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Thermal degradation of lyocell/poly-N-isopropylacrylamide graft copolymers gels

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Abstract In the present work Lyocell fibers were subjected to graft copolymerization of poly-N-isopropylacrylamide (pNIPAAm) thermosensitive polymer. The thermal degradation and stability of lyocell/pNIPAAm copolymers gels were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). pNIPAAm/lyocell copolymers are thermally stable and more resistant to temperature than lyocell fibres. Thermal characterization was analyzed as a function of percentage by mass of the pNIPAAm grafted. It has been shown that for pNIPAAm/lyocell copolymers, degradation occurs at higher temperature when increasing the degree of grafting.

Keywords Cellulose · DSC · Graft copolymers · Lyocell · Hydrogel · N-isopropylacrylamide · TG

Introduction

Poly-N-isopropylacrylamide (pNIPAAm) is a temperature-sensitive hydrogel which has attracted considerable attention due to its drastic swelling transition at its lower critical solution temperature (LCST) of 32 °C. Below LCST the pNIPAAm gel is swollen, however, above it the gel dehydrates to the collapsed state due to the change of the hydrophilic/hydrophobic balance in its network structure [1]. This temperature sensitive behavior has been widely investigated for many biomedical and pharmaceutical applications, such as drug delivery systems, molecular separation and tissue culture scaffolds [2].

On the other hand, pNIPAAm can be applied for surface modification of solid substrates to obtain environment sensitive copolymers by graft copolymerization reaction of N-isopropylacrylamide (NIPAAm) on several solid supports which has attracted considerable attention [3]. Among the different solid materials used for this purpose, research has been mainly focused on solid polysaccharide substrates, such as cellulose [4] because of its appropriate properties: is abundant, renewable and a biodegradable resource. Among the cellulose substrates, lyocell is a regenerated cellulose material that has particular properties as it is produced via an advanced closed loop organic solvent (N-methyl morpholine-N-oxide, NMMO) spinning process [5], and it also has interesting mechanical properties in dry and wet environments which are different to those of any other cellulose substrate [6].

Due the importance, for its application, of the thermal behavior of the grafted copolymers obtained, the present work is devoted to the study of the thermal behavior of the lyocell – pNIPAAm copolymers obtained by radical copolymerization using cerium (IV) ammonium nitrate as initiator following a previous study developed in our laboratory [7]. Calorimetry (DSC) and thermogravimetry (TG) were the techniques applied in this work to study the thermal behavior of the synthesized pNIPAAm/lyocell graft copolymers due to the convenience and good results obtained for the thermal characterization and stability

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analysis of cellulose by many authors [8, 9]. In addition, it has been shown that DSC and TG analysis is a useful method to characterize the LCST and the stability of thermosensitive pNIPAAm hydrogels [10, 11] and their copolymers [12, 13].

Materials and methods

Lyocell fibres, kindly supplied by Lenzing AG (Austria), with an average lineal density of 1.7 dtex (1.7×10^{-4} g m^{-1}), average length of 38 mm and diameter of 13.4 µm, were the fibres used for the experimental analysis. The fibres were first washed in a bath at 80 °C containing 1 g/L of a nonionic surfactant with a 50/1 (v/w) liquor ratio during 60 min. After the washing step, the fibres were rinsed with deionised water and dried in an air oven at 60 °C for 48 h.

N-isopropylacrylamide (or NIPAAm from Aldrich, Spain) was recrystallized from a mixture of hexane and benzene 1:1 (v/v). Ammonium cerium (IV) nitrate (CAN), hexane, benzene and nitric acid (analytical grade, Panreac Química S.A., Spain) were used as received.

Graft copolymerisation of NIPAAm onto Lyocell was carried out with a 1/4 (volume of bath, in ml/weight of fibre, in mg) liquor ratio at 25 °C in a nitric acid 0.1 M solution using 5 mM of CAN as an initiator and 1 M of NIPAAm under a nitrogen atmosphere. In a closed reactor, a 5 mM of CAN solution (used as initiator) in nitric acid (0.1 M) was purged with nitrogen atmosphere for 5 min. Then 100 mg of the washed lyocell fibres were introduced bubbling nitrogen for 30 more minutes. After the initiation step, the previously recrystallized NIPAAm was introduced into the reactor and lyocell fibres were copolymerized under nitrogen for 15 and 24 h. Once the sample was grafted, it was rinsed and washed and the pNIPAAm non reacted was removed by swelling (in deionized water at 26 °C for 2 h) and deswelling cycles (fresh deionized water at 45 °C for 2 h more) above and below the LCST respectively. This procedure was repeated until no more turbidity in the warm water was seen. Then the copolymer was transferred to an oven at 60°C for at least 24 h.

In order to calculate the degree of grafting (DG, %), the weight increase of lyocell was measured to constant weight at room temperature and calculated as Eq. 1.

$$DG = \frac{\left(w_g - w_o\right)}{w_o} \times 100 \tag{1}$$

where: DG, represents the degree of grafting, and w_o and w_g represent the mass of dried sample before and after graft copolymerization, respectively, determined after drying the sample in an air oven at 60 °C for 48 h and keeping the sample in a desiccator for 24 h at room temperature.

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 standards of In and Pb. The samples were heated from 30 °C to 600 °C at a rate of 10 K min^{-1} and with synthetic air as a purging gas at a flow rate of 13 ml min^{-1}. Air was used because air is the real work condition of the fibres.

Thermogravimetry analysis was performed in a TGA/851e Mettler at a heating rate of 10 K/min in air from 30 °C to 600 °C.

Results and discussion

The results of DSC measurements of lyocell fibres, pNIPAAm/lyocell grafted copolymers with different degree of grafting (DG) and pNIPAAm homopolymer hydrogels are displayed in Figs. 1 and 2 for the ranges of 30 to 200 °C and 200 to 600 °C, respectively.

In the range 30–200 °C (Fig. 1) an endothermic peak is observed for each of the analysed samples showing a maximum in the range 60–130 °C. For the lyocell's DSC curve (Fig. 1a) a small endothermic peak with a maximum around 70 °C is seen. It is related to water desorption process which can be explained in terms of migration of bubbles generated in the bulk, caused by the hydrophilic behaviour of lyocell [14, 15]. DSC curve obtained for pNIPAAm (Fig. 1d) shows second order glass transition temperature (Tg) at 120 °C, determined at the peak of the thermal event. DSCs of the copolymers (Fig. 1b and c) show a decrease of the glass transition temperature compared to pNIPAAm homopolymer and which increases with the degree of pNIPAAm grafted onto lyocell fibres, with Tg values of 75 and 90 °C for grafting degrees of 40 and 60%, respectively. This behaviour indicates interaction

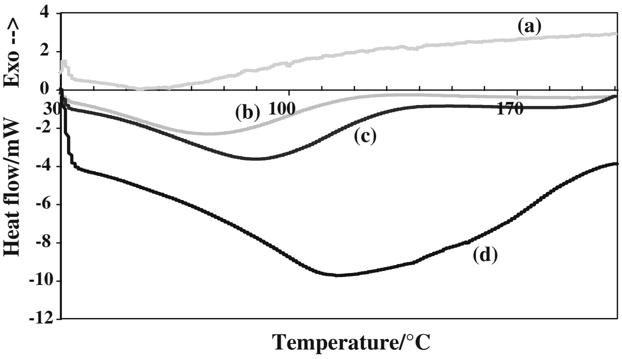

Fig. 1 DSC curves in the temperature range of 30 to 200 °C for: **a** lyocell fibers; **b** lyocell/pNIPAAm copolymers with DG = 41% (time of grafting 15 h); **c** lyocell/pNIPAAm copolymers with DG = 61% (time of grafting 24 h) and **d** pNIPAAm homopolymer

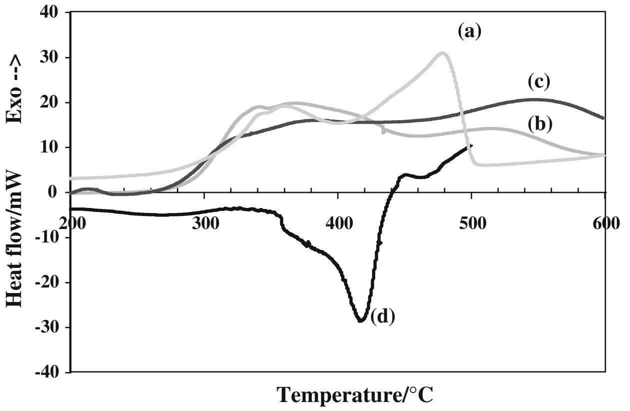

Fig. 2 DSC curves in the temperature range of 200 to 600 °C for: **a** lyocell fibers; **b** lyocell/pNIPAAm copolymers with DG = 41% (time of grafting 15 h); **c** lyocell/pNIPAAm copolymers with DG = 61% (time of grafting 24 h) and **d** pNIPAAm homopolymer

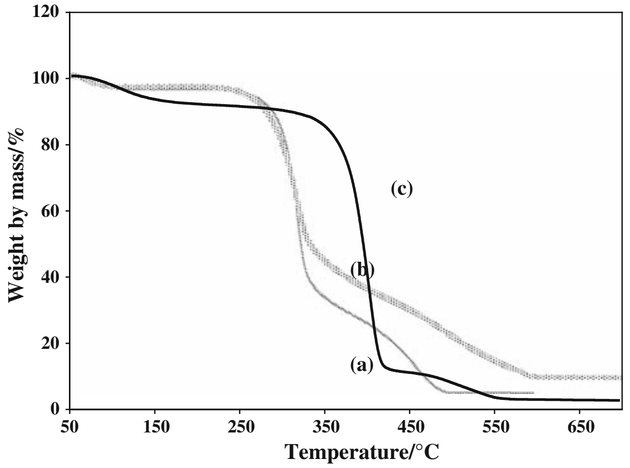

Fig. 3 Thermogravimetry. **a** Lyocell, **b** Copolymer with 61% of pNIPAAm grafted, **c** pNIPAAm homopolymer

in the copolymer between pNIPAAm and lyocell, which increases the mobility of the pNIPAAm chains probably due to a reduction of the chain entanglement in the pNIPAAm structure by the interference of lyocell's cellulose chains. Then, lower temperatures are needed to promote mobility of pNIPAAm chains grafted to lyocell substrates. Moreover, the increase of grafted pNIPAAm onto lyocell promotes pNIPAAm chain interactions and higher temperature is necessary to produce mobility of the molecules, resulting in higher Tg values.

At higher temperatures (Fig. 2) a broad exothermic peak, characterized by two thermal events, is observed for lyocell (Fig. 2a) and pNIPAAm/lyocell copolymers (Fig. 2b and c) and an endothermic peak was recorded for pNIPAAm homopolymer (Fig. 2d). The results of DSC of the lyocell fibers corroborated that thermal degradation of lyocell fibres in air shows a similar trend that thermal degradation of cellulose [16]: between 250 to 400 °C decomposition and combustion of cellulose occurs. Above 400 °C volatile products (such as CO_2, CO) are produced due to the char oxidation after the thermo oxidative decomposition. The lyocell thermograme shows two exothermic peaks: the first one with maximum heat flow at 360 °C and the second one at 480 °C. The behaviour of the pNIPAAm homopolymer is quite different; it shows an endothermic peak at 414 °C and after it an exothermic peak appears until 500 °C.

It has been shown (Fig. 2) that for pNIPAAm/lyocell copolymer, cellulose degradation occurs at higher temperature. pNIPAAm/lyocell copolymer of 60% degree of grating shows two exothermic peaks at 362 °C and at 520 °C, showing higher values than the obtained for lyocell support at 360 °C and 480 °C, respectively. These two exothermic peaks observed in the degradation of the copolymers shift to higher temperatures when grafting with pNIPAAm because of the higher thermo stability of pNIPAAm and these peaks become smoother due to the balance between the exothermic/endothermic degradation of cellulose and pNIPAAm, respectively. This behaviour was corroborated with the thermogravimetry analysis (Fig. 3).

The TG curves obtained for lyocell, pNIPAAm and pNIPAAm/lyocell copolymer at 61% of grafting are shown on Fig. 3. Before 100 °C, only a minor weight by mass loss (5–10%) due to the water evaporation is observed for lyocell. Lyocell degradation starts at 298 °C with a peak temperature of 318 °C. From 298 to 395 °C, the degradation rate is high (weight by mass loss of 65,5%), and then the weight by mass loss rate decreases until 500 °C when all the fibre is degraded. The pNIPAAm degradation process was quite different: 10% of weight by mass is lost by water evaporation in the first stage until 368 °C. Next, there is a fast second weight by mass loss (68%) between 368 °C and 494 °C. From 494 °C to 580 °C, the sample that remains was degraded at a slower rate (weight by mass loss of 6%). On the other hand, for the copolymer, the TG curve shows a similar behaviour to lyocell until 295 °C, showing similar initial thermal decomposition temperature. Above this temperature, from 295 to 580 °C (65% weight by mass loss), the evolution of its weight by mass as a function of the temperature is quite different from the evolution observed for pNIPAAm homopolymer and a temperature of 580 °C is needed to degrade entirely the copolymer. The degradation temperature (determined at the peak of the thermal event) of the copolymer (583 °C) is higher than the degradation temperature of its two components independently (454 °C and 529 °C for lyocell and pNIPAAm homopolymer, respectively). In addition, at 425 °C, lyocell and the pNIPAAm homopolymer were degraded with a weight by mass loss of 90%, in front of the 65% weight by mass loss observed in the pNIPAAm/

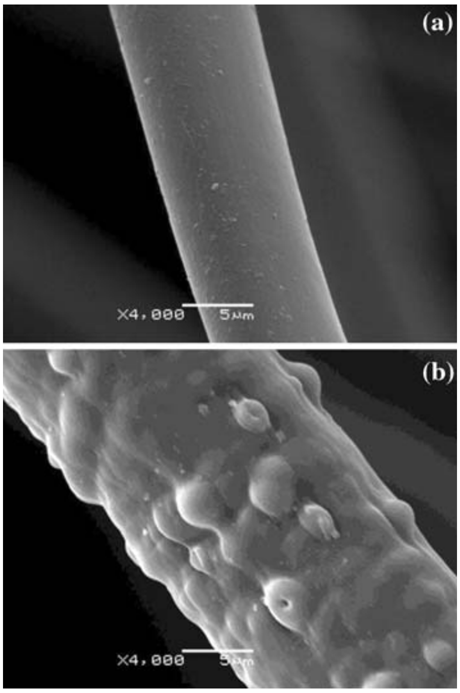

Fig. 4 SEM micrographs of lyocell (**a**) and poly-NIPAAm/lyocell copolymer at 41% of grafting (**b**)

lyocell copolymer sample. In addition, resulted pNIPAAm/lyocell copolymers keep similar thermosensitivity behaviour, with similar lower critical solution temperature (LCST) that pNIPAAm homopolymer alone [7].

Morphology of lyocell and lyocell/pNIPAAm copolymers with a grafting degree of 41% were analyzed by scanning electronic microscopy (Fig. 4). Lyocell fibres show a smooth surface before grafting (Fig. 4a). When pNIPAAm is grafted to lyocell, the micrographs (Fig. 4b) reveal pNIPAAm chains distributed at lyocell surface.

Conclusions

Thermal analysis of lyocell, pNIPAAm/lyocell copolymer and pNIPAAm homopolymer was performed by differencial scanning calorimetry and through thermogravimetric analysis. Thermal degradation behavior of the lyocell fibres changed when pNIPAAm were grafted and higher temperatures than for lyocell and pNIPAAm homopolymer components independently were needed to degrade the obtained copolymers. pNIPAAm/lyocell copolymers prepared are thermally stable and more resistant to temperature than lyocell fibres alone. The resulted copolymers showed pNIPAAm layers distributed at lyocell surface as it was corroborated by scanning electron miscroscopy analysis. In addition, an increase of the glass transition temperature of the copolymers was observed when increasing the degree of pNIPAAm grafted onto lyocell fibres due to the interaction between the pNIPAAm and lyocell.

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