Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 117–121

THERMAL BEHAVIOR OF CELLULOSE FIBERS WITH ENZYMATIC OR Na_2CO_3 TREATMENT

J. J. Suñol[1*], *D. Miralpeix*[1], *J. Saurina*[1], *F. Carrillo*[2] *and X. Colom*[2]

[1]Grup de Recerca en Materials i Termodinàmica, Campus Montilivi, Universitat de Girona, 17071 Girona, Spain
[2]EUETIT - Universitat Politècnica de Catalunya, 08222 Terrasa, Spain

New regenerated cellulose fibers were developed during the last decades as environmentally friendly systems. In this work, three fibers: lyocell, modal and viscose were subjected to an enzymatic treatment. Likewise, different lyocell fibers were washed in a Na_2CO_3 solution under severe conditions. Analysis was performed by means of differential scanning calorimetry, thermogravimetry and scanning electron microscopy. In all samples, at low temperature, water desorption was detected. Furthermore, thermal analysis shows wide exothermic processes that began between 250 and 300°C corresponding to the main thermal degradation and it is associated to a depolymerization and decomposition of the regenerated cellulose. It is accompanied with mass more than 60% mass loss. Kinetic analysis was performed and activation energy values 152–202 kJ mol^{-1} of the main degradation process are in agreement with literature values of cellulose samples.

Keywords: *cellulose fibers, degradation, DSC, lyocell, modal, TG, viscose*

Introduction

During last decades, the scientific and technological interest in the development of environmentally friendly systems based in the use of non-aqueous solvents for dissolution of cellulose has increased [1–3]. Pollutant emission is one of the main problems in the textile industry of manufactured fibers from regenerated cellulose. There have been numerous efforts to find an alternative to the use of carbon disulphide, CS_2, for regenerated cellulose fiber production [4–6]. Nowadays, the most promising is the NMMO process [7, 8], which uses the monohydrate of N-methylmorphine-N-oxide, and offers a viable commercial alternative to the other proposed production methods [9]. No derivation, as alkalinization and reaction with carbon disulphide in the case of xanthate process is required [10]. Based on the lyocell technology, also other cellulose products, such as membranes, filaments and films, are currently developed or are already commercially produced [11, 12]. For example, the production predicted in 2005 is approximately of 300,000 tons [13].

When cellulose fibers are thermally treated on heating, a series of physical changes occur. The physical properties affected include enthalpy, mass, color, strength, crystallinity degree and orientation [14]. Furthermore, several chemical reactions are interrelated with the physical changes. The analysis of the thermal degradation and stability of cellulose fibers have been performed by many authors [15–17]. In this work, we analyze the thermal behavior and degradation kinetics of several samples: lyocell, viscose and modal under different treatment conditions. Furthermore, it is important to control if cellulose fibers present fibrillation that adversely affects the launderability of the product in textile end uses.

Experimental

Materials and methods

Lyocell (Tencel) as well as conventional viscose and modal fibers, with an average linear density of 1.7 dtex (0.17 g/1000 m), were analyzed. All products were obtained from the cellulose polymerization and submitted by textile industries. Two lyocell fibers were subjected to an enzymatic treatment: fabric sample+enzymes, L-A, and fabric sample with industrial fibrillation+enzymes, L-B. Comparison with viscose, V, and modal, M, fibers treated with enzymes was performed. Enzymatic treatment is performed to improve mechanical properties. Furthermore, other lyocell samples were washed in a Na_2CO_3 solution to analyze related wear under aggressive conditions: L-C (non-fibrillated), L-D (fibrillated) and L-E (fibrillated+enzymatic treatment). Details on sample preparation were given in [14–18].

Thermal treatments were performed by means of differential scanning calorimetry (DSC) and thermogravimetry (TG). DSC analysis was conducted using a Mettler TA4000 thermo-analyzer coupled with a low temperature DSC30 calorimeter. TG was performed in

---

[*] Author for correspondence: joanjosep.sunyol@udg.es

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

a TGA851 Mettler Toledo equipment. The fabric sample was cut to obtain fibers and ~3 mg of sample was used. The DSC and TG curves were usually obtained in the temperature range of 50 to 400ºC at a heating rate of 10 K min^{-1}. Air atmosphere was used because air is the real work condition of the fibers.

The microstructure of samples was characterized by scanning electron microscopy (SEM) in a Zeiss DSM 960 device. Resolution was 4.5 nm, acceleration voltage was 15 kV, and working distance was between 15 and 25 mm. Samples had been sputtered previously with a K550 Emitech equipment.

Results and discussion

The dynamic thermal behavior of the samples was analyzed using heat flow DSC. Figure 1 shows the DSC scans of fibers subjected to enzymatic treatment. The samples were heated to temperatures reaching 400ºC. At low temperature, an endothermic process was detected, with a maximum at about 80ºC. This process is associated to water desorption [19] and caused by the hydrophilic behavior of cellulose polymers. Re-heating the samples, previously heated until 200ºC and cooled to room temperature, this process disappears. Likewise, if a second heating is performed after one hour in air atmosphere the process is present, as found in other cellulose samples [19] and associated to a new water absorption–desorption. Moreover, the broad exothermic polymer decomposition process begins between 250 and 300°C. Figure 2 corresponds to the DSC curves of samples treated with Na_2CO_3. In this case, fibrillation produce more changes than enzymatic treatment. Furthermore, the onset temperature decreases about 8ºC.

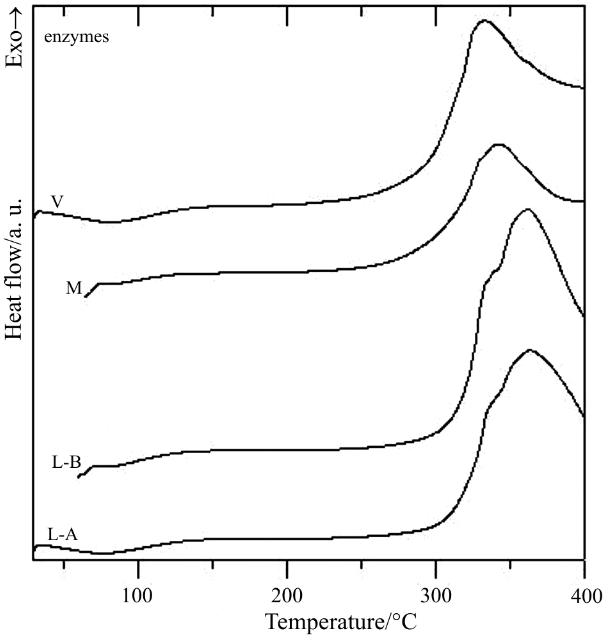

Fig. 1 DSC scans of textile fibers with enzymatic treatment: L-A – lyocell, L-B – fibrillated lyocell, M – modal and V – viscose

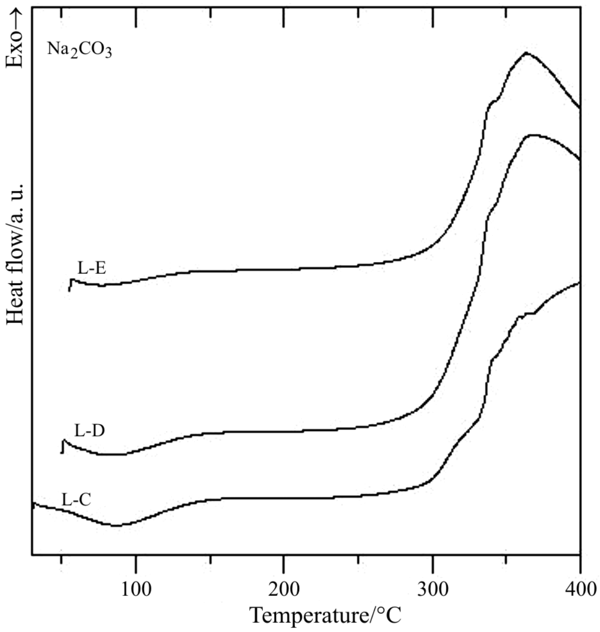

Fig. 2 DSC scans of textile lyocell fibers after Na_2CO_3 treatment: L-C, L-D – fibrillated and L-E – fibrillation and enzymatic treatment

In all samples, the DSC shape of the decomposition part indicates the presence of several processes. Generally, the thermal reactions involved on heating over 200ºC the cellulose fibers can be grouped in different reactions overlapped related with the decomposition of the glycosyl units of cellulose by evolution of water, carbon dioxide and carbon monoxide and to depolymerization of the molecule by cleavage of glycosil units to form mainly 1,6-anhydro-β-D-glucopyranose [20]. Likewise, parameters as heating rate or atmosphere influence the decomposition process [21].

The onset and peak temperatures of decomposition, T_0 and T_p, as well as the partial (until 400ºC) normalized enthalpy, obtained from the DSC area, are given in Table 1 and compared with data collected in other works [14, 22, 23]. A higher onset temperature is associated with higher thermal stability. From thermal analysis, we can state that usually lyocell fibers are the most thermally stable if compared with modal and viscose. Other advantages of lyocell are its excellent mechanical properties: high modulus and tenacity, specially in wet environments [24]. Na_2CO_3 produces a diminution (about a half) of the enthalpy area. The solar radiation provokes a diminution, about 10ºC and 25%, on thermal stability and enthalpy.

Mass loss during heating was analyzed from TG measurements. Figure 3 shows the mass loss during

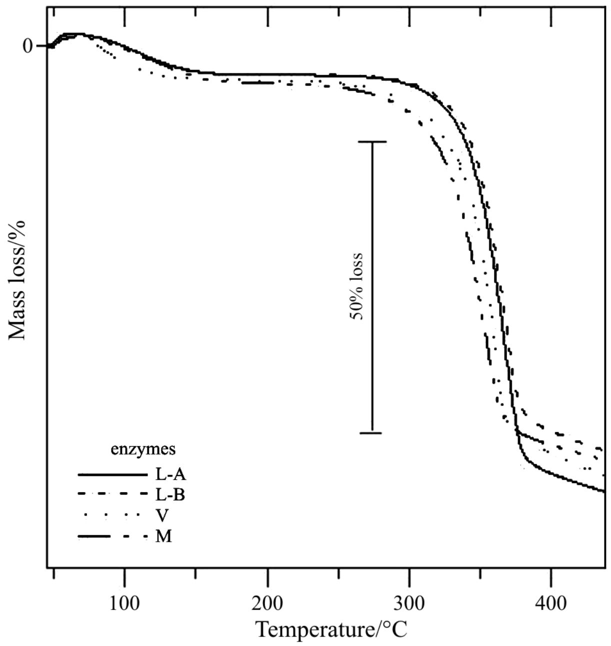

Fig. 3 TG scans of textile fibers with enzymatic treatment: L-A – lyocell, L-B – fibrillated lyocell, M – modal and V – viscose

Table 1 Characteristic parameters of thermal decomposition obtained from DSC and TG scans. (SOL and UV indicates subjected to solar and UV degradation, respectively)

Sample	T_0/°C	T_p/°C	Area/J g^{-1}	T_0/°C (TG)
lyocell	305	365	1459	315
modal	296	351	1610	297
viscose	282	350	1748	297
L–UV	298	356	1850	305
M–UV	297	347	1969	297
V–UV	285	345	1852	288
L–SOL	294	354	1543	302
M–SOL	287	352	1532	294
V–SOL	272	347	1489	286
L-A	306	360	1912	312
L-B	308	358	1737	316
M	282	343	1251	297
V	280	328	1671	293
L-C	298	–	852	306
L-D	297	362	1034	308
L-E	300	362	875	317

heat treatment in air atmosphere of samples treated with enzymes. The overall mass loss can be divided into different stages [22]. The first mass loss that occurs at about 100ºC is generally attributed to the evaporation of sorbed water from the fibers. Re-heating the samples, in the same way as performed by DSC confirms it. The main mass loss represents more than 60% of mass loss. The beginning shows a slow mass decrease represented by a shoulder. The onset temperature is given in Table 1. The results are consistent with DSC analysis. Finally, the last process beginning at about 350ºC corresponds to prolonged char oxidation stages and the slope diminishes.

Figure 4 corresponds to TG scans of lyocell fibers washed in a Na_2CO_3 aggressive solution. The general shape of the TG curves indicates a similar behavior to the samples treated with enzymes. The mass loss is lower (about 10%) than for lyocell fibers non-treated with enzymes. Furthermore, sample L-E is the most stable.

The kinetics of the degradation process was performed from the non-isothermal TG experiments using the Broido formula [25] as shown in Eq. (1):

$$\ln\left[\ln\left(\frac{1}{\alpha}\right)\right]=-\frac{E}{RT}+\left(\frac{RZ}{E\beta}\right)T_{\mathrm{m}}^{2} \qquad (1)$$

where Z is a frequency factor, β is the heating rate, T_m is the temperature at the maximum reaction rate and E is the activation energy. The last term of Eq. (1) is considered as a constant. The term α corresponds to:

$$\alpha=\frac{m-m_{\mathrm{e}}}{m_0-m_{\mathrm{e}}} \qquad (2)$$

where m_e being the mass at the end of the process and m_0 being the mass at the beginning. Figure 5 shows the differential thermogravimetry (DTG) curves of two sam-

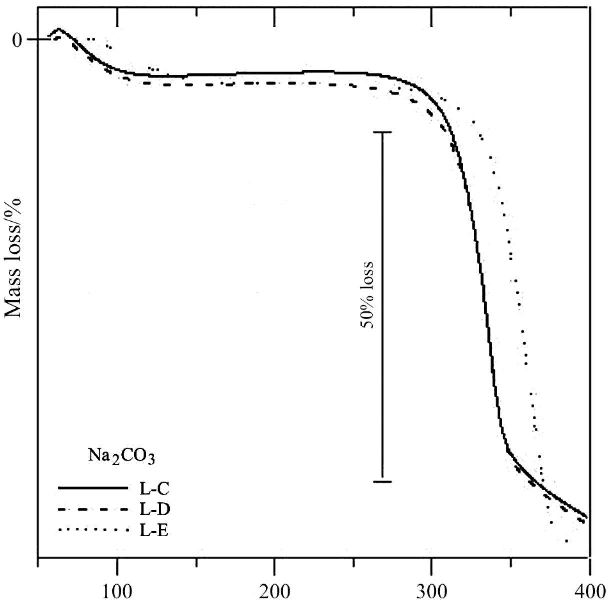

Fig. 4 TG scans of textile lyocell fibers after Na_2CO_3 treatment: L-C, L-D – fibrillated and L-E – fibrillation and enzymatic treatment

ples. The main process is related with the beginning of the degradation process. This kinetics of this process was used in the range around the DTG peak. The activation energy values are shown in Table 2 and compared with values obtained with other authors [17, 26–29]. The values are similar to the cellulose. A high value of E and T_m points to a stable substance because the process begins at higher temperature and the energy is related to the reaction of degradation of the substance. Samples treated with Na_2CO_3 have high energy but the decrease in the degradation temperature provokes lower thermal stability. Ulterior analysis of isothermal data can confirm this behavior.

Figure 6 shows the micrographs corresponding to lyocell (a) and modal (b) fiber after thermal treatment in the DSC. The fibers maintain their aspect but the diameter of the fiber is reduced at about a half if compared with the original (from ~12 to ~6 μm). The same phenomenon is observed in the other samples. Micrographie (c) corresponds to viscose fiber before DSC treatment. In this study, fibrillation effect was not produced. It is known that fibers produced with the cellulose/NMMO/water system fibrillate under condition of wet abrasion [30] and there are several methods to reduce the tendency of lyocell fibers to fibrillate [31].

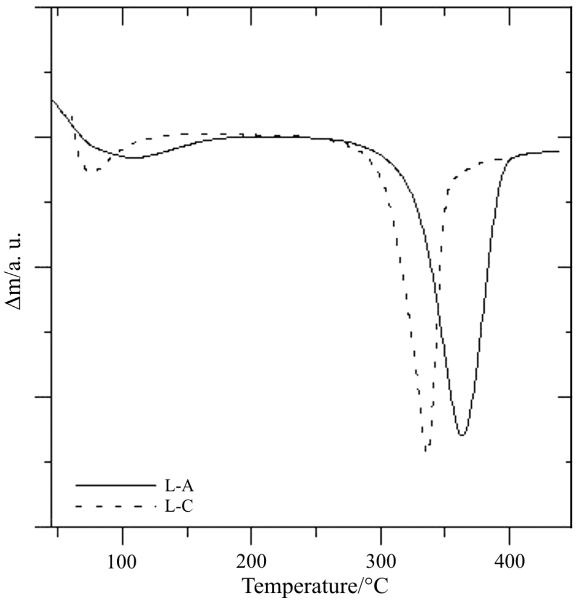

Fig. 5 DTG scans of textile lyocell fibers L-A and L-C

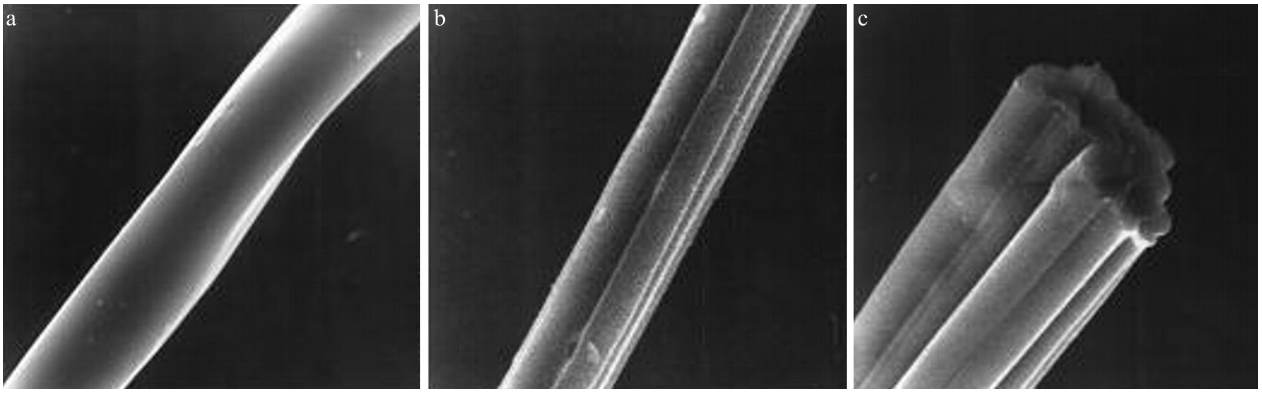

Fig. 6 SEM micrographs corresponding to fiber: a – lyocell, b – modal and c – viscose

Table 2 Activation energy, E, values and characteristic T of the main degradation process from this work and the literature

Sample	Atmosphere	T_m/°C	E/kJ mol^{-1}	Reference
cellulose	nitrogen	339	182	26
cellulose	helium	not given	203	27
retted flax	helium	377	188	27
cellulose	air	355–365	193–228	28, 29
flax	air	324.57	123.7	17
flax	nitrogen	319.89	117.2	17
retted flax	air	344.13	202.9	17
retted flax	nitrogen	348.99	181	17
lyocell-A	air	363	176	this work
lyocell-B	air	367	174	this work
viscose	air	352	170	this work
modal	air	347	152	this work
lyocell-C	air	336	202	this work
lyocell-D	air	335	200	this work
lyocell-E	air	362	191	this work

Conclusions

Lyocell, viscose and modal fibers are analyzed with enzymatic or Na_2CO_3 treatment. The process involved on heating were water desorption, as confirmed by ulterior cooling and reheating process, and complex thermal decomposition. Lyocell fibers are the most thermally stable if compared with modal and viscose. The main mass loss represents more than 60% of mass loss and the decomposition that continues after 350ºC with a lower mass loss slope is related to prolonged char oxidation stages. Furthermore, from the kinetic analysis of non-isothermal data the activation energy of the main degradation process was calculated, varies between 152 and 202 kJ mol^{-1}, values closer to cellulose as found in literature. Combination of high degradation temperature and activation energy is associated to thermal stability. Lyocell fiber usually is the most stable under thermal degradation conditions. Na_2CO_3 aggression provokes higher activation energy but lower degradation temperature. Fibrillation of the fibers was undetected.

Acknowledgements

Financial support from DURSI (project 20001SGR-00190) is acknowledged.

References

1 H. Chanzy, J. Polym. Sci. Polym. Phys., 18 (1980) 1137.
2 A. S. Chegolya, D. D. Grinshpan and E. Z. Burd, Textile Res. J., 59 (1989) 501.
3 Y. K. Hong, K. H. Chung and W. S. Lee, Textile Res. J., 68 (1998) 65.
4 E. M. Aizenshtein, Fibre Chem., 30 (1998) 281.
5 S. P. Papkov, Fibre Chem., 28 (1996) 1.
6 C. L. McCormick and P. A. Callais, Polymer, 28 (1987) 2317.
7 T. Rosenau, A. Potthast, H. Sixta and P. Kosma, Prog. Polym. Sci., 26 (2001) 1763.
8 P. Weigel, J. Gensrich and H. P. Finck, Lenz Ver., 74 (1994) 31.
9 J. Taylor, JDSC, 114 (1998) 191.
10 I. Marini and F. Brauneis, Textilveredlung, 31 (1996) 182.
11 H. P. Fink, P. Weigel, H. J. Purz and A. Bohn, Recent. Res. Dev. Polym. Sci., 2 (1998) 1909.
12 C. Beyer, F. Meister and E. Taeger, Biotechnol., 10 (1999) 38.
13 Chem. Fibres Int., 48 (1998) No. 1.
14 F. Carrillo, Thesis, Universitat Politècnica de Catalunya, 2002.
15 K. Ciesla, H. Rahier and G. Zakrzewska-Trznadel, J. Therm. Anal. Cal., 77 (2004) 279.
16 K. Stanakleinschek, T. Kreze, V. Ribitsch and S. Strnad, Colloids Surf., A, 195 (2001) 275.
17 K. Vandevelde and P. Kiekens, J. Appl. Polym. Sci., 83 (2002) 2634.
18 F. Carrillo, X. Colom, J. Valldeperas, D. Evans, M. Huson and J. Church, Textile Res. J., 73 (2003) 1024.
19 J. J. Suñol, J. Saurina, D. Miralpeix, F. Carrillo and X. Colom, Revista de Química Textil, 156 (2002) 92.
20 F. Shafizadeh, in Cellulose Chemistry and its Application, T. P. Nevell and S. H. Zeronian, Eds, Thomas Percy, Horwood, Chichester, UK 1985, p. 267.
21 N. Marin, A. Krzton, A. Koch, D. Robert and J. V. Weber, J. Therm. Anal. Cal., 55 (1999) 765.
22 J. J. Suñol, J. Saurina, F. Carrillo and X. Colom, J. Therm. Anal. Cal., 72 (2003) 753.
23 F. Carrillo, X. Colom, J. J. Suñol and J. Saurina, Eur. Polym. J., 40 (2004) 2229.
24 I. Marini and E. Firgo, Lenzing Lyocell, Lenzinger Berichte, 9 (1994) 53.
25 A. Broido, J. Polym. Sci. Part A-2: Polym. Phys., 7 (1969) 1762.
26 A. M. A. Nada and M. L. Hassan, Polym. Degrad. Stab., 67 (2000) 111.
27 B. Wielage, Th. Lampke, G. Marx, K. Nestler and D. Starke, Thermochim. Acta, 337 (1999) 169.
28 R. Shing, S. Arora and K. Lal., Thermochim. Acta, 289 (1996) 9.
29 C. M. Tian, H. Z. Guo, H. Y. Zhang, J. Z. Xu and J. R. Shi, Thermochim. Acta, 253 (1995) 243.
30 J. Lenz and J. Schurz, Cellulose Chem. Technol., 24 (1990) 679.
31 S. A. Mortimer and A. A. Péguy, J. Appl. Polym. Sci., 60 (1996) 305.