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X-ray diffraction and thermogravimetry data of cellulose, chlorodeoxycellulose and aminodeoxycellulose

Edson C. da Silva Filho · Sirlane A. A. Santana · Júlio C. P. Melo · Fernando J. V. E. Oliveira · Claudio Airoldi

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Abstract Cellulose was chemically modified with $SOCl_2$ to obtain chlorodeoxycellulose, followed by a reaction that gave bonded ethylene-1,2-diamine (en), producing 6-(2′-aminoethylamino)-6-deoxycellulose. The reactions were carried out without the presence of solvent, in water or in *N*,*N*′-dimethylformamide, in which the highest amount of amino compound was incorporated onto the biopolymer backbone. The X-ray diffraction patterns for the chlorodeoxycellulose indicate new crystallinities that result from hydrogen bonds established through bonded chorine atoms and the remaining hydroxyl groups, while all the aminodeoxycelluloses were amorphous compounds. Thermal stabilities, for all aminated celluloses gave lower final mass losses than for the chlorinated biopolymer, whose value is lower than unmodified cellulose.

Keywords Ethylene-1,2-diamine · Cellulose · Solvent-free · Thermogravimetry · X-ray

E. C. da Silva Filho (✉)
Química, Universidade Federal do Piauí, Bom Jesus, Piauí 64900-000, Brazil
e-mail: edsonfilho@ufpi.edu.br

S. A. A. Santana
Departamento de Química, UFMA, São Luiz, Maranhão 65080-540, Brazil

J. C. P. Melo · F. J. V. E. Oliveira · C. Airoldi
Institute of Chemistry, University of Campinas, UNICAMP, P.O. Box 6154, Campinas, SP 13084-971, Brazil

Introduction

A great variety of pristine or chemically modified organic or inorganic polymeric materials have been and continue to be the focus of many studies [1], including the two most abundant biopolymers, cellulose [2, 3] and chitosan [4, 5], as well as synthetic and natural inorganic polymers, such as silicas [6–8], phyllosilicates [9–11], phosphates [12, 13], chrysotile [14], clays [15, 16] etc. The increasing usefulness of these classes of materials is closely related to chemical surface modifications, explored to change the chemical and physical properties and also the activity of the available functional groups attached on pendant chains. For any support, the original hydroxyl reactive centers on the surface are of great utility to graft desirable molecules in single-step procedures or using a sequence of reactions [17].

Many studies concerning the synthesis and characterization of modified surfaces have been reported in the last half-century [18–20]. Thus, surfaces modified with basic centers, such as the ethylene-1,2-diamine moiety, are applied in different areas for cation removal from aqueous solution [20], in chromatography [21], in catalysis [22], for pre-concentration of trace chemical species in solution [23], andin ion-exchange processes [24].

This investigation deals with the most abundant natural biopolymer, cellulose, with the objective to improve its applicability, by exploring the limited reactivity of the hydroxyl groups bonded to the polymeric structure [17, 25]. After cellulose chlorination on carbon 6 the synthetic procedure enables the incorporation of the ethylene-1,2-diamine molecule, exploring different features with polar or solvent-free routes. As the characterization of these synthetic products is not an easy task, the elemental analysis results associated with those obtained from X-ray diffraction and thermogravimetric tools, contribute to

rapidly clarify the chemical and structural changes of the newly synthesized compounds.

Experimental

Materials

Microcrystalline cellulose (Merck), thionyl chloride (Chemika), *N*,*N*′-dimethylformamide (DMF) (Synth), ammonium hydroxide (Aldrich) and ethylene-1,2-diamine (en) (Aldrich) were all reagent grade and were used without prior purification. Activated cellulose and the corresponding chemically modified compounds were stored in flasks under dry nitrogen.

Synthesis of 6-chlorodeoxycellulose

A sample of 10 g of cellulose (Cel) previously activated at 353 K for 12 h was suspended in 200 cm^3 of DMF followed by the slow addition of 35 cm^3 of thionyl chloride ($SOCl_2$) at 353 K, under mechanical stirring. After the addition, stirring was continued at the same temperature for another 4 h. The cooled suspension containing the cellulose chloride (CelCl) was washed with several portions of dilute ammonium hydroxide solution. The supernatant in each operation was eliminated with pH control to bring its value to neutral. To complete the washing the suspension was exhaustively treated with distilled water. Finally, the solid was then separated by filtration and dried under vacuum at room temperature [13].

Synthesis of 6-ethylenodiamino-deoxycellulose

A sample of 1.0 g of CelCl was reacted with 5.0 cm^3 of en under reflux and with mechanical stirring for 3 h [2, 13] with variation of the quantity of solvent (water or DMF), or without solvent, as shown in Fig. 1, followed by filtration using a sintered glass filter. The solid (Celen) was dried under vacuum at room temperature for 24 h.

Physical measurements

The amounts of en pendant chains anchored onto the cellulose surface were calculated based on percent nitrogen, determined through elemental analysis with a Perkin Elmer, model 2400, elemental analyzer. XRD patterns were obtained on a Shimadzu XRD7000 diffractometer for powdered samples. The voltage applied was 40 kV, current of 30 mA, with a CuKα ($\alpha = 0.154$ nm) radiation source scanned from 1.4 to 50°. The thermogravimetric curves for powdered samples were obtained on a Dupont TA 9900 instrument in an argon atmosphere of 1.67 $cm^3\ s^{-1}$, using a heating rate of 0.167 K s^{-1}, from room temperature to 1,273 K, with an initial mass of approximately 10 mg of solid sample.

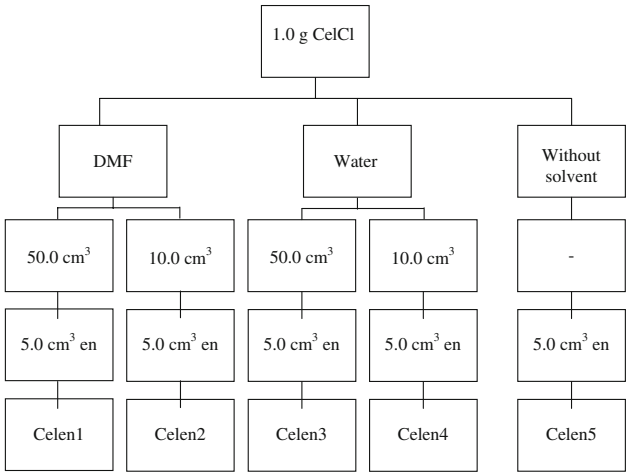

Fig. 1 Variations in the preparation of the five aminated biopolymers

Results and discussion

Elemental analysis, based on incorporated nitrogen, was used to determine the amount of en molecules chemically bonded to the cellulose backbone to give the aminated biopolymer, originating from the chlorodeoxycellulose precursor, as shown in Scheme 1 and the results are listed in Table 1. The chlorinated cellulose gave a high degree of substitution, 0.99 ± 0.01, of the hydroxyl groups preferentially on carbon 6 (C6) and this expected favorable process is due to its high reactivity compared to other positions. Thus, the following decreasing sequence in reactivity of the hydroxyls of the cellulose presents the order: $C_6 >> C_3 > C_2$, due to the fact that C_6 bear a primary hydroxyl and the differences between C_3 and C_2

Scheme 1 Reaction sequence to prepare CelCl and Celen

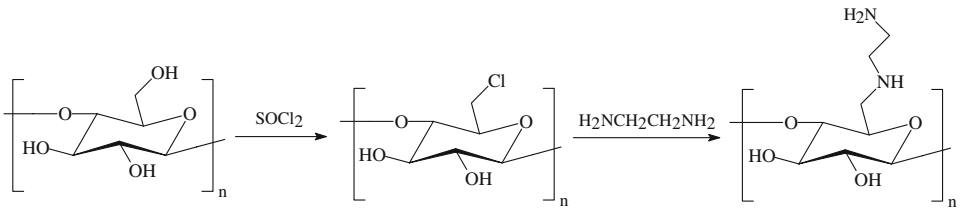

Table 1 Percent of nitrogen for CelenX (X = 1–5) biopolymers, the degrees of substitution (DS) and incorporation (DI)

CelenX	N (%)	DS	DI (mmol g^{-1})
1	3.96 ± 0.01	0.28	1.41 ± 0.01
2	5.78 ± 0.06	0.42	2.06 ± 0.02
3	1.04 ± 0.02	0.07	0.37 ± 0.01
4	5.84 ± 0.06	0.42	2.08 ± 0.03
5	8.50 ± 0.03	0.61	3.03 ± 0.01

are mainly to their acidities [25]. The unequivocal biopolymer modification was previously confirmed through ^{13}C NMR, where the spectra clearly demonstrated the chemical shift from 65 to 44 ppm for carbon 6, without notable change for carbons 2 and 3 [2].

The most encouraging fact to support this reaction is the high value found for nitrogen percentage on Celen5, as listed in Table 1, where the incorporation was performed without adding solvents, as is desirable under Green Chemistry principles [26]. A sequence of attaching groups, whose decreasing values are in agreement with the amount and polarity of solvent used in these reactions, to give the following order: Celen5 > Celen4 > Celen2 > Celen1 > Celen3.

An important feature to compare in these syntheses is related to the same solvent, but the quantities employed varied. For example, for the biopolymers prepared using DMF, as less of this solvent was used, the amount of en molecule bonded to the surface increased. The same result can be observed when water was used as solvent. On the other hand, when the different solvents are compared for the same final volume, for example, 50 cm^3, the synthesis was more effective in DMF than in water, as reflected the amount of incorporated groups. However, when 10 cm^3 was used the more favorable solvent was water, although the nitrogen quantities were close.

For the solvent-free process of incorporation, an increase of 31% was detected when compared to Celen4, which corresponded to the highest value when solvent was employed. In addition to the great increment on incorporation, an important advantage is the absence of solvent for preparing new functional polymers, a procedure that brings many environmental benefits, including reduction in costs and easier process control [27]. For Celen5 the data demonstrate that the solvent-free procedure gave larger amounts of pendant amino groups.

Cellulose and its various derivatives were among a series of polymers for which phase transitions in the solid and semisolid state were first studied. For instance, when compared with other biopolymers, cellulose shows a distinct tendency for crystallization, probably caused by the relative stiffness of the glucosidic chains and the hydrogen-bonding capacity of the hydroxyl groups. The shape of the rings and the spatial distribution of the hydroxyl groups appear to favor the formation of ribbon-shaped laterally ordered sheets, which exhibit a three-fold anisotropy as far as bonding strength is concerned [17, 28–30].

Perpendicular to the polymeric chains, in the plane of the anhydroglucose rings, representing the a-axis direction of the lattice, the hydrogen bonds between the hydroxyl groups and the ring oxygen atoms are responsible for this interaction. Finally, perpendicular to the chains and to the plane of the anhydroglucose rings and parallel to the c-axis of the lattice, the only existing attraction is due to van der Waals interactions between the anhydroglucose rings and their constituents. This system of bonding can be considered as a reasonable starting point for the explanation of the crystallization tendency of cellulose. It leads to the existence of elongated thin sheets with high lateral order, which can explain in a satisfactory way the observed macroscopic mechanical and flow properties of cellulose fibers and films in the dry and swollen state [17, 28–30]. To explore such biopolymer properties, the X-ray diffraction patterns are shown in Fig. 2 (I).

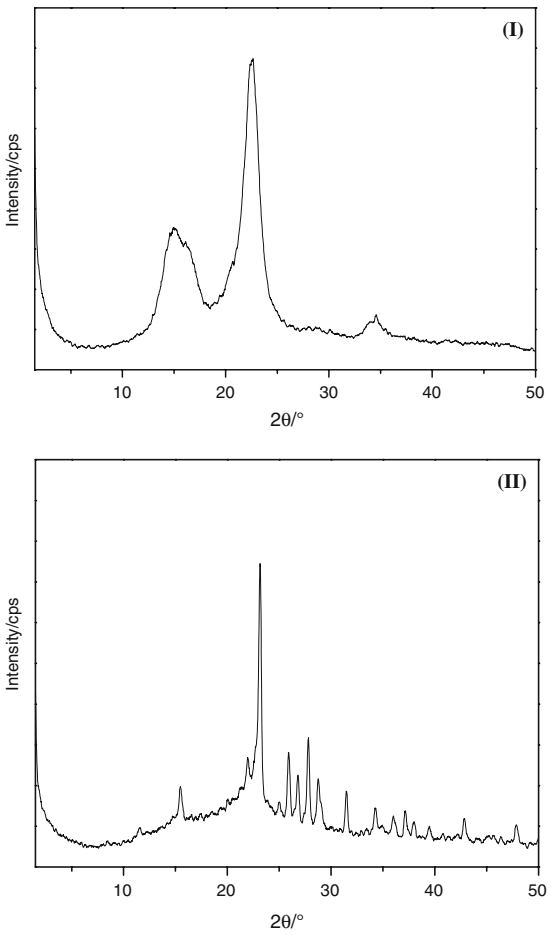

Fig. 2 X-ray diffraction patterns for microcrystalline cellulose (**I**) and chlorodeoxycellulose (**II**)

The X-ray diffraction patterns of chlorinated cellulose, shown in Fig. 2 (II), indicate that the corresponding degree of crystallinity is smaller and differs from that found for the precursor cellulose, which has the original microcrystalline properties. The new assembly is now formed through bonded chlorine atoms and remaining hydroxyl groups, where depolymerization processes can occur due to the effect of a hydrochloric acid reaction. Similar behavior was also observed for other biopolymers where mainly hydrogen bonding occurs with available hydroxyl groups [17, 28–30]. Thus, when cellulose is chlorinated the hydrogen bonding should be partially disrupted, to favor the entrance of chlorine atoms concomitantly with the leaving of the hydroxyl group, yielding a new network with distinct features. From the integration of the main peak, between 20 to 30°, the values demonstrate a decrease of 70% in crystallinity for the chlorinated biopolymer, which can be very interesting mainly when other modifications are intended, such as anchoring an ethylene-1,2-diamine molecule.

The oxidative chlorination process on cellulose consists in substituting the hydroxyl group by a chlorine atom in the original biopolymer structure. The chemical modification occurs initially in the less ordered polymeric regions related to the para-crystalline or amorphous regions. The hydroxyl groups of cellulose bear two electron lone pairs and one bonded hydrogen. On the other hand, chlorine atoms covalently bonded to the biopolymer can potentially make available three free pairs of electrons to be shared through the formation of hydrogen bonds**.** Therefore, as chlorine atoms, in the progress of the reaction, substitute the hydroxyl groups, other hydrogen bonds can be formed with different characteristics from the earlier ones, being established between the chlorine atoms and hydrogen from unreacted hydroxyl groups, by causing new chemical structural arrangements of the modified biopolymer. These characteristics change the crystallinity due to the new chain arrangement [17, 28–30].

The cellulose structure reacting with thionyl chloride to obtain Cel-Cl sample is shown in Scheme 1. According to earlier publication, IR spectra confirm substitution of hydroxyl groups from the original cellulose by the chlorine species [2]. The typical bands assigned at 709 and 752 cm^{-1} correspond to the stretching vibration of the C–Cl bond, from the branched part of the original polymer. The displacement and decreasing size of the band originally observed in the cellulose at 894 cm^{-1}, is now shifted to 865 cm^{-1} in the CelCl compound and has disappeared in Celen. This fact corroborates with the chemical substitution of the OH groups by chlorine atoms in this proposed reaction. The appearance of a new band at 2,844 cm^{-1} is assigned to C–H stretching of the symmetric CH_2 group, due to ethylene-1,2-diamine molecule immobilization. The displacement of the band at 1,632 cm^{-1} that corresponds to the deformation of OH groups and also the angular deformation for the N–H amine band at 1,659 cm^{-1} are unequivocal facts that confirm the ethylene-1,2-diamine immobilization on the cellulosic matrix [2].

Microcrystalline celullose, named type I cellulose, is normally found with a degree of crystallinity between 40 to 60%. Some heterogeneous reactions are able to modify only the surface of the polymer and sometimes can also modify the internal layers, as well as having a high probability of reacting in the amorphous regions. Here, the X-ray diffraction patterns show the appearance of new peaks, in addition to those associated with the original solid, demonstrating a different crystalline structure, even though present at low intensity. The decrease in intensity of the peaks suggests that only small crystallites are present due to the hydrogen bonding involving chlorine atoms. This behavior decreases the space between the chains, resulting in the displacement of the peaks to give higher θ values. Again the confinement of bonded chlorine atoms allows them to form hydrogen bonds that could be differentiated from those found on the surface of the material [17, 28–30].

The crystalline regions found in the bulk material were formed as a consequence of the intensity of the intermolecular interactions and result in an ordered lattice dominated by the lower availability of hydroxyl groups. To the contrary, the amorphous region presented weak interactions, causing a low ordered lattice while the hydroxyl groups have increased abilities to access chemicals. This fact was demonstrated through ^{13}C NMR with clear indications that the consumption of the amorphous part of cellulose is followed by the disappearance of C(4) and C(6) signals of the chloride cellulose [2]. These concomitant processes address the increase crystallinity of cellulose-chloride part in comparison to the unmodified cellulose.

For cellulose with amino pendant groups, as shown in Fig. 3, a drastic decrease in crystallinity is observed in

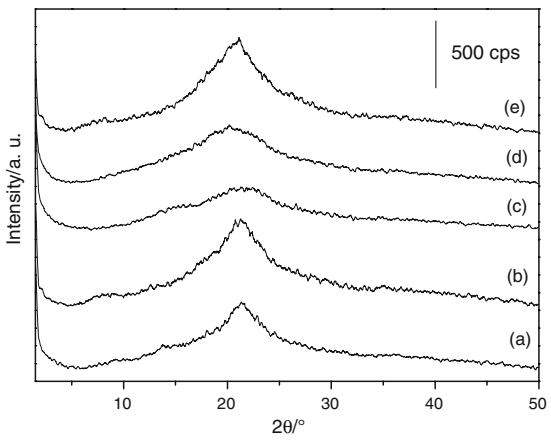

Fig. 3 X-ray diffraction patterns for CelenX: 1 (*a*), 2 (*b*), 3 (*c*), 4 (*d*) and 5 (*e*)

comparison with the original and the chlorine-containing celluloses. These data suggest that the aminated biomaterial resulted in an amorphous structure. This result is independent on the synthetic route and the amount of amine groups attached to the pendant chains [31, 32]. However, in the newly obtained biopolymers using water as solvent, the amorphous characteristics were intensified, as observed in Fig. 3c and d. This change occurs due to the substitution of a chlorine atom by ethylene-1,2-diamine, it means that this molecule is capable to increase the effectiveness of the hydrogen bonds. Taking into account the decrease in the crystallization process, the data are in agreement that the bonded en molecules do not establish an ordered assembly, resulting in these amorphous aminated biopolymers.

A careful investigation of the thermal decomposition of the modified materials was performed using thermogravimetry. The curves of pure cellulose, chloride-cellulose and cellulose modified with en, using DMF and water as solvents, as well as that prepared without any solvent, are shown in Figs. 4, 5, 6.

For pure cellulose only one mass loss between 563 and 647 K was observed, composing 92% of the thermal decomposition. These curves are shown in Fig. 4 (I). For CelCl the curve shows three mass losses corresponding to: (i) loss of water adsorbed on the surface in the 386–430 K interval, (ii) mass losses attributed to loss of hydrochloric acid and to condensation of hydroxyl groups present on carbons 2 and 3 in the 430 to 534 K range, and (iii) the decomposition of the organic framework above 521 K. The curves for CelCl are shown in Fig. 4 (II) and the corresponding mass losses are listed in Table 2. Based on these results, it could be supposed that CelCl presented higher mass loss due to formation of hydrochloric acid that catalyzes bulk oxidation.

The ethylene-1,2-diamine incorporated biopolymers also presented three mass losses that were attributed to loss of water and possibly carbon dioxide, pendant group decomposition plus condensation of hydroxyl groups and, finally, thermal decomposition of the organic support.

The thermogravimetric curves for en modified celluloses synthesized using DMF as solvent and also for that obtained without solvent are shown in Fig. 5 (I), presenting the same order of final mass loss as previously detected, given as: Celen1 > Celen2 > Celen5. The curves for cellulose chemically modified using water as solvent are shown in Fig. 6 (I), where the behavior

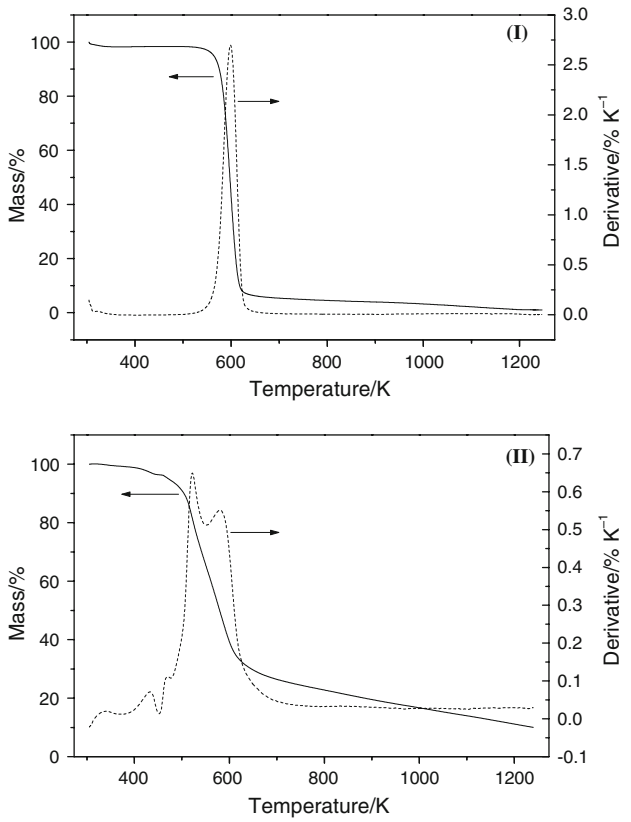

Fig. 4 Thermogravimetric and differential curves for pristine cellulose (**I**) and chlorodeoxycellulose (**II**)

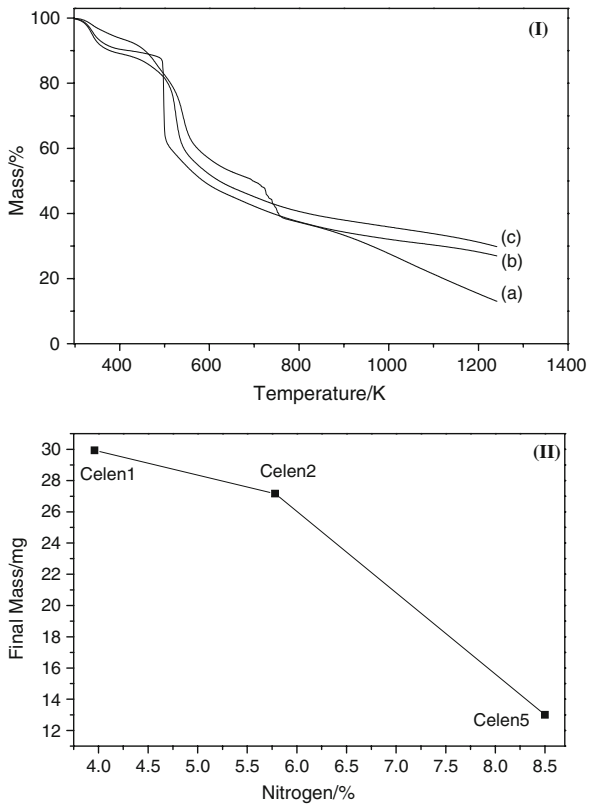

Fig. 5 Thermogravimetric curves for Celen5 (*a*), Celen2 (*b*) and Celen1 (*c*) biopolymers (**I**) and residue of mass loss from thermogravimetric data as a function of the percentage of nitrogen for Celen5, Celen2 and Celen1 biopolymers (**II**)

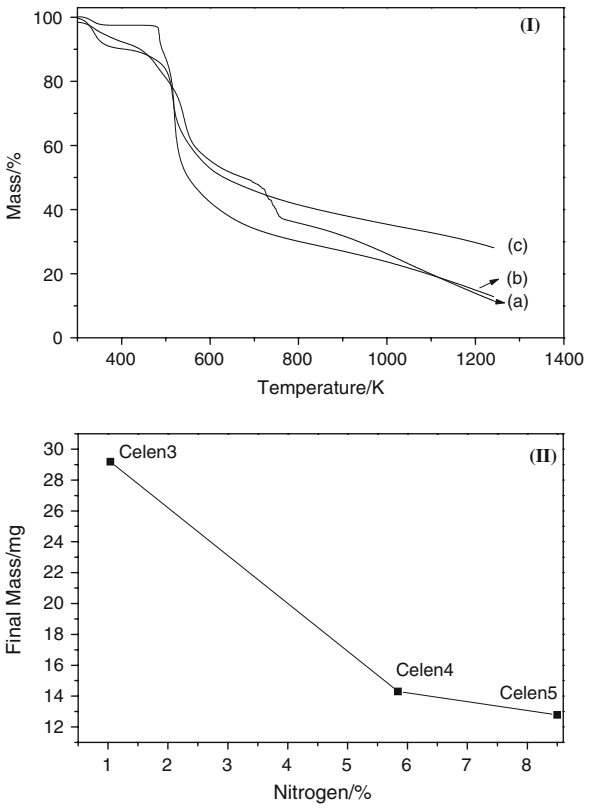

Fig. 6 Thermogravimetric curves for Celen5 (*a*), Celen4 (*b*) and Celen3 (*c*) biopolymers (**I**) and residue of mass loss from thermogravimetric data as a function of the percentage of nitrogen for Celen5, Celen4 and Celen3 biopolymers (**II**)

Table 2 Variation in temperature (ΔT), percent of mass losses for each step of decomposition (Δm) and residue (Δm_r) for biopolymers (Biop) Cel, CelCl and CelenX (X = 1–5)

Biop	ΔT (K)	Δm (%)	Δm_r (%)
Cel	298–343	2	1
	523–647	92	
	647–1273	5	
CelCl	298–430	3	10
	430–534	23	
	534–1273	64	
Celen1	298–452	13	30
	452–1273	57	
Celen2	298–497	13	27
	497–1273	60	
Celen3	298–481	13	28
	481–1273	59	
Celen4	298–481	2	14
	481–1273	84	
Celen5	298–450	10	13
	450–1273	77	

observed was: Celen3 > Celen4 > Celen5. From this relationship an inverse behavior was obtained for all biopolymers, when the residues were at 1273 K were considered, as shown in Fig. 5 (II). For these an analogous graphical representation is obtained by relating the final residue as a function of the nitrogen percentage, as shown in Fig. 6 (II). As observed, the final mass of the chemically modified cellulose is equivalent to the amount of en immobilized.

A higher thermal stability is clearly observed when compared with the unmodified cellulose and chloride modified biomaterials, to give the thermal stability order as follows: Celen > CelCl > Cel, suggesting that biopolymers with fewer incorporated en groups gave higher thermal stability [3, 31, 33, 34].

A summary of thermogravimetric results is presented in Table 2, indicating all decomposition processes, comparing the precursors and chemically modified biopolymers in all steps involved. As expected, the amount of residue after final decomposition depends on the amount immobilized. For the Celen1-5 biopolymers the second interval presented in Table 2 corresponds to two events of different decompositions, as previously described.

Conclusions

The results from this investigation are a relevant advance for this branch of materials science, due to the fact that elemental analysis associated with X-ray diffraction and thermogravimetric tools were successfully applied to characterize cellulose chemically modified with ethylene-1,2-diamine, taking into account that the new compounds were synthesized in available polar solvents and in a special methodology without solvent. The highest amine group incorporations were synthesized through the solvent-free condition, which is a very convenient method of great interest for reducing the generation of toxic wastes and also making the process less expensive.

X-ray diffraction is a useful technique to follow the change in cellulose crystallinity as the sequence of reactions progressed. Thus, a decrease in crystallinity occurred after chlorination, probably due to glucosidic chains and the hydrogen-bonding capacity of the hydroxyl groups, which was further reduced in the next step when ethylene-1,2-diamine was incorporated onto the biopolymer backbone.

The thermogravimetric data of the chemically modified biopolymers indicated smaller total decompositions than the respective cellulose and cellulose chloride precursors. Based on the incorporation results, lesser amounts of ethylene-1,2-diamine attached to the precursor lead to higher total decompositions. For all systems, the final mass was inversely proportional to the amount of the en molecule incorporated.

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References

1. Airoldi C. The weighty potentiality of nitrogenated basic centers in inorganic polymers and biopolymers for cation removal. Quim Nova. 2008;31:144–53.
2. da Silva Filho EC, de Melo JCP, Airoldi C. Preparation of ethylenediamine-anchored cellulose and determination of thermochemical data fot the interaction between cations and basic centers at the solid/liquid interface. Carbohydr Res. 2006;341:2842–50.
3. de Melo JC, da Silva, Santana SA, Airoldi, C. Maleic anhydride incorporated onto cellulose and thermodynamics of cation-exchange process at the solid/liquid interface. Colloids Surf A. 2009.
4. Lopes ECN, Sousa KS, Airoldi C. Chitosan-cyanuric chloride intermediary as a source to incorporate molecules—thermodynamic data of copper/biopolymer interactions. Thermochim Acta. 2009;483:21–8.
5. Sousa KS, Silva Filho EC, Airoldi C. Ethylenesulfide as a useful agente of incorporation into the biopolymer chitosan in a solvent-free reaction for use in cátion removal. Carbohydr Res. 2009. doi: 10.1016/j.carres.2009.05.028.
6. Arakaki LNH, Alves APM, da Silva Filho EC, Fonseca MG, Oliveira SF, Espínola JGP, Airoldi C. Sequestration of Cu(II), Ni(II), and Co(II) by ethyleneimine immobilized on silica. Thermochim Acta. 2007;453:72–4.
7. Sales JAA, Petrucelli GC, Oliveira FJVE, Airoldi C. Some features associated with organosilane groups grafted by the sol-gel process onto synthetic talc-like phyllosilicate. J Colloid Interface Sci. 2006;297:95–103.
8. Sales JAA, Airoldi C. Calorimetric investigation of metal ion adsorption on 3-glycidoxypropyltrimethylsiloxane + propane-1,3-diamine immobilized on silica gel. Thermochim Acta. 2005;427:77–83.
9. da Fonseca MG, da Silva Filho EC, Machado Júnior RSA, Arakaki LNH, Espínola JGP, Airoldi C. Zinc phyllosilicates contaning amino pendant groups. J Solid State Chem. 2004;177:2316–22.
10. da Fonseca MG, Airoldi C. Mercaptopropyl magnesium phyllosilicate—thermodynamic data on the interaction with divalent cations in aqueous solution. Thermochim Acta. 2001;359:1–9.
11. Sales JAA, Petrucelli GC, Oliveira FJVE, Airoldi C. Mesoporous silica originating from a gaseous ammonia epoxide ring opening and the thermodynamic data on some divalent cation adsorptions. J Colloid Interface Sci. 2006;297:426–33.
12. da Silva OG, da Fonseca MG, Arakaki LNH. Silylated calcium phosphate and their new behavior for copper retention from aqueous solution. Colloids Surf A. 2007;301:376–81.
13. da Silva OG, da Silva Filho EC, da Fonseca MG, Arakaki LNH, Airoldi C. Hydroxyapatite organofunctionalized with silylating agents to heavy cátion removal. J Colloid Interface Sci. 2006;302:485–91.
14. da Fonseca MG, da Silva Filho EC, Machado Júnior RSA, Arakaki LNH, Espínola JGP, Oliveira SF, et al. Anchored fibrous chrysotile silica and its ability in using nitrogen basic centers on cátion complexing from aqueous solution. Colloids Surf A. 2003;227:85–91.
15. da Fonseca MG, Almeida RKS, Arakaki LNH, Espínola JGP, Airoldi C. Vermiculite as a useful host for guest cyclic aliphatic amine intercalation, fllowed by cation adsorption. Colloids Surf A. 2006;280:39–44.
16. Morais CC, da Silva Filho EC, da Silva OG, da Fonseca MG, Arakaki LNH, Espínola JGP. Thermal characterization of modified phyllossilicates with aromatic heterocyclic amines. J Thermal Anal Calorim. 2007;87:767–70
17. Klemm D, Heublein D, Fink HP, Bohn A. Cellulose: fascinating biopolymer and sustainable raw material. Angew Chem Int Ed. 2005;44:3358–93.
18. Jal PK, Patel S, Mishra BK. Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions. Talanta. 2004;62:1005–28.
19. Arakaki LNH, da Fonseca MG, da Silva Filho EC, Alves APM, de Sousa KS, Silva ALP. Extraction of Pb(II), Cd(II), and Hg(II) from aqueous solution by nitrogen and functionality grafted to silica gel measured by calorimetry. Thermochim Acta. 2006;450:12–15.
20. Tashiro T, Shimura Y. Removal of mercuric ions by systems based on cellulose derivatives. J Appl Polym Sci. 1982;27:747–56.
21. Silva CR, Airoldi C, Collins KE, Collins CH. Influence of the TiO_2 content on the chromatographic performance and high pH stability of C_{18} titanized phases. J Chrom A. 2006;1114:45–52.
22. Valkenberg HM, Hölderich WF. Preparation and use of hybrid organic-inorganic catalysts. Catal Rev. 2002;44:321–74.
23. Prado AGS, Airoldi C. Adsorption, preconcentration and separation of cations on silica gel chemically modified with the herbicide 2,4-dichlorophenoxyacetic acid. Anal Chim Acta. 2001;432:201–11.
24. Pehlivan E, Altum T. The study of various parameters affecting the ion exchange of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution on Drowex 50W synthetic resin. J Hazard Mater. 2006;134:149–56.
25. Martin AI, Sanchez-Chaves M, Arranz F. Synthesis, characterization and controlled release behaviour of adducts from chloroacetylated cellulose and α-naphthylacetic acid. React Funct Polym. 1999;39:179–87.
26. Warner JC, Cannon AS, Dye KM. Green chemsitry. Env Imp Ass Rev. 2004;24:775–99.
27. Tanaka K, Toda F. Solvent-free organic synthesis. Chem Rev. 2000;100:1025–74.
28. Ott E, Spurlin HM, Grafflin MW. Cellulose and cellulose derivatives. New York: Interscience Publishers; 1954.
29. Zugenmaier P. Conformation and packing of various crystalline celllose fibers. Prog Polym Sci. 2001;26:1341–417.
30. O'Sullivan AC. Cellulose: the structure slowly unravels. Cellulose. 1997;4:173–207.
31. Kim UJ, Kuga S. Thermal decomposition of dialdehyde cellulose and its nitrogen-containing derivatives. Thermochim Acta. 2001;369:79–85.
32. Cunha AP, Freire CRS, Silvestre AJD, Pascoal Neto C, Gandini A, Orblin E, et al. Characterization and evaluation of the hydrolytic stability of trifluoroacetylated cellulose fibers. J Colloid Interface Sci. 2007;316:360–6.
33. Liu CF, Sun RC, Zhang AP, Ren JL, Geng ZC. Polym Degrad Stab. 2006;91:3040–7.
34. Yin C, Li J, Xu Q, Peng Q, Liu Y, Shen X. Chemical modification of cotton cellulose in supercritical carbon dioxide: synthesis and characterization of cellulose carbamate. Carbohydr Polym. 2007;67:147–54.