Thermochimica Acta, 132 (1988) 101-109
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

THERMOGRAVIMETRIC ANALYSIS OF FLAX FIBRES

H.S.S. SHARMA *

Plant Pathology Research Division, Department of Agriculture for Northern Ireland, Newforge Lane, Belfast BT9 5PX (Northern Ireland)

K. KERNAGHAN

Lambeg Industrial Research Association, Lambeg, Lisburn BT29 4RJ (Northern Ireland)

(Received 14 December 1987)

ABSTRACT

An increase in the heating rate of thermogravimetric analysis from 5 °C min^{-1} to 150 °C min^{-1} displaced the integral curves towards higher temperature depending on the amount of residual non-cellulosic polysaccharides present along with the fibre cellulose. The differences in the quality of fibres may be detected by quantitative estimation of the differences in the thermal spectrum. Sequential processing of the grey fabric with NaOH, NaOCl, H_2O_2 and $NaClO_2$ decreased the content of an amorphous fraction in the fabric samples. This may have been a result of the loss of the amorphous non-cellulosic components of the fibres and the degradation of the unordered regions of the flax fibre. However, mercerisation at each stage of processing of the fabric samples revealed an increase in the amorphous fraction, confirming the decrease in crystallinity. Mercerised fabric may be more susceptible to thermal degradation than unmercerised fabric.

INTRODUCTION

The physical and chemical properties of celluloses have been examined [1]. Most of the earlier work relates to cotton cellulose for textiles and ligno-celluloses for paper making. The physicochemical properties of linen cellulose complex were examined by Butterworth and Elkin [2]. During retting and scutching of flax fibres, most of the non-cellulosic components are removed. However, the fibres may contain as much as 25% of hemicellulose, pectin and lignin [3,4]. These fibres are further processed by alkali boil followed by peroxide treatment. It is known that many of the processes involved in the production of linen change the properties of the fibres by removal of non-cellulosic material and by alteration of the physical condition of the remaining cellulose component. These changes are usually

---

* Offprint requests should be sent to H.S.S. Sharma.

0040-6031/88/$03.50

detected during the determination of fibre fineness, viscosity and degree of polymerisation [5].

The thermal analysis of cellulose in cotton fibres has been studied extensively [6,7]. Studies on the influence of crystallinity on the thermal properties of cellulose have produced conflicting results, because the results obtained, especially from thermal analysis, are difficult to correlate owing to differences which exist between different types of amorphous cellulose, e.g. degree of polymerisation, carboxyl content and carbonyl content. Cabradilla and Zeronian [8] studied the relationship between crystallinity and thermal behaviour of a cellulose sample. Flax fibre is highly crystalline [9] and the non-cellulosic component of the fibre influences the physical and chemical characteristics. Some of the physical changes in flax fibres brought about by mercerisation were described by Herzog [9] and later by Sponsler and Dore [10], but there is little information on the effect of mercerisation of flax fibres on the degree of decrystallisation and on the changes in the thermal properties of the treated fibres. The presence of the residual polysaccharide and lignin in the fibre may influence the thermal stability of the structural cellulose of the flax fibre. The present investigation is designed to study the differences in thermal stability of fibres at different heating rates and the changes which occur in the thermal spectrum and in crystallinity as a result of flax processing.

MATERIALS AND METHODS

The fibres used in this investigation were of the following types: good quality, Belgian water-retted fibre and Continental, dew-retted fibre. Since processing of flax fibre is easier in a fabric form, grey fabric woven from dew-retted fibre was used.

Fabric processing

The grey fabric samples (16) were given a sequential treatment of NaOH, NaOCl, H_2O_2 and $NaClO_2$. The fabric samples (400 g) were first treated with NaOH solution (2 g l^{-1}) containing the sequestrant ethylenediaminetetraacetic acid (EDTA, Trilon TB, BASF; 2.6 ml l^{-1}) and a surfactant Warcoadet K (anionic, 0.1 g l^{-1}) in a fabric : liquor ratio of 1 : 10 maintained at 90 °C for 2 h. They were then washed in running cold water for 30 min., prior to partial bleaching with sodium hypochlorite solution (15 ml^{-1}) (2 g l^{-1} available Cl_2 at 20 °C in a fabric : sodium hypochlorite solution ratio of 20 : 1 for 2 h). The samples were again washed in running cold water for 1 h to remove all traces of chlorine and were then dried overnight at 20 °C. They were further bleached in a solution containing sodium carbonate (7.5 g l^{-1}), sodium silicate (7.5 g l^{-1}), hydrogen peroxide (16.5 ml l^{-1}) (130 vol) and EDTA (2.6 ml l^{-1}). The sodium carbonate, sodium silicate and EDTA were dissolved in water at 40 °C and then the hydrogen peroxide was added and the temperature was raised to 85 °C for about 90 min. The bleached fabric samples were again washed and dried as already described, then treated with sodium chlorite solution (1 g l^{-1}) to enhance their whiteness. For this treatment the pH of the liquor was adjusted to 4 with nitric acid (3.1 ml l^{-1}) and the fabric : liquor ratio was maintained at 1 : 10 (liquor : sample) at 90 °C for 1 h. At each stage of the sequential treatment, half of the fabric samples were also mercerised in NaOH (15%) at 20 °C for 2 h in a stoppered glass bottle. The alkali was filtered off and the samples were washed in several changes of distilled water before being steeped in 0.1% acetic acid for 15 min. The samples were rewashed in water until they were free of acetic acid and were then dried at room temperature [1]. All the treatments including the controls were done twice.

Moisture regain

Moisture regain is the amount of moisture absorbed by the dried material, expressed as a percentage of the dry weight. The dry weights of the fibres were obtained after drying in an oven maintained at 105 °C for 24 h. The dried samples were exposed for a week to air at 20 °C and 65% RH. The sorption ratio (SR) is defined as the ratio of moisture regain of the sample to that of the starting material at the same relative humidity and temperature. Amorphous fraction F_{am} was calculated according to Valentine's equation [11], $F_{am} = SR/2.6$. The sorption ratio of completely accessible (amorphous) cellulose is 2.60; this corresponds to a moisture regain of about 19.3% at 65% RH at 20 °C [12].

Fluidity

The fibre samples were separated into a fibrous state and cut into 1 cm lengths. The fluidity test was carried out in a controlled environment maintained at 20 °C and 65% RH. The non-cellulosic components of the fibre samples were extracted by boiling in 2% w/v NaOH for 4 h. The fluidity n of the solutions of the fibre samples (2 g) in cuprammonium hydroxide (100 ml) were determined viscometrically to study the differences in the cellulosic component of the fibres retted by different means [2].

Thermogravimetric (TG) system

The samples were ground to pass through a 10 mesh screen and sample weights used ranged between 3 and 5 mg. Fibre samples were suspended from a Stanton Redcroft microbalance with a platinum wire. Changes in sample mass were converted to a recorded voltage output using a Stanton

Redcroft TG 750. A temperature programmer (Dats 2), a computer-controlled recorder and an atmospheric controlling system were also connected to the TG system. The TG system was then flushed with air at 10 ml $\min^{-1}$. The TG runs were set 5 and 150 °C $\min^{-1}$ from room temperature to the end point temperature (1000 °C) for the dew-retted and water-retted fibres. All the fabric samples were tested at a temperature rise of 20 °C $\min^{-1}$. At the end point of each run, the residual samples were discarded and the crucible was cleaned by firing in air at about 600 °C. The treatments were done twice.

RESULTS

Physical characteristics of the fibre and fabric samples

The moisture regain was significantly ($P < 0.01$) higher for water-retted fibre than for dew-retted fibre (Table 1). The reduction in caustic weight loss of dew-retted fibre was significantly ($P < 0.01$) higher than water-retted fibre or the fabric samples. The fluidity of water-retted fibre was slightly higher than that of dew-retted fibre. However the fluidities for both types of fibre were low (Table 1). From the determination of the amorphous fraction it was apparent that fibres of the mercerised fabric samples absorbed more moisture from the atmosphere than fibres of the non-mercerised fabric samples (Table 2). Fibres of the non-mercerised fabric contained a smaller amorphous fraction than fibres of the mercerised fabric. During the fabric processing, the amorphous fraction present in the sample was reduced and the lowest fraction was detected after the chlorite treatment (Table 2).

Effect of different heating rates on decomposition temperature

The dew- and water-retted fibres decomposed and pyrolysed at near 329 °C and 321 °C, respectively, when subjected to a heating rate of 5 °C $\min^{-1}$. However, the peak decomposition temperatures advanced further to

TABLE 1

The fluidity n, moisture regain (%) and caustic weight loss (%) of the dew-retted (DR), water-retted (WR) and the grey fabric.

Samples	Fluidity	Moisture regain	Caustic weight loss
DR	1.2	9.1	25.1
WR	1.5	9.3	23.0
Fabric	1.2	8.4	23.5
SE of means		0.06	0.14

TABLE 2

The change in amorphous fraction F_{am} during the sequential treatment of the fabric samples with NaOH (B), NaOCl (D), H_2O_2 (P) and $NaClO_2$ (C) and mercerisation at each stage of processing

Fabric treatment	F_{am} (before mercerisation)	F_{am} (after mercerisation)
B	0.36	0.41
D	0.36	0.43
P	0.35	0.42
C	0.34	0.43

TABLE 3

The active temperature of pyrolysis, weight loss (%) and char (%) of the dew-retted (DR) and water-retted (WR) fibre samples at two rates of heating (5 and 150 °C min^{-1})

Heating rates (°C min^{-1})		Temp. of active pyrolysis (°C)			Weight loss (%)	Char (%)
		I	M	F		
5	DR	210	329	350	65	0
	WR	210	321	350	56	8
150	DR	250	347	410	67	12
	WR	275	394	475	73	10

I = initial; M = maximum; F = final.

TABLE 4

The peak temperature (°C) of active pyrolysis (primary peak, PP; shoulder to the primary peak, SPP; secondary peak, SP), weight loss (%) during the decomposition char (%) remaining at the end of the analysis of the fabric samples (untreated (UT), sequentially treated with NaOH boil (B), NaOCl dip (D), hydrogen peroxide (H), chlorite (C) and mercerisation (merc) by NaOH treatment at each stage of the fabric treatment)

Sample	Temperature of active pyrolysis (°C)			Weight loss (%)		Char (%)
	PP	SPP	SP	PP+SPP	SP	
UT	330	–	398	56	16	0
UT merc	329	–	–	65	–	0
B	334	–	–	68	–	0
B merc	326	–	–	62	–	0
D	336	–	–	62	–	0
D merc	334	336	445	80	9	0
H	341	–	–	69	–	12
H merc	326	328	430	77	11	0
C	338	–	–	61	–	10
C merc	318	319	426	79	8	0

347 °C and 394 °C for dew- and water-retted fibres at a higher heating rate of 150 °C min^{-1} (Table 3). Similarly weight losses were higher at the higher heating rate for both dew- and water-retted fibres. The pyrolysis of the fibre samples at higher heating rates also increased the amount of char remaining at the end of the TG run.

Thermogravimetric analysis of the fabric

The treatment of the grey fabric material with NaOH boil, followed by an NaOCl dip, did not change the peak decomposition temperature even though the weight loss was slightly reduced. At the end of the pyrolysis, char was not detected after treatment of NaOH followed by sodium hypochlorite. On treatment of the boiled and dipped fabric samples with peroxide and chlorite, the main decomposition temperatures shifted to higher values: 341 and 338 °C for bleached and chlorite-treated samples, respectively, (Table 4). The weight losses at the active decomposition peaks were higher than in the control samples and the char remaining at the end of the pyrolysis was

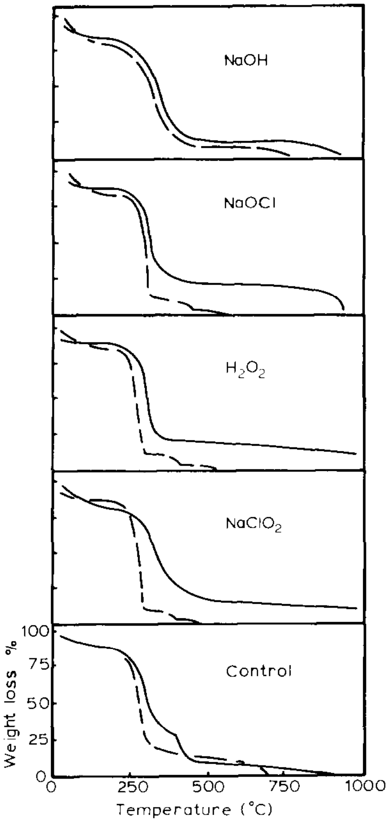

Fig. 1. Thermogravimetric analysis of mercerised fabric samples (— — —) sequentially treated (———) with NaOH, NaOCl, H_2O_2, $NaClO_2$ and untreated samples (control).

between 10% and 12% of the total weight of the samples. On pyrolysis of the untreated fabric samples the active temperature of decomposition was detected at 300 °C (Table 4). At the end of the pyrolysis char was not detected in either the mercerised or the control samples. Mercerisation caused the individual fibres to increase in diameter and consequently to shrink. Derivative thermal analysis of the fabric treated with 2% NaOH followed by mercerisation revealed a slight reduction in the peak decomposition temperature to 326 °C. However, mercerising the fabric at each sequential stage of the treatment of hypochlorite, peroxide and chloride revealed a reduction in the active decomposition temperature and a shoulder appeared just after the main decomposition peak. This was followed by an extra peak at above 400 °C (Table 4). The weight losses were above 77% and 85% for the main peak including the shoulder and the minor peak, respectively. All the mercerised samples were burnt off without leaving any char at the end of the thermal analysis (Fig. 1). Mercerisation of the hypochlorite-treated fabric limited the main TG weight loss to a narrow band (250–320 °C) of temperature compared with the decomposition temperature band (250–475 °C) of the unmercerised-hypochlorite-treated fabric samples. The treatment of the fabric samples with peroxide and chlorite did not change the TG weight loss curve of the mercerised samples (Fig. 1).

DISCUSSION

Derivative thermogravimetry of flax fibres has confirmed that cellulose is the main component [3]. The fluidity measurements and thermal spectra of the fibres obtained by dew retting or water retting suggest that the damage to cellulose fibres during retting is minimal. An increase in the heating rate displaces the integral thermogravimetric curve towards higher temperature depending on the amount of non-cellulosic polysaccharides present in the fibre samples and the results agree with earlier reports [13]. The differences between good- and bad-quality fibres may be detected by thermogravimetric analysis of the samples at a high rate of heating (150 °C min^{-1}) in conjunction with other methods of thermal analysis.

During treatment of the grey fabric with NaOH, some of the residual non-cellulosic polysaccharides were removed, and as a result, the amorphous content of the fibre was reduced. Since significant changes in the weight-loss curve for the treated fabrics only appeared after mercerisation, this process may have influenced the arrangement of the crystalline and amorphous regions of the flax fibre. Just as crystallinity and crystallite dimensions appear to increase together in acid hydrolysis, they also appear to decrease together when cotton is swollen by sodium hydroxide or ethylene amine [14]. Similarly, when flax was mercerised with NaOH, crystallinity was decreased as shown by the increase in the amorphous content.

At the end of the TG analysis, the mercerised fabrics did not form any char, which further confirms that mercerised cellulose is more susceptible to thermal decomposition, because of greater translational and segmental movement [15]. Since hypochlorite is a non-specific oxidizing agent, it will attack the cellulose molecule as well as lignin, the residual cross-linking component of the fibre cellulose. Attack on the cellulose chain during hypochlorite treatment was indicated by the gradual decrease in the α-cellulose content [16]. Consequently, the TG weight loss curve of the mercerised fabric was active in a narrow band of temperature. Mercerisation of the fabric samples prior to hypochlorite treatment resulted in increased degradation of the cellulose. This was confirmed by the appearance of a shoulder near the main peak which was followed by an extra peak after mercerisation of the fabric. Electron microscopic studies carried out on cotton fibres which had been mercerised revealed that the microfibrils were swollen, crimped and disoriented along the length of the fibre [17]. Under scanning electron microscopy, mercurised flax microfibrils were found to be swollen but not crimped (Sharma, unpublished data). In peroxide bleaching of the fabric, perhydroxyl ions solubilize and decolourize the impurities in the cellulose and other residual non-cellulosic components [18].

The uptake of moisture by cellulose varies according to its purity, crystallinity, and possibly, its morphology [19]. The crystalline area in the fibre is encased in a sheath of less crystalline material. The outer sheath has different degrees of disorder in the longitudinal dimension of the elementary fibril. This may be due to concentrations of stress from distortion in the radial fissures during mercerisation. Studies using X-ray analysis have shown that water molecules do not penetrate the crystalline regions [20,21]. Thus the moisture must be absorbed in the less-ordered regions and on the surface of the crystallites. The results from the present investigation confirmed that the rate of moisture uptake changes during the different stages of processing, suggesting that changes in the crystal lattice and decrystallization probably occurred. A few mixed chains of xylan and cellulose may have been present and these may account for the extreme stability of a small proportion of the xylan which resists extraction by NaOH [15].

The sharp definition of the spots on the X-ray diagram shows that untreated flax cellulose molecules are highly oriented in a direction nearly parallel to the longitudinal axis of the fibre, and that the fibre is highly crystalline [3]. The X-ray analysis of the mercerised cotton revealed that changes in the X-ray pattern only take place after treatment of the fabric with a high concentration of NaOH ($\geqslant 13\%$) [22]. As a result of the penetration of the alkali into the cellulose lattice, internal hydrogen bonds are broken and the number of hydroxyl groups is increased by 25%. The effect of mercerisation of flax fibres is to move the molecular chains further apart, thereby increasing the thickness of the fibre. The water–hydroxyl linkages formed during mercerisation may be in the amorphous regions and on the surface of the crystallites of the flax fibre.

ACKNOWLEDGMENT

We thank Mr. J. Bingham for his excellent technical help.

REFERENCES

1 J.T. Marsh, Mercerising, Chapman and Hall, London, 1941, pp. 458.
2 E. Butterworth and H.A. Elkin, Lambeg Industrial Research Association, Res. Inst. Mem. No. 63, 1929, p. 294.
3 A.J. Turner, J. Text. Inst., 39 (1948) 150–161.
4 H.S.S. Sharma, Ann. Appl. Biol., Test Agrochem. Cult., 7 114–115.
5 A.J. Turner, Quality in Flax, Lambeg Industrial Research Association, 1954, pp. 149.
6 J.S. Crighton and A. Das, Thermochim. Acta, 29 (1979) 319–322.
7 M.V. Ramiah, J. Appl. Polym. Sci., 14 (1970) 1323–1337.
8 K.E. Cabradilla and S.H. Zeronian, in F. Safizadeh, K.V. Sarkansen and D.A. Tillman (Eds.), Thermal Uses and Properties of Carbohydrates and Lignins, Academic Press, New York, 1976, pp. 73–96.
9 A. Herzog, Textilber, 1 (1920) 136.
10 O.L. Sponsler and W.H. Dore, J. Am. Chem. Soc., 50 (1928) 1940–1950.
11 L. Valentine, Chem. Ind. (London), (1956) 1279.
12 A.J. Turner, J. Text. Inst., 40 (1949) 857–868.
13 R.D. Cardwell and P. Lunar, Adv. Chem. Ser., 164 (1977) 362–381.
14 N.B. Patil, N.E. Dweltz and T. Radhakrishnan, Text Res. J., 32 (1962) 460–471.
15 R. Whistler and J. Teng, in K.W. Britt (Ed.), Handbook of Pulp and Paper Technology, Van Nostrand Reinhold, London, 1970, pp. 13–17.
16 L.E. Larsen, in K.W. Britt (Ed.), Handbook of Pulp and Paper Technology Van Nostrand Reinhold, London, 1970, pp. 269–274.
17 S.H. Zeronian, J. Appl. Polym. Sci., 9 (1965) 313–332.
18 F.L. Fennell in K.H. Britt (Ed.), Handbook of Pulp and Paper Technology, Van Nostrand Reinhold, London, 1970, pp. 315–321.
19 S.H. Zeronian, M.L. Coole, K.W. Alger and J.M. Chandler, J. Appl. Polym. Sci., Appl. Polym. Symp., 37 (1983) 1053–1069.
20 L. Valentine, J. Polym. Sci., 27 (1958) 313.
21 P.H. Hermans and A. Weidinger, J. Polym. Sci., 4 (1949) 135.
22 W.D. Bancroft and J. Calkin, J. Phys. Chem., 39 (1935) 1245.