THERMAL STABILITY AND DEGRADATION KINETIC STUDY OF WHITE AND COLORED COTTON FIBERS BY THERMOGRAVIMETRIC ANALYSIS

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Thermal degradation behavior using thermogravimetry (TG), chemical composition and crystallinity by X-ray diffraction of white and naturally colored cotton fibers (ruby, beige, brown and green) were studied. Flynn–Wall–Ozawa method was used to investigate the thermal decomposition kinetics of the different fibers. The white cotton fiber has higher thermal stability and higher apparent activation energy (E_a) value compared to the colored fibers. There are no significant differences in initial temperature of degradation in air or in nitrogen atmosphere for the same type of fiber. Chemical composition and crystallinity influenced the thermal degradation behavior of the fibers studied.

Keywords: Flynn–Wall–Ozawa method, naturally colored cotton fibers, thermal degradation

Introduction

Brazilian researchers have used genetic breeding of cotton fibers in order to increase the production and to develop new species more appropriate to Brazil's soil and climate. Furthermore, naturally colored cotton fibers are considered potential eco-friendly materials for textile industries because they avoid the use of synthetic pigments which in general, contain toxic chemicals such as heavy metals. In this context, some species of colored cotton with different colors were developed by Embrapa Algodão (Paraíba, Brazil), which was denominated according to their relative colors as: ruby, beige, brown, green and ruby. Beside the use of cotton fibers in textile industries, they have potential for application as reinforcement to polymer composites [1–3].

The understanding of the thermal behavior of these fibers is very important since in general several conventional techniques used in plastic processing industry, carried out at high temperature. In this work thermal degradation behavior by thermogravimetry (TG), chemical composition and crystallinity by X-ray diffraction of white and four naturally colored cotton fibers were studied.

Experimental

Materials

Cotton fibers were supplied by Embrapa Algodão (Campina Grande, PB, Brazil).

Chemical composition

The cotton fibers were chopped in a knife mill using a sieve of 10 mesh and extracted by Soxhlet extraction system using subsequently ethanol:hexane 1:1 (*v/v*) solution and hot water at boiling temperature. The extracted samples were dried for 24 h at 60°C. The lignin content of the fibers was determined by reaction with sulfuric acid according to the standard methods of TAPPI-T222 om-88. The holocellulose (cellulose+hemicellulose) content was determined according to TAPPI T19m-54. The α-cellulose was removed from holocellulose (cellulose+hemicellulose) by alkaline extraction [4]. The hemicellulose content was obtained by subtracting the α-cellulose part from the holocellulose content. An average on three samples was taken for all mentioned analyses.

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Methods

Thermogravimetry (TG)

The fibers were analysed using TG and derivative thermogravimetry (DTG) using a TA Q500 instrument (TA Instruments, New Castle, DE, USA). TG/DTG curves of the cotton fibers were recorded in air and nitrogen atmospheres at 10°C min⁻¹ heating rates. For kinetic study the experiments were carried out in nitrogen atmosphere at 5, 10, 15 and 20°C min⁻¹. All measurements were performed at a flow rate of 60 mL min⁻¹ of purging gases, platinum crucible, sample mass around 5 mg.

X-ray diffraction (XRD)

Diffractograms were recorded using a Rigaku diffractometer. Scattered radiation was detected in the $2\theta=5–40°$ range at a speed of $2°$ min⁻¹. The extent of crystallinity (I_c) was estimated by means of Eq. (1) using the height of the 200 peak (I_{200}, $2\theta=22.6°$) and the minimum between the 200 and 110 peaks (I_{am}, $2\theta=18°$). I_{200} represents both crystalline and amorphous materials while I_{am} represents the amorphous material.

$$I_c=(I_{200}-I_{am}/I_{200})\cdot100\% \qquad (1)$$

Results and discussion

Principal constituents (lignin, cellulose and hemicellulose) of white and colored cotton fibers are presented in Table 1. It was observed that the colored cotton fiber have higher lignin and hemicellulose content than the white fiber; the green cotton fiber has higher lignin content than the other fibers.

The TG/DTG curves under nitrogen and air atmospheres at 10°C min⁻¹ for white cotton and colored cotton fibers are shown in Fig. 1. A progressive mass loss was observed from 50 to 120°C associated with water release. The decomposition of lignocellulosic components (hemicellulose, cellulose and lignin) for all cotton fibers showed only one distinct peak in the DTG curves in nitrogen atmosphere, whereas in air two distinct peaks related to degradation process were observed (DTG curves in Fig. 1). It is well known from the literature that lignocellulosic fibers degrade in several steps. The hemicellulose degrades at about 240–310°C, whereas the cellulose degrades between 310–360°C and the lignin has been shown to degrade in wide temperature interval (200–550°C) [5, 6]. It is not possible to separate the different degradation processes of the fiber components because the reactions are very complex and overlap in the range of 220–360°C. In both atmospheres, the first thermal event is due to breakdown of lignocellulosic components and the second event that occurs only in air atmosphere is due to oxidation of the partially decomposed components [7].

Initial temperature of degradation, the maximum temperatures of the thermal decomposition peak and the residual mass at 700°C (in air and nitrogen atmospheres) were determined from TG/DTG curves (Fig. 1) and are shown in Table 2. No significant difference in the initial temperature of degradation was observed in both atmospheres for the same type of fiber. The white cotton fiber started to decompose at higher temperature than colored fibers. Between the

Table 1 Principal constituents of white and colored cotton fibers

	White/%	Ruby/%	Brown/%	Beige/%	Green/%
Hemicellulose	8.0±0.3	11.3±2.6	9.9±0.4	12.5±3.4	8.7±0.9
Cellulose	88.3±0.3	73.6±2.3	78.7±0.4	81.4±2.2	80.3±0.8
Lignin	4.8±0.5	13.8±0.1	9.9±0.1	7.2±0.4	15.6±1.7

Table 2 Parameters obtained from TG/DTG curves of white and colored cotton fibers at N_2 and air atmospheres: temperature range of thermal degradation, mass losses and mass residue at 700°C

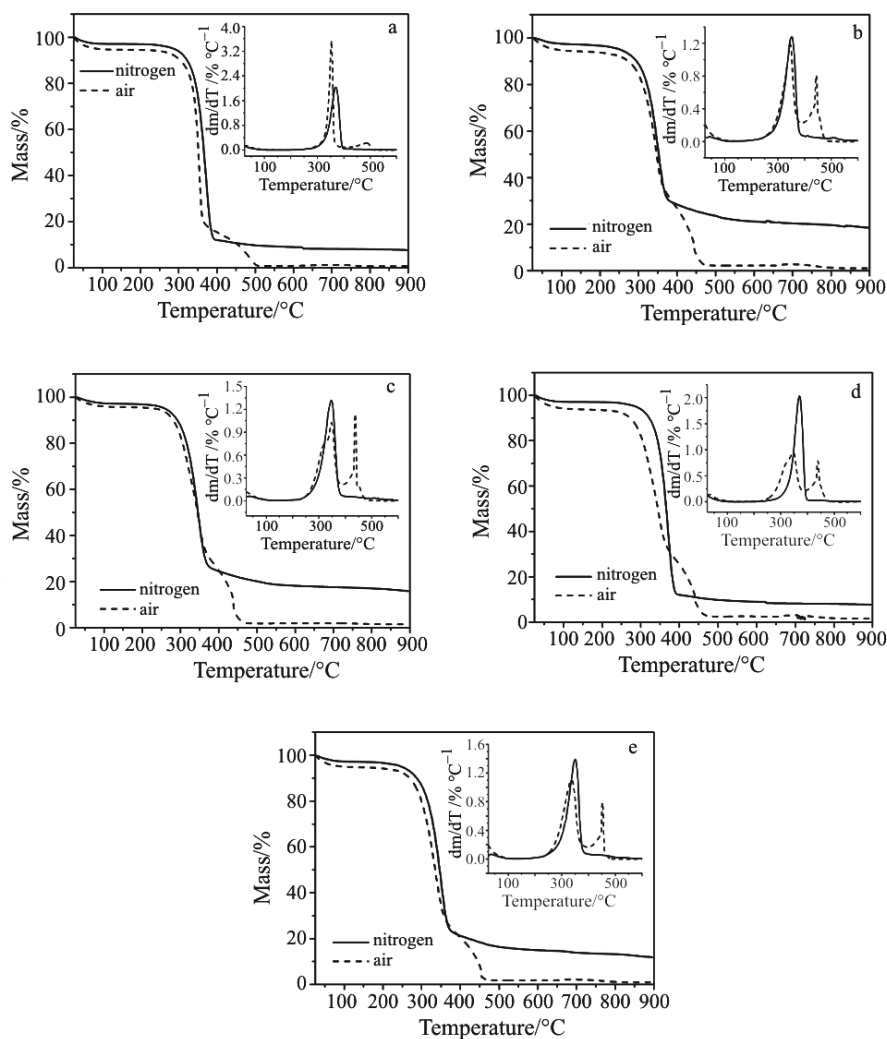| Fiber	Atmosphere (10°C min⁻¹)	Temperature range/°C	Mass loss/%	Residue at 700°C/%
White	air	241–550	93.8	1.1
	nitrogen	245–550	85.0	8.8
Ruby	air	196–560	91.2	3.6
	nitrogen	201–560	75.1	19.8
Beige	air	186–565	93.4	1.6
	nitrogen	192–565	79.4	17.5
Brown	air	194–560	90.7	2.4
	nitrogen	203–560	87.6	8.5
Green	air	186–550	92.9	2.2
	nitrogen	196–550	82.2	13.2

Fig. 1 TG and DTG curves for cotton fibers in nitrogen and air a – white, b – ruby, c – beige, d – brown and e – green

colored cotton fibers no serious differences in the thermal stability was observed. The differences in the thermal behavior between colored and white cotton fibers can be due to the variations in their composition. The white fiber has higher cellulose content, whereas the colored cotton fibers beside higher lignin and hemicellulose contents than the white fiber, have pigmentations which might belong to flavonoids substances [8]. However, these pigments in colored fibers are essentially unknown [9]. The residue after the thermal degradation at 700°C in both atmospheres is inorganic ash, naturally present as a constituent of fibers. The residue content was lower for the white fiber than that was observed for most colored cotton fibers.

The apparent activation energy (E_a) for different cotton fibers was obtained applying the isoconversional method Flynn, Wall and Ozawa (Eq. (2)) [10–13].
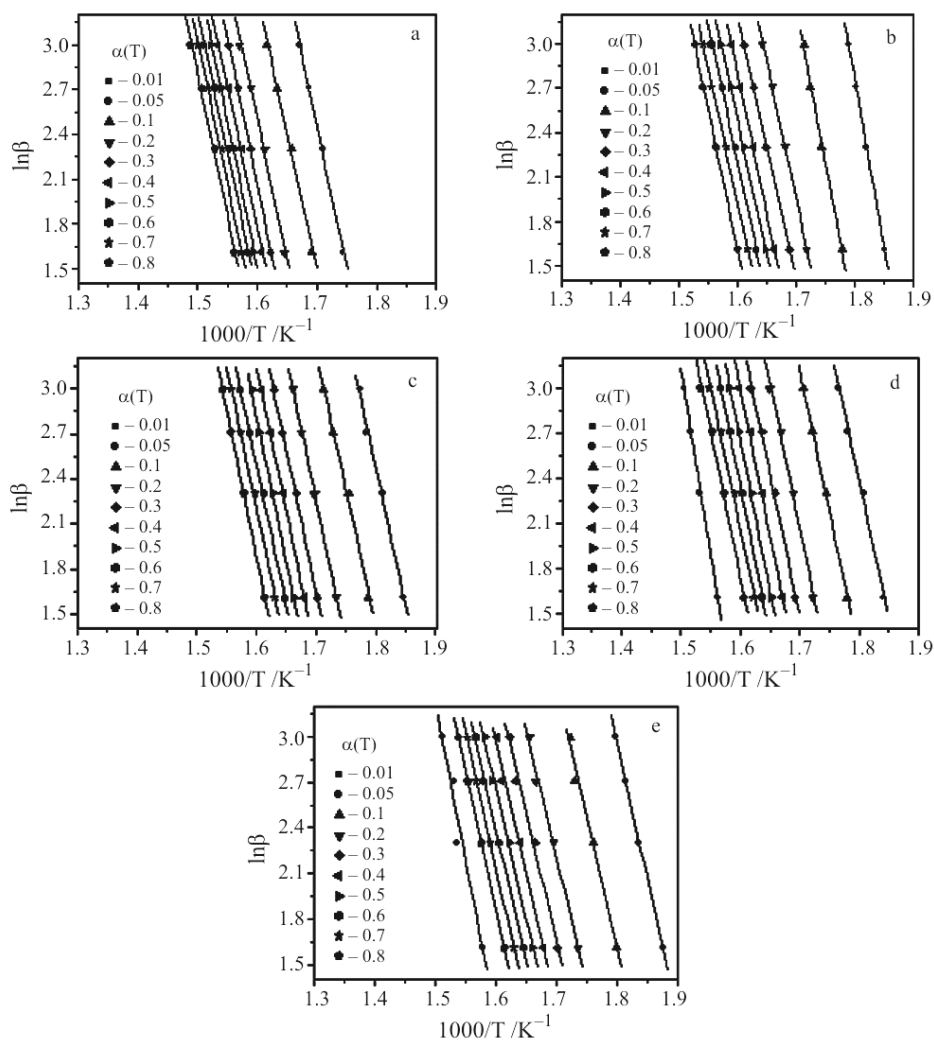
$$\ln\beta = \ln\left[Af(\alpha)\frac{d\alpha}{dT}\right] - \frac{E}{RT} \qquad (2)$$

where β is the heating rate, E_a is the apparent activation energy, R is the gas constant, T is the absolute temperature, A is the pre-exponential factor and $f(\alpha)$ is the mathematical expression related to the TG curve.

Table 3 shows reaction limits taken from TG/DTG curves obtained at 5, 10, 15 and 20°C min^{-1} in nitrogen atmosphere which were employed to obtain E_a. For each fixed fractional conversion (α), $0.1 \leq \alpha \leq 0.80$, the apparent activation energy E_a was calculated from the slope of $\ln\beta$ vs. $1000/T$ (K^{-1}) plot (Eq. (1)). These plots for the cotton fibers are shown in Fig. 2, which presented correlation coefficients larger than 0.995. It is observed that the fitted lines are nearly parallel, which indicates approximate activation energies at different fractional conversions and consequently implies possible single reaction mechanisms or the unification of multiple reaction mechanisms [14]. According to the isoconversional method, the reaction rate at a constant extent of conversion is only a function of temperature and the independence

Table 3 Temperature range taken from TG/DTG curves to obtain apparent activation energy (E_a), mass loss, average E_a and crystallinity index (X_c) obtained from X-ray diffractograms of white and colored cotton fibers

Fiber	Heating rate/°C min⁻¹	Temperature range/°C	Mass loss/%	Average E_a/kJ mol⁻¹	X_c/%
White	5	216–560	87.6		
	10	223–560	87.3		
	15	233–560	87.1	150.4±3.6	77.0
	20	244–560	88.4		
Ruby	5	180–560	75.1		
	10	186–560	72.6		
	15	188–560	73.9	151.7±12.3	77.0
	20	190–560	73.5		
Beige	5	182–565	77.8		
	10	185–565	77.5		
	15	189–565	78.2	150.1±4.1	77.0
	20	190–565	77.1		
Brown	5	175–560	76.4		
	10	183–560	74.1		
	15	187–560	75.5	151.3±4.4	75.0
	20	190–560	76.5		
Green	5	175–550	82.0		
	10	178–550	84.8		
	15	180–550	81.7	137.7±4.5	63.0
	20	181–550	83.0		

Fig. 2 $\ln\beta$ *vs*. $10^3/T$ plots for cotton fibers: a – white, b – ruby, c – beige, d – brown and e – green
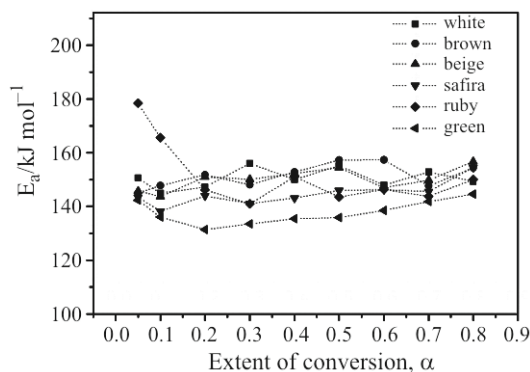
Fig. 3 Dependence of the activation energy on the extent of conversion obtained from isoconversional method regarding the thermal decomposition of white and colored cotton fibers
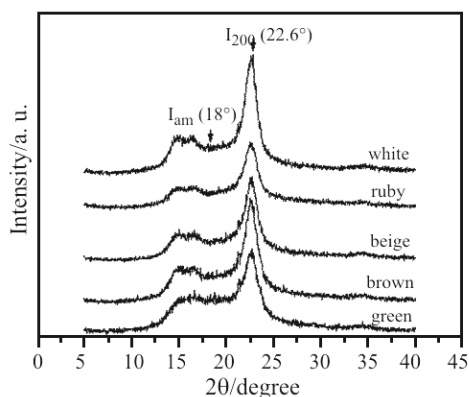

Fig. 4 X-ray diffraction patterns of white and colored cotton fibers

of E_a from α and T may be tested by determining E_a at various α [15, 16]. The E_a vs. α plot of cotton fibers is shown in Fig. 3. In general, the activation energy changed with increasing degree of conversation for all cotton fibers. This variation in E_a values was expected because when more than one degradation mechanism takes place, energy will be not always constant [17]. The average E_a values obtained for cotton fibers were lower than those data reported for jute (184.2±5.8), kenaf (170.3±1.6), cotton stalk (169±5.1), hemp (177.9±3.9) [18]. These differences could be related to chemical composition and structural differences of respective fibers. The average E_a values obtained for all colored cotton fibers except for the green cotton fiber were nearly the same than that obtained for the white cotton fiber. The lowest value of E_a of the green fiber can be due to its lower crystallinity (Table 3). The crystallinity indexes were calculated from X-ray diffractograms shown in Fig. 4. There is a coherent correlation between the activation energy and the crystallinity index of the studied cotton fibers, i.e. the higher crystallinity index values are standing together with higher E_a values.

Conclusions

The white cotton fiber presents higher thermal stability and higher E_a value than colored cotton fibers. There are no significant differences in the initial temperature of degradation in air or nitrogen atmosphere for the same type of fiber. Chemical composition and crystallinity index had influence on the thermal degradation behavior of the studied cotton fibers.

Acknowledgements

References

1 X. Zhang, M. D. Do and A. Bilyk, Biomacromolecules, 8 (2007) 1881.
2 M. A. S. A. Samir, F. Alloin, J. Y. Sanchez and A. Dufresne, Biomacromolecules, 6 (2005) 612.
3 A. K. Mohanty, M. Misra and L. T. Drzal, J. Polym. Environ., 10 (2002) 19.
4 B. L. Browning, Methods of Wood Chemistry; Wiley, New York 1967, p. 499.
5 V. Alvarez and A. Vázquez, Polym. Degrad. Stab., 84 (2004) 13.
6 V. Alvarez,.E. Rodrigues and A. T. Vázquez, J. Therm. Anal. Cal., 85 (2006) 383.
7 P. Aggarwal, D. Dollimore and K. Heon, J. Thermal Anal., 50 (1997) 7.
8 Y. Dutt, X. D. Wang, Y. G. Zhu and Y. Y. Li, Plant Breeding, 123 (2004) 145.
9 Y. H. Xiao , Z. S. Zhang, M. H. Yin, M. Luo, X. B. Li and L. H. Pei, Biochem. Biophys. Res. Commun., 358 (2007) 73.
10 M. E. Brown, D. Dollimore and A. K. Galwey, Reaction in the Solid State: Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam 1980, p. 22.
11 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1995) 1881.
12 J. H. Flynn and L. A. Wall, J. Nat. Bur. Stand., 70 (1966) 487.
13 J. H. Flynn and L. A. Wall, J. Polym. Sci. Pt. B, 4 (1966) 323.
14 J. H. Flynn, J. Thermal Anal., 34 (1988) 367.
15 J. H. Flynn, Thermochim. Acta, 300 (1997) 83.
16 S. Vyazovkin and C. A. Wight, Int. Rev. Phys. Chem., 17 (1998) 407.
17 J. H. Chan and S. T. Balke, Polym. Degrad. Stab., 57 (1997) 135.
18 F. Yao, Q. Wu, Y. Lei, W. Guo and Y. Xu, Polym. Degrad. Stab., 93 (2008) 90.