Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 1, 41–44

THERMAL DEGRADATION OF LYOCELL, MODAL AND VISCOSE FIBERS UNDER AGGRESSIVE CONDITIONS

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Lyocell, modal and viscose fibers were subjected to mercerization or to solar degradation. The ulterior thermal degradation was analyzed by means of differential scanning calorimetry (DSC). Thermal analysis shows wide exothermic processes that began between 250 and 300°C corresponding to the main thermal degradation and are associated to a depolymerization and decomposition of the regenerated cellulose. Thermal degradation was analyzed as a function of concentration and time. Lyocell fiber is the most stable under thermal degradation conditions. Furthermore, mercerized samples are initially more degraded and present a lower thermal stability.

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

Introduction

Cellulose is generally regarded as being the most abundant and useful renewable material, due to its excellent physical properties, such as its specific gravity, gloss and pleasant touch [1]. However, it is known that conventional processes to obtain regenerated cellulose fibers have serious environmental and economical problems. In the typical xanthate process, alcalisation and reaction with carbon disulphide, CS_2, is required [2]. In the xanthate process, the choice of manufacturing conditions during regeneration and coagulation steps leads to diversity of structure and properties of cellulose fibres. Direct coagulation in acid bath leads to regular viscose and when coagulation and stretch occur together, before regeneration and crystallization of cellulose, modal type fibres are manufactured [3]. In addition, CS_2 is known to provoke serious damage to human body upon chronic exposure. For it, the scientific and technological interest in the development of non-contaminant processes with organic solvents of cellulose was increased. N-methyl morpholine-N-oxide (NMMO) monohydrate is an organic solvent able to dissolve natural polymers and already used in the industry of man-made regenerated cellulose fibres [4, 5]. Direct dissolution of cellulose in NMMO monohydrate is established as the well-known lyocell process [6–8]. Based on the lyocell technology, several cellulose products, such as membranes, filaments and films, are currently developed or are already commercially produced [9]. Several studies were performed to compare new lyocell with conventional viscose or modal fibres. Lyocell presents excellent mechanical properties [10], higher degree of crystallinity and molecular orientation [11] and higher thermal stability [12].

Thermal degradation and stability analysis of cellulose have been performed by many authors [13, 14] using calorimetry (DSC) and thermogravimetry (TG) techniques. DSC technique was used in this work to study the thermal behavior of lyocell, modal and viscose fibers under simulated solar radiation or mercerization.

Experimental

Materials and methods

Lyocell, viscose and modal fibres, supplied by Lenzing AG, with an average lineal density of 1.3 dtex (0.13 g/1000 m) were used to develop the experimental analysis. To avoid the uncontrolled influence of added substances, we proceed previously to the fiber purification. Several fibers were introduced in a climatic chamber to simulate 30, 60, 90 and 120 days of solar radiation. Furthermore, other samples were mercerized with sodium hydroxide at different concentrations from 5.0 to 50.0 g/100 mL^{-1}. Details on sample preparation were given in [15].

The dynamic thermal behavior of the samples was analyzed with heat flow DSC. The measurements were made in a DSC 30 Mettler apparatus coupled with a TA4000 thermoanalyser. The calibration of the temperatures and energies was made with standard samples of In and Pb. The samples were heated from 30 to 450°C. The measurements were performed at a heating of 10 K min^{-1} and with synthetic air as a purging gas at a flow rate of 40 mL min^{-1}. From the analysis of DSC

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1388–6150/$20.00

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curves, it was determined the onset temperature of the decomposition and the activation energy of the first degradation process using the Kissinger approach [16]. 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

Information about thermal behavior is obtained from DSC scans. Figure 1 shows the comparison of the DSC scans of lyocell, modal and viscose fibers before and after a mercerization treatment at a concentration of 18.0 g 100 mL^{-1}. The low temperature endothermic process detected, with a maximum at about 80°C is related to water desorption [17]. This water desorption can be explained in terms of migration of bubbles generated in the bulk [18]. Re-heating the samples, previously heated until 100°C and cooled to room temperature, this process disappears as shown for example in lyocell scan. Degraded fibers are more sensitive to water absorption.

At higher temperature a broad exothermic peak begins. The DSC shape of the exothermic part indicates the presence of several processes. In the non-treated fibers, the onset temperature of this process varies between 290 and 300°C. Generally, the thermal reactions involved on heating over 250°C the cellulose fibers can be grouped in different pathways detailed in [19]: decomposition of the glycosil units, depolymerization, oxidation of the products, etc. However, all these reactions can overlap. The process beginning at about 400°C corresponds to prolonged char oxidation stages.

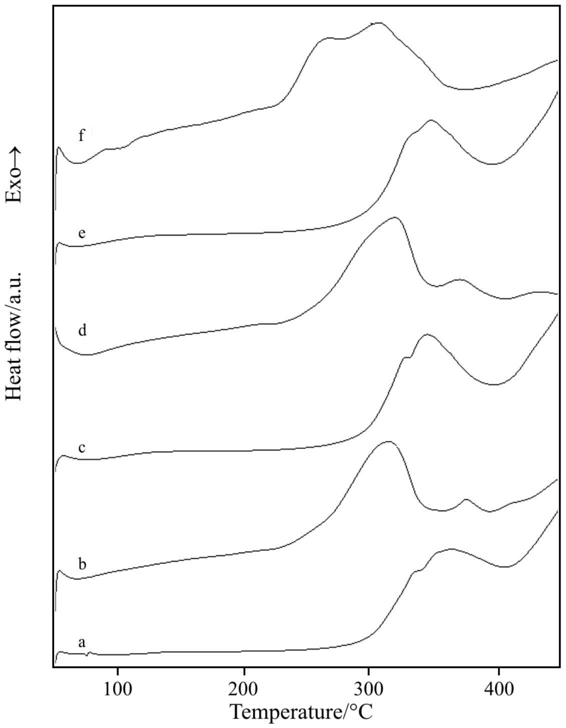

Fig. 1 DSC scans of textile fibers before and after degraded 18.0 g/100 mL NaOH: a – lyocell, b – lyocell degraded, c – modal, d – modal degraded, e – viscose and f – viscose degraded

Temperature values are similar to those reported (between 279 and 295°C) in experiments performed in nitrogen atmosphere in different cellulosic fibers [20]. The onset temperature values as a function of NaOH concentration are given in Fig. 2. The mercerization process causes changes in crystallinity and orientation of fibrils in cellulosic fibres. Previous studies [21] that has been pointed out that caustic concentrations of up to 10 g NaOH/100 mL produce a decrease in crystallinity, and there is evidence of a certain amount of recrystallization under alkaline conditions at lower concentrations. This behavior is in agreement with the high initial onset temperature values obtained at low caustic concentration followed by a noticeable decrease of this parameter at high NaOH concentrations. The higher initial onset temperatures correspond to lyocell fibers. As expected, mercerization provokes a diminution (>50°C) of the onset temperature. The most important diminution corresponds to viscose fiber. Furthermore, the peak temperature of this degradation process is also moved to lower temperatures. This can be explained by the lower orientation and crystallinity of viscose in front of modal and lyocell fibres.

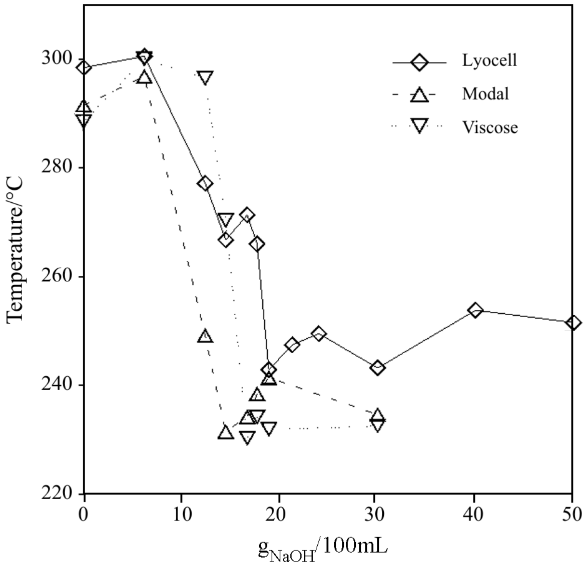

Fig. 2 Onset temperature of the thermal degradation process as a function of NaOH concentration in the previous fiber treatment

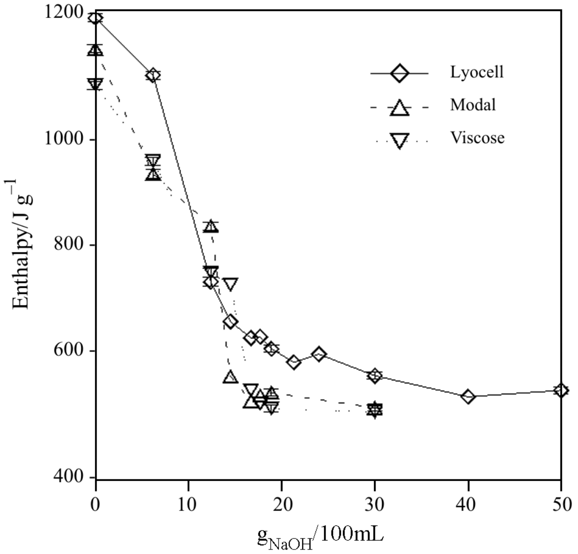

Fig. 3 Enthalpy (J g^{-1}) of the thermal degradation process as a function of NaOH concentration in the previous fiber treatment

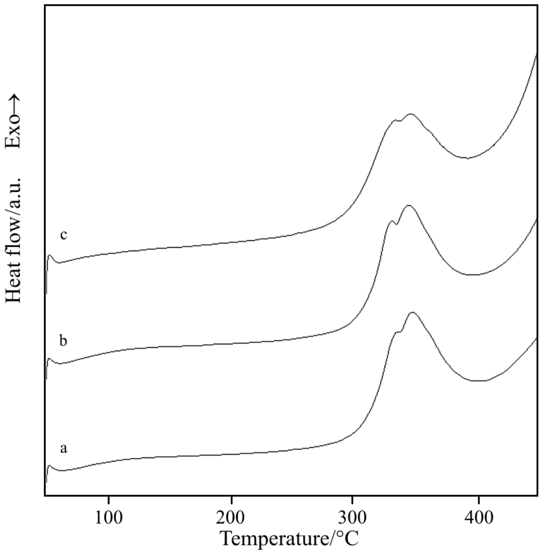

Fig. 4 DSC scans of fibers under 120 days of simulated solar radiation: a – lyocell, b – modal and c – viscose

Figure 3 shows the enthalpy value of the first degradation process. Initial values are between 1050 and 1200 J g^{-1}. As increasing the concentration over 15.0 g mol^{-1} NaOH the enthalpy diminishes at values lower than 650 J g^{-1}. This diminution is produced by the degradation under aggressive conditions. From the data, lyocell fiber is the most thermally stable.

Other lyocell, modal and viscose fibers were subjected to simulated solar radiation. Radiation causes the degradation of cellulose compounds accompanied by depolymerization of the cellulose and formation of compounds with carbonyl and carboxy groups, as well as formation of hydrogen, carbon dioxide, and carbon monoxide [22]. Figure 4 corresponds to DSC scans of fibers subjected to a simulated solar radiation of 120 days. We remark that this degradation does not provoke a significant variation in the onset temperature of the degradation process. The enthalpy value only diminishes at about 12% in all cases after 120 days. Slight diminution of the onset temperature (about 10°C) and a diminution of enthalpy of 25% were found after more than seven months [23]. We can state that the chemically treated fibers are less thermally stable than solar degraded ones.

To analyze the thermal stability of all samples, higher values of the onset temperature and the apparent activation energy of the first degradation process are needed, because structural changes were induced during the degradation process and resultant fibers present a loss of properties [19, 20]. The apparent activation energy, E, for the degradation process of several fibers has been evaluated using the Kissinger equation: $\ln(\beta/T_p^2)$ *vs.* $1/T_p$ with β the heating rate and T_p the peak temperature. The crystallization data have been collected from DSC curves, obtained with different heating rates (2.5, 5, 10, 20 and 40 K min^{-1}). Figure 5 shows the activation energy values obtained. The poor thermal stability corresponds to the mercerized fibers analyzed in this work. In the bibliography the values ranged between 90 and 210 kJ mol^{-1} [13, 20, 24]. We can state that lyocell is the most thermally stable considered the onset temperature and the activation energy of the degradation process. Furthermore, it is known that lyocell is characterized by high crystallinity, long crystallites, high degree of orientation and well-oriented amorphous regions resulting in a very high dry and wet tensile strength, a high wet modulus and high loop tenacity [12, 25]. Viscose fiber presents low thermal stabil-

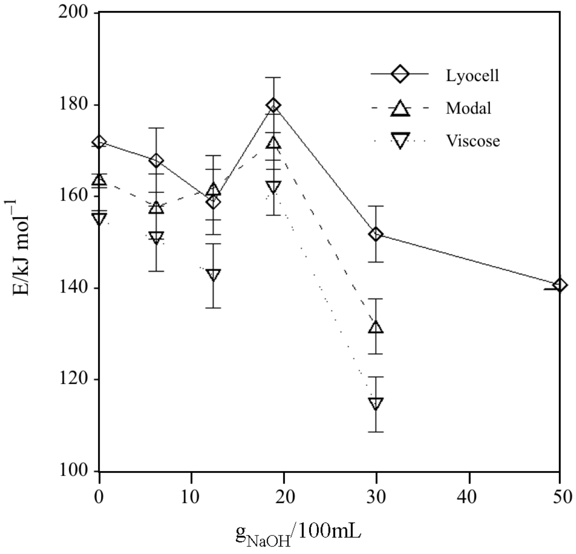

Fig. 5 Apparent activation energy values obtained from Kissinger fittings

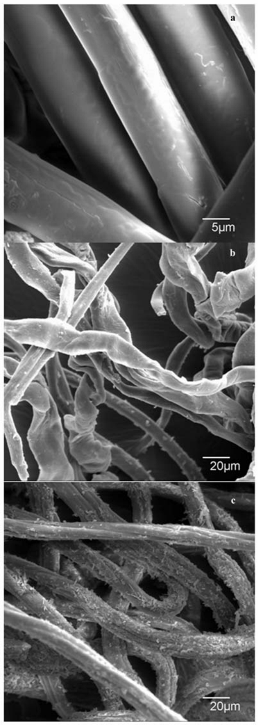

Fig. 6 SEM micrographs corresponding to degraded fibers: a – lyocell, b – modal and c – viscose

ity. Nevertheless, modern viscose fiber production allows significantly reducing environmental difficulties [26]. Viscose textile fibers are special important for processing fabrics for linens and linings.

Complementary morphology analysis by SEM confirms the degradation of the treated fibers. As an example, Fig 6 shows several micrographs of lyocell (a), modal (b) and viscose (c) fibers degraded under aggressive conditions.

Conclusions

Lyocell as well as conventional viscose and modal fibers were performed under NaOH, aggressive conditions and simulated solar radiation. Lyocell, viscose and modal fibers present a similar thermal behavior. The enthalpy of the first degradation process diminishes from 1050–1200 J g^{-1} to values lower than 650 J g^{-1} at concentrations higher than 15.0 g mol^{-1} NaOH. Minor changes were detected in fibers subjected to simulated solar radiation. The activation energy value varies between 180 and 115 kJ mol^{-1}. We can state that lyocell is the most thermally stable, considered the onset temperature and the activation energy of the degradation process, because of their structure: high crystallinity and orientation are less affected by the treatments. Viscose fiber presents low thermal stability. The poor thermal stability corresponds to the mercerized fibers caused by a decrease in the crystallinity of the fibres.

Acknowledgements

Financial support from DURSI 2005-SGR-00201, MAT 2003-00275 and DURSI 2005-SGR-00716 is acknowledged.

References

1 I. S. Kim, J. P. Kim, S. Y. Kwak, Y. S. Ko and Y. K. Kwon, Polymer, 47 (2006) 333.
2 T. Rosenau, A. Pottash, H. Sixta and P. Kosma, Prog. Polym. Sci., 26 (2001) 1763.
3 C. Woodings Editor, Regenerated Cellulose Fibres, Woodhead Publishing Ltd., England, (2001) 199.
4 J. Gassan and A. K. Bledski, J. Appl. Polym. Sci., 71 (1999) 623.
5 E. Marsano, P. Corsini, C. Arosio, A. Boschi, M. Mormino and G. Freddi, Inter. J. Biological Macromolecules, 37 (2005) 179.
6 H. Chanzy, J. Polym. Sci. Polym. Phys., 18 (1980) 1137.
7 J. Lenz, J. Schurz and E. Wrebtschur, J. Appl. Polym. Sci., 35 (1988) 1887.
8 H. Firgo, K. Eibl, W. Kalt and G. Meister, Lenz. Ver., 8 (1994) 81.
9 C. Beyer, F. Meister and E. Taeger, Biotechnol., 10 (1999) 38.
10 I. Marini and E. Firgo, Lenzing Lyocell, Lenzinger Berichte, 9 (1994) 53.
11 K. Stana-Kleinschek, T. Kreze, V. Ribitsch and S. Strnad, Colloids Surf. A, 195 (2001) 275.
12 F. Carrillo, X. Colom, J. J. Suñol and J. Saurina, Eur. Polym. J., 40 (2004) 2229.
13 K. Vandevelde and P. Kiekens, J. Appl. Polym. Sci., 83 (2002) 2634.
14 K. Ciesla, H. Rahier and G. Zakrzewska-Trznadel, J. Therm. Anal. Cal., 77 (2004) 279.
15 F. Carrillo, X. Colom, J. Valldeperas, D. Evans, M. Huson and J. Church, Textile Res. J., 73 (2003) 1024.
16 H. Kissinger, Anal. Chem., 29 (1957) 1702.
17 J. J. Suñol, J. Saurina, D. Miralpeix, F. Carrillo and X. Colom, Rev. Quím. Textil, 156 (2002) 92.
18 T. Kojima, M. Tsuchiya, K. Ishimaru and T. Yamada, J. Therm. Anal. Cal., 80 (2005) 137.
19 F. Shafizadeh, in Cellulose Chemistry and its application, T. P. Newell and S. H. Zeronian, Eds., Thomas Percy, Horwood, UK, Chichester 1985, p. 267.
20 P. Yang and S. Kokot, J. Appl. Polym. Sci., 60 (1996) 1137.
21 X. Colom and F. Carrillo, Eur. Polym. J., 38 (2002) 2225.
22 G. O. Phillips, P. J. Baugh and J. F. McKellar, Interaction of Radiation with Cellulose in the Solid State and Photochemistry of Lignocellulosic Materials, Cyril Heitner, Editor and J. C. Scaiano Editor, Am. Chem. Soc., Washington D.C., USA 1993.
23 J. J. Suñol, J. Saurina, F. Carrillo and X. Colom, J. Therm. Anal. Cal., 72 (2003) 25.
24 J. J. Suñol, D. Miralpeix, J. Saurina, F. Carrillo and X. Colom, J. Therm. Anal. Cal., 80 (2005) 117.
25 R. Kruger, Cellulosic filament yarn from the NMMO process. Lenz Ver, 74 (1994) 49.
26 K. E. Perepelkin, Fibre Chem., 35 (2003) 241.

DOI: 10.1007/s10973-006-7801-1