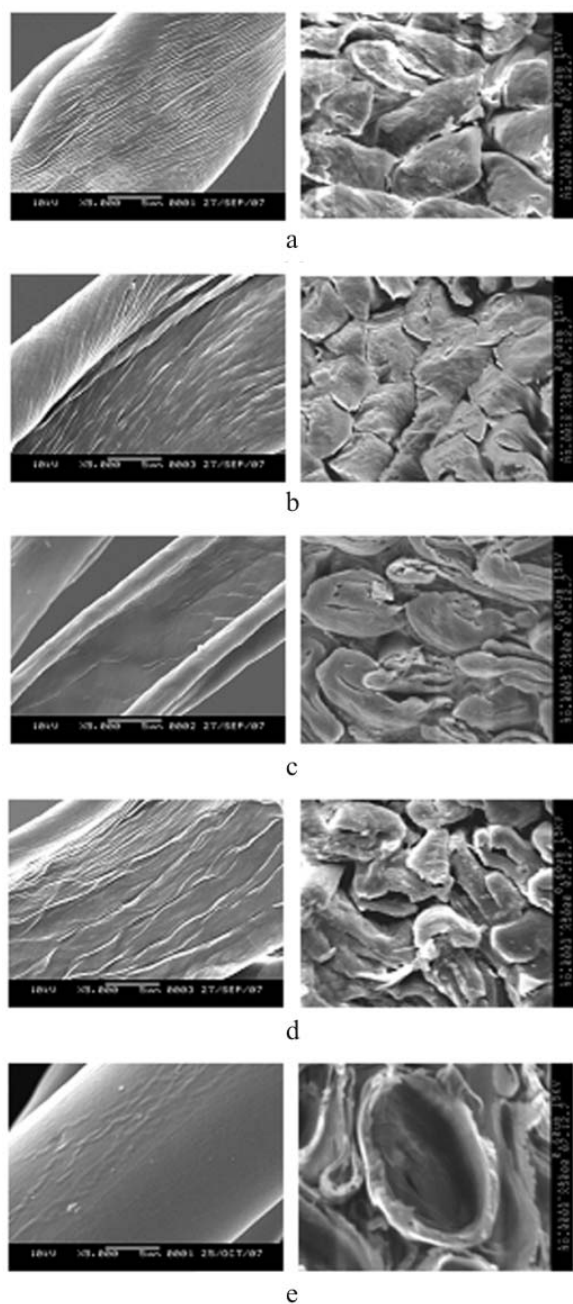


Fig. 4 The SEM photograph of natural colored cottons, bombax cotton and white cotton at the surface and cross-section (Magnification \times 5000); a – white cotton; b – brown cotton; c – bottle green cotton; d – laurel green cotton; e – bombax cotton

shown in Table 2. The crimpness of the two green cottons was the highest; the next was brown cotton and white cotton. Bombax cotton is cylindrical with smooth surface and hardly any curve. The lengths of brown cotton and green cottons are 28 and 25–26 mm, respectively, which are much lower than that of white cotton fiber (36 mm). Bombax cotton has the shortest length, only 15 mm; therefore it is hardly to be used in spinning.

Table 2 Morphological character parameters of natural colored cottons, bombax cotton and white cotton

Cottons	Line density/dtex	Average length/mm	Curliness	R
White	1.50	36	17	2.1
Brown	1.66	28	22	2.4
Bottle green	1.30	25	26	3.0
Laurel green	1.39	26	24	2.8
Bombax	0.77	15	4	20

There are remarkable differences among the cross-sections of these cottons (Fig. 4), especially bombax cotton has a lumen structure with the cell width of 15 μm , whereas the wall thickness of only 0.75 μm (Fig. 4e). The percentage of hollowness in bombax cotton is as high as 83% and the ratio of the width of the cell and the thickness of the wall (indicated as R) is as high as 20, as shown in Table 2. Therefore, despite bombax cotton hardly to be used in spinning, it has many advantages to be used as warm fillings. White cotton is the plumpest with the thickest wall of cell. By comparison, the wall of cell in natural green cotton is thinner than others. The R value of laurel green cotton is 2.8 and bottle green cotton is 3.0, which are obviously higher than 2.1 of the white cotton and 2.4 of the brown cotton.

X-ray diffraction analysis

X-ray diffractogram of natural colored cottons and bombax cotton are shown in Fig. 5 and the results are shown in Table 3. The empirical crystallinity (CrI) is consistent with the crystallinity (X_d) calculated by deconvolution method, of course, the crystallinity of white cotton is the highest. Obviously, the amorphous components such as lignin, hemicellulose result in the lower crystallinity of natural colored cotton and bombax cotton, especially bombax cotton whose crystallinity is the lowest. The crystallinity of brown cotton is higher than other two-kind green cottons among these natural colored cottons.

The crystallinity and crystallite size of laurel green cotton are less than those of bottle green cotton and especially the crystallite sizes of 101, 021 and 002 lattice plane. As shown in IR spectra analysis, there has higher suberin content in laurel green cotton, which can result in the lack of the $\text{O6-H}\cdots\text{O}$ bridge bond in cellulose. Therefore, it seems to that suberin has a notable impact on the formation of cellulose crystallite. Being similar to crystallinity, the crystallite sizes in bombax cotton are the least among these cottons.

In spite of the lowest crystallinity and crystallite size in bombax cotton, its crystallite orientation along the fiber axis is the best among these cottons.

Table 3 Crystallinity, crystallite size and crystallite orientation of natural colored cottons, bombax cotton and white cotton

Cottons	Crystallinity/%		Crystallite size/nm				Crystallite orientation/%	
	CrI	X_d	101	10 $\bar{1}$	021	002	OG	OGI
White	81.81	73.33	3.82	4.75	4.85	4.86	83.4	66.1
Brown	80.54	70.05	3.83	4.32	3.01	4.98	83.5	66.0
Bottle green	77.14	66.87	3.83	4.48	3.03	4.81	78.9	59.7
Laurel green	74.14	63.46	3.80	4.05	2.89	4.51	76.8	55.5
Bombax	66.32	48.50	3.66	3.25	2.79	3.96	88.0	73.8

Table 4 Thermal degradation data of natural colored cottons, bombax cotton and white cotton

Cotton	$T_i/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T_{1/2}/^\circ\text{C}$	$T_d/^\circ\text{C}$	$\left(\frac{d\alpha}{dt}\right)_{p^*}/\% \text{ min}^{-1}$	$T_p - T_i/^\circ\text{C}$	$T_e - T_i/^\circ\text{C}$
White	306.2	343.7	344.0	358.0	11.4	37.5	51.8
Brown	308.7	341.4	341.4	355.5	13.0	32.7	46.8
Bottle green	336.6	356.1	357.1	375.6	15.5	19.5	39.0
Laurel green	308.5	343.1	342.1	356.1	13.2	34.6	47.6
Bombax	293.3	338.4	332.3	358.1	11.1	45.1	64.8

*The highest velocity of decomposition.

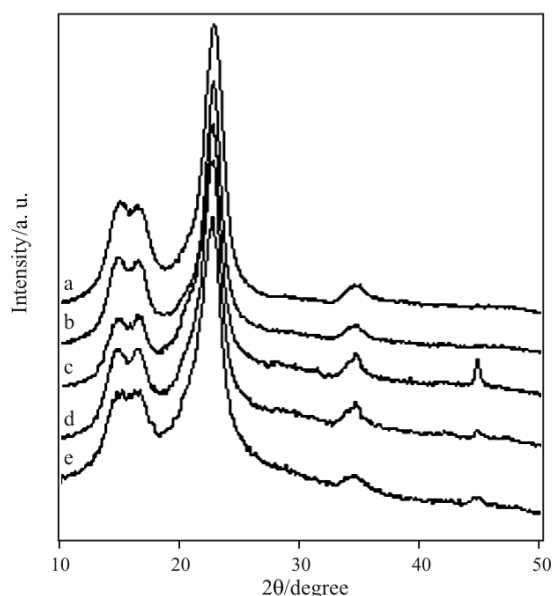


Fig. 5 X-ray diffractogram curve of natural colored cottons, bombax cotton and white cotton; a – white cotton; b – brown cotton; c – bottle green cotton; d – laurel green cotton; e – bombax cotton

The crystallite orientation of brown cotton is similar to that of white cotton; however, the green cottons have the minimal crystallite orientation, especially laurel green cotton (Table 3).

Thermogravimetric analysis

DTG curves of fiber samples are shown in Fig. 6, respectively. Obviously, at the first peak between 40 and 100°C in DTG curve, the mass loss is due to water

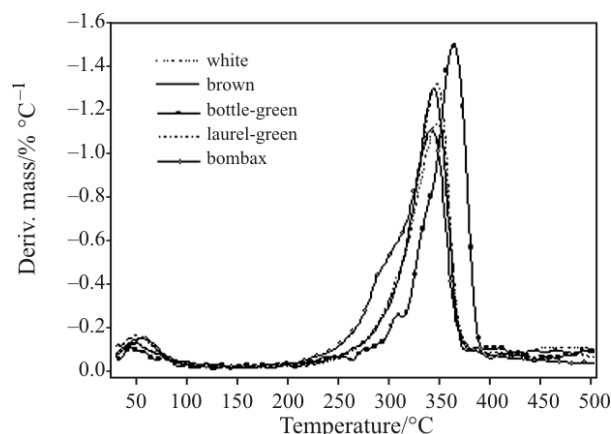


Fig. 6 DTG curves of natural colored cottons, bombax cotton and white cotton

vaporization (drying). In this region, the mass loss of white cotton is the highest, the secondary is bombax cotton and the three natural colored cottons are the least, especially bottle green cotton. It is consistent with the foregoing test result of moisture regain.

These cottons show a larger difference in the next region of DTG curve corresponding to main degradation peaks. Bombax cotton has a big shoulder peak at 280°C, but the bottle green cotton has a little shoulder peak at about 300°C. Obviously, the former can be attributed to the abundant hemicellulose degradation in bombax cotton [17], but the latter is likely induced by the waxiness because the waxiness content in bottle green cotton is the highest. Judged from DTG curves, the thermal degradation processes of brown cotton and laurel green cotton are relatively similar.

The thermal degradation data of these cottons are shown in Table 4. Initial degradation temperature

T_i was used as an index to judge the thermal stabilities of these five-kind cottons [18]. It could be found that thermal property of bottle green cotton was the most stable, whose degradation temperature is higher of 30°C than that of common white cotton, but that of laurel green cotton and brown cotton was only slightly more than of white cotton. Studies of Ouajai and Shanks proved that more crystalline structures were favourable to improve the thermal stabilities of cellulose [19]. As analyzed before, the crystallinity and crystallite size of bottle green cotton are larger than those of laurel green cotton. Furthermore, studies of Ramiah *et al.* indicated that thermal decomposition temperature of hemicellulose was the lowest and thermal stabilities of lignin was the best in three-kind of plant materials of hemicellulose, cellulose and lignin [20]. Accordingly, the higher lignin content is one of the reasons for the high thermal decomposition temperature of bottle green cotton. Among these cotton fibers, the thermal degradation temperature of bombax cotton is the lowest. Obviously, the low crystallinity in bombax cotton and the excessive hemicellulose content are the main reasons. Being similar to the T_i , other characteristic indexes such as T_p (the temperature in the most speed of thermal degradation), T_e (the end temperature of decomposition) and $T_{1/2}$ (the temperature degraded to 50%) also show the same rule.

From Table 4 it can be seen that, as far as these fibers are concerned, the order of the two temperature differences of (T_p-T_i) and (T_e-T_i) are coincident, that is, bombax cotton > white cotton > natural laurel green cotton > brown cotton > natural bottle green cotton. Whether the temperature span from initial temperature to the highest speed of decomposition temperature (T_p-T_i) or the whole temperature interval of decomposition (T_e-T_i) , bombax cotton is maximal and bottle green cotton is minimal. It is shown that although thermal decomposition temperature of natural bottle green cotton is the highest, it reaches the highest decomposition speed and makes decomposition finish in a very short time once its thermal decomposition begins. Bombax cotton is just the reverse.

Conclusions

Green cotton has the high waxiness contents, especially suberin, for which laurel green cotton is higher than bottle green cotton. The excess content of suberin makes the lack and disappearance of O6-H•••O bridge bond, therefore, the crystallinity and crystallite size of laurel green cotton are lower than those of bottle green cotton and those of brown cotton were similar to of white cotton. Bombax cotton has the lowest crystallinity and crystallite size, but the degree of crystallite orientation is the highest. The cellulose

content of green cotton is very low among natural colored cottons, especially bottle green cotton. This was proved by SEM observation because the cellulose microfibrillar structure, which could be observed in white and brown cotton, hardly can be observed in two green cottons. Natural colored cottons, especially bottle green cotton, showed a higher thermal stability compared with white cotton. Bombax cotton has the lowest thermal degradation temperature, however, its (T_e-T_i) and (T_p-T_i) are the highest among these cottons.

References

- 1 B. L. Williams and P. Horridge, *Text Tech. Int.*, (1997) 31.
- 2 M. J. Van Zandt, P. Horridge and J. K. Dever, *Clothing Text Res J.*, 15 (1997) 246.
- 3 H. L. Chen and A. I. Yokochi, *J. Appl. Polym. Sci.*, 76 (2000) 1466.
- 4 U. S. Elesini and P. Alenka, *Acta. Chim. Slov.*, 49 (2002) 815.
- 5 K. Hori, M. E. Flavier and S. J. Kuga, *Wood Sci.*, 46 (2000) 401.
- 6 J. He, Y. Tang and S. Y. Wang., *Iran Polym. J.*, 16 (2007) 807.
- 7 L. Segal, L. Creely A. E., Martin and C. M. Conrad, *Textiles Res. J.*, 29 (1959) 786.
- 8 A. Bohn, H. P. Fink, J. Ganster and M. Pinnow, *Macromol. Chem. Phys.*, 201 (2000) 1913.
- 9 Q. A. Andreeva, L. A. Burkova, A. N. Grebenkin and A. A. Grebenkin, *Russ. J. Appl. Chem.*, 75 (2002) 1513.
- 10 K. Iiyama, T. B. T. Lam, N. Kasuya and B. A. Stone, *Phytochemistry*, 35 (1994) 959.
- 11 K. H. Gardner and J. Blackwell, *Biochim. Biophys. Acta*, 343 (1974) 232.
- 12 T. Kondo, *Cellulose*, 4 (1997) 281.
- 13 Y. Marechal and H. Chanzy, *J. Mol. Struct.*, 523 (2000) 183.
- 14 S. Kokot, B. Czarnik and Y. Ozaki, *Biopolymers*, 67 (2002) 456.
- 15 J. Sugiyama, J. Persson and H. Chanzy, *Macromolecules*, 24 (1991) 2461.
- 16 L. Y. Yatsu, K. E. Espelie and P. E. Kolattukudy, *Plant Physiol.*, 73 (1983) 521.
- 17 M. Katharina, Picker-Freyer, *J. Therm. Anal. Cal.*, 89 (2007) 745.
- 18 E. S. Sashina, G. Janowska, M. Zaborski and A. V. Vnuchkin, *J. Therm. Anal. Cal.*, 89 (2007) 887.
- 19 S. Ouajai and R. A. Shanks, *Polym. Degrad. Stab.*, 89 (2005) 327.
- 20 M. V. Ramiah, *J. Appl. Polym. Sci.*, 14 (1970) 1323.

Received: April 26, 2008

Accepted: June 11, 2008

OnlineFirst: November 12, 2008

DOI: 10.1007/s10973-008-9206-9