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COMPARISON OF THE THERMAL BEHAVIOR OF THREE CELLULOSE FIBERS MERCERIZED OR SUBMITTED TO SOLAR DEGRADATION

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Abstract

Comparison of Lyocell, modal and viscose fibers was performed by means of differential scanning calorimetry, thermogravimetry and scanning electron microscopy. Thermal analysis was performed in air atmosphere. Samples were mercerized (21.3 g 100 mL^{-1}) or submitted to solar radiation (seven months). Solar degraded samples presents a higher thermal stability and are initially less degraded. Furthermore, Lyocell fiber is the most stable under thermal degradation conditions. Heating produces a reduction of the fiber diameter (about 50%).

Keywords: cellulose fibers, degradation, DSC, Lyocell, modal, TG, viscose

Introduction

Pollutant emission is one of the main problems in the textile industry of manufacturated fibers from regenerated cellulose. Research works on cellulose fibers are traditionally performed for its technological interest [1–4]. The innovation with new production ways and materials permits to solve it, at least partially. There have been numerous efforts to find an alternative to the use of carbon disulphide, CS_2, for regenerated cellulose fiber production. During the last decade, the scientific and technological interest in the development of non-contaminant processes with organic solvents of cellulose was increased. A fiber, known as Lyocell presents the best properties if compared with other cellulosic fibers, as viscose or modal.

In the Lyocell process described in reference [5], N-Methylmorpholine-N-oxide monohydrate (NMMO) is used as a solvent for direct dissolution of cellulose in industrial fiber-making. Other solvents are: dimethylformamide/dinitrogen tetraoxide (DMF/N_2O_4), and N,N-dimethylacetamide/lithium chloride (DMAc/LiCl) [6]. The NMMO process offers a commercial and viable alternative to the pre-existent methods of textile fiber production [7]. Several labels essentially designate similar products, namely Lyocell fibers, which are cellulosic fibers spun from cellulose solutions in NMMO. The commercial products are: Tencel (Courtaulds), Lyocell (Lenzing),

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Newcell (Akzo Nobel) and Alceru (TITK Rudolstadt). Based on the Lyocell technology, also other cellulose products, such as membranes, filaments and films, are currently developed or are already commercially produced [8–10].

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. 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 [11–13]. In this work, we analyze the thermal behavior of several samples: Lyocell, viscose and modal under different treatment conditions.

Experimental

Several textile fibers were analyzed: Lyocell (Tencel) and conventional viscose and modal fibers 1.7 dtex. All products were regenerated cellulose fibers submitted by textile industries. One of the most important treatments that are carried out in the cellulosic fibers, is mercerization. This process is significantly aggressive and, in consequence, changes in fine structure, morphology and conformation of the cellulose fibers occur. In this work, treatments of aqueous solutions with sodium hydroxide at various concentrations, i.e. the relation 21.3 g 100 mL^{-1}, were performed. Furthermore, in other samples seven months of solar radiation were simulated in a climatic chamber. Details on sample preparation are given in reference [14]. In both cases, sample changes on thermal degradation and thermal stability were produced.

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 a TGA851 Mettler Toledo equipment. The fabric sample was cut to obtain fibers and ~4 mg of sample was used. The DSC and TG curves were obtained in the temperature range of 50 to 400°C at a heating rate of 10°C 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. The aim is to observe microstructure changes resulting from the degradation phenomena related to simulated solar radiation or to mercerization.

Results and discussion

Information about thermal behavior is obtained from DSC scans. Figure 1 shows the DSC scans of fibers subjected to simulated thermal radiation. At low temperature, an endothermic process was detected, with a maximum at about 80°C. This process is associated to water desorption [15]. Reheating the samples, previously heated un-

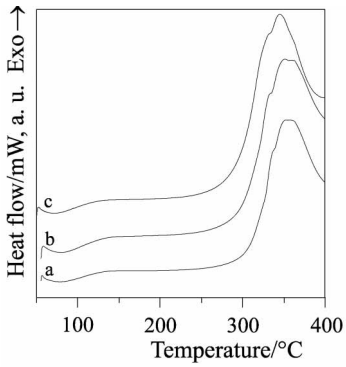

Fig. 1 DSC scans of textile fibers after solar degradation (about seven months): a – Lyocell, b – modal and c – viscose

til 200°C and cooled to room temperature, this process disappears. Nevertheless, if a second heating is performed after one hour in air atmosphere the process is present. This phenomenon is associated to a new water sorption-desorption.

Furthermore, a broad exothermic peak begins between 280 and 300°C. A higher increase of the onset temperature of this process can be associated to a 'higher thermal stability' because structural changes were induced during the degradation process and resultant fibers present a loss of properties [15, 16]. Thus, comparison of the thermal behavior of fibers before and after solar radiation treatment can be performed. We remark that solar degradation provokes a lower value (about 10°C) in the onset temperature of the exothermic process in Lyocell and modal fibers. From DSC scans, we can state that Lyocell fiber is the 'most thermally stable' considered the onset temperature of the degradation process as the experimental criterion. Figure 2 corresponds to the DSC curves of mercerized samples (21.3 g 100 mL^{-1}). The processes involved are the same as in the solar degraded. Nevertheless, the enthalpy values associated to the exothermic part decrease in one third (from 2000 J g^{-1} to 700 J g^{-1}). In this case, modal is the most affected by NaOH solution. From the onset temperature

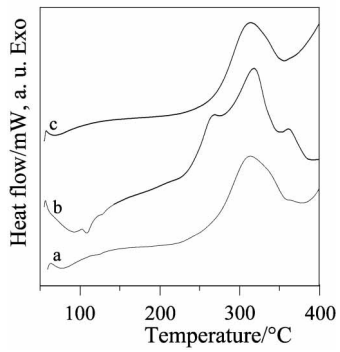

Fig. 2 DSC scans of textile fibers after mercerization process (21.3 g 100 mL^{-1}): a – Lyocell, b – modal and c – viscose

of the exothermic part, the chemically treated fibers are less thermally stable than solar degraded ones.

The DSC shape of the exothermic part indicates the presence of several processes. Generally, the thermal reactions involved on heating over 200°C the cellulose fibers can be grouped in different pathways detailed in [16]: decomposition of the glycosil units, depolymerization, etc. However, all these reactions overlap.

Complementary information can be obtained from TG measurements. Figure 3 shows the mass loss during heat treatment in air atmosphere of the textile samples. It can be seen from the TG curves that the overall mass loss can be divided into four different stages. This behavior is typical of cellulose fabrics [15]. The first mass loss that occurs at about 100°C is generally attributed to the evaporation of sorbed water from the fibers. Reheating the samples, in the same way as performed by DSC confirms it.

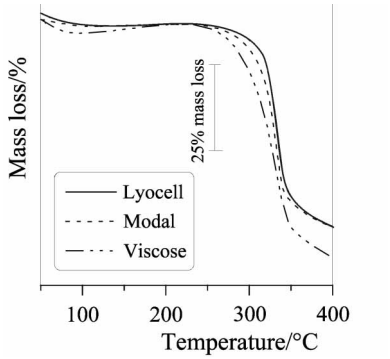

Fig. 3 TG scans of Lyocell, modal and viscose fibers after solar degradation (about seven months)

The second mass loss, which began at about 250–270°C, and is reflected in a slow mass decrease represented by a shoulder. This is the initial stage of thermal degradation. Thus, an increase of the onset temperature of this process can be associated to a 'higher thermal stability' as considered in DSC measurements. The high thermal stability corresponds to lowest contamination process fiber, Lyocell. This result is consistent with DSC analysis.

The third mass loss corresponds to an accelerating mass loss reflecting major thermal degradation. It is known that the rate of pyrolisis of cellulose is inversely proportional to the square root of the degree of polymerization, to the additives and to the atmosphere [17]. About 50% of the mass loss is associated to this process. Finally, the last process beginning at about 350ºC corresponds to prolonged char oxidation stages and the slope diminishes.

Figure 4 corresponds to samples mercerized. The general shape of the TG scans indicates a similar behavior to solar degraded. As expected, the mass loss associated to humidity is higher than in the solar degraded samples. Likewise, the main mass loss slope is lower in samples treated with NaOH. Moreover, all fibers have been to other subjected processes as UV radiation, treatment with H_2SO_4, industrial fibrillation, enzymatic treatment. All the analysis performed confirms that the best thermal behavior corresponds to

Lyocell fiber [14, 18]. The poor thermal stability corresponding to the mercerized fibers analyzed in this work. 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 [14, 19–21].

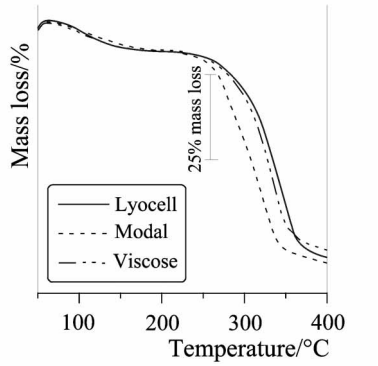

Fig. 4 TG scans of Lyocell, modal and viscose fibers after mercerization process (21.3 g 100 mL^{-1})

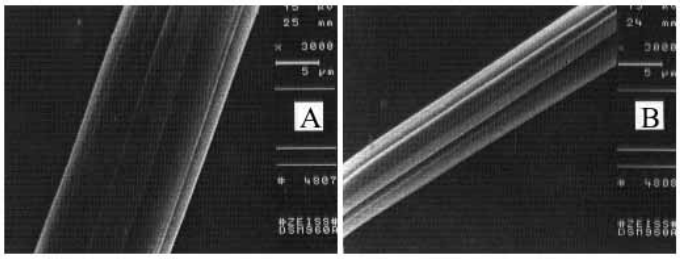

Fig. 5 SEM micrographs corresponding to viscose fiber: a – before DSC treatment, b – after DSC treatment until 400°C

Morphology analysis by SEM confirms the mass loss of samples thermally treated. As an example, Fig. 5 shows the micrographs corresponding to viscose fiber before and after thermal treatment in the DSC. The fiber maintain their aspect but the diameter of the fiber is reduced (from 14.5 to 7.3 μm). The same phenomenon is observed in the other samples. Complementary studies of the mechanical properties and fiber structure were developed in the Universitat Politècnica de Catalunya (EUETIT center).

Conclusions

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 and thermogravimetry. At low temperature, water desorption was detected being lower the mass loss in the fibers subjected to previous solar radiation degradation. 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 by a mass loss of about 50%. The process beginning at about 350°C corresponds to prolonged char oxidation stages with a lower mass loss rate. Lyocell fiber is the most stable under thermal degradation conditions. Furthermore, mercerized samples are initially more degraded and present a lower thermal stability.

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