A physical organic chemistry approach to dissolution of cellulose: effects of cellulose mercerization on its properties and on the kinetics of its decrystallization

Ludmila A. Ramos,[a] Daniella L. Morgado,[a] Fergus Gessner,[a] Elisabete Frollini,[a]
and Omar A. El Seoud[b]*

[a]Institute of Chemistry of São Carlos, University of São Paulo, P.O. Box 780,
13 560 970 São Carlos, SP, Brazil
[b]Institute of Chemistry, University of São Paulo, P.O. Box 26.077,
05513-970 São Paulo, SP, Brazil
E-mail: elseoud@iq.usp.br

Dedicated to Professors Rita H. Rossi, Julio C. Podestá, Manuel González Sierra,
and Oscar S. Giordano

DOI: http://dx.doi.org/10.3998/ark.5550190.0012.734

Abstract

The effects of alkali treatment on the structural characteristics of cotton linters and sisal cellulose samples have been studied. Mercerization results in a decrease in the indices of crystallinity and the degrees of polymerization, and an increase in the α-cellulose contents of the samples. The relevance of the structural properties of cellulose to its dissolution is probed by studying the kinetics of cellulose decrystallization, prior to its solubilization in LiCl/*N*,*N*-dimethylacetamide (DMAc). Our data show that the decrystallization rate constants and activation parameters are only slightly dependent on the physico-chemical properties of the starting celluloses. This multi-step reaction is accompanied by a small enthalpy and large, negative, entropy of activation. These results are analyzed in terms of the interactions within the biopolymer chains during decrystallization, as well as those between the two ions of the electrolyte and both DMAc and cellulose.

Keywords: Cotton linters, sisal, mercerization, cellulose dissolution, decrystallization, kinetics

---

Introduction

Most organic solvents, including strongly dipolar ones, *e.g.*, DMSO cause swelling, but not dissolution of cellulose. The reason is that the biopolymer has a semi-crystalline structure, a consequence of the strong intra- and intermolecular hydrogen-bonding between the OH groups of its anhydroglucose units (AGU). Solvents that are able to disrupt these hydrogen bonds dissolve cellulose samples, even those with very high degree of polymerization, DP, *e.g.*, bacterial cellulose. Examples of solvents that dissolve cellulose physically, *i.e.*, without forming covalent bonds are LiCl/*N*,*N*-dimethylacetamide, DMAc, quaternary ammonium fluorides/DMSO and, more recently, ionic liquids.[1,2] The resulting cellulose solutions have been employed, *inter alia*, for the analysis of cellulose,[3,4] and the preparation of a myriad of derivatives, whose properties are much better controlled than those that are prepared under heterogeneous conditions (solid biopolymer/liquid derivatizing agent).[1,5-10] However, the homogeneous reaction scheme is complex and multi-step, including cellulose activation, dissolution, and subsequent reaction with the derivatizing agent. Understanding the mechanism of each step is essential for process optimization.[11] Cellulose dissolution is a critical step in this reaction scheme, *e.g.*, the dissolution of cotton linters in LiCl/DMAc is sluggish; mercerization is a frequently employed pretreatment step in order to speed up dissolution. The reason usually advanced for this difficulty is the high DP and index of crystallinity, Ic of this cellulose. Therefore, a clearer understanding of the effects of cellulose properties, including purity, DP, and Ic, on the ease of its dissolution is required for a better control of derivatization under homogeneous reaction conditions; this is the subject of the current paper. An additional source of interest is that the celluloses employed are extracted from rapidly-growing plants, sisal and cotton linters (hereafter designated as “sisal” and “linters”, respectively), as opposed to wood, which is obtained from long life-cycle trees.[5,6,8,11]

Results and Discussion

Cellulose characterization

Table 1 shows the structural properties of the cellulose samples studied, along with some results from a previous study.[11]

As the results of Table 1 show, mercerization of both cellulose samples has lead to an initial decrease of $\overline{DPv}$; further treatment has no measurable effect on the physical integrity of the biopolymer. The increase in the α-cellulose content of sisal, 7.9%, is related to its higher hemicellulose content. The effect of alkali treatment on the purity of sisal is relevant to its derivatization, for several reasons: (a) The competition between cellulose and hemicellulose for the derivatizing reagent leads to a decrease of both the yield of the desired product (*e.g.*, cellulose ester), and its degree of substitution, DS; (b) The presence of hemicellulose increases cellulose aggregation in solution, hence decreases its accessibility.[1] Cotton, on the other hand, is practically free of hemicellulose; the increase of its α-cellulose content, 5.5%, is due to the elimination of residual pectins that were not removed during scouring (alkali treatment).[3] During the latter process, cellulose can be degraded by hydrolysis, which can lead to a low average molecular weight sample, as the one employed in the present study.

Table 1. $\overline{DPv}$ (viscosity-based average degree of polymerization), α-cellulose content, Ic (crystallinity index), and crystallite size ($\bar{L}_{002}$ and $\bar{L}_{10\bar{1}}$) of unmercerized and mercerized cellulose samples

Cellulose	$\overline{DPv}$ ± 3.0	α-Cellulose content (%) ± 1.0	Ic ± 0.02	$\overline{L_{002}}$ (nm) ± 0.3	$\overline{L_{10\bar{1}}}$ (nm) ± 0.3
Linters[a]	400	91	0.80	5.9	-
Linters M1h[b]	370	92	0.71	4.1	4.9
Linters M2h[a]	377	92	0.71	3.6	3.9
Linters M3h	370	95	0.72	3.7	4.0
Linter M4h	370	96	0.72	3.9	3.6
Sisal[a]	642	89	0.67	3.9	-
Sisal M1h	574	97	0.64	2.7	3.1
Sisal M2h[a]	544	97	0.65	2.7	3.4
Sisal M3h	544	95	0.65	2.8	3.7
Sisal M4h	544	96	0.65	3.2	3.2

[a]Data taken from reference 11. [b]M1h to M4h denote cellulose samples mercerized for 1 to 4 h, respectively.

The X rays diffractograms of untreated and mercerized linters and sisal (not shown) exhibit the typical diffraction of the polymorphic form attributed to cellulose I, that is, diffraction at, 2θ: 23º (plane 002), 21º (plane 021), 17º (plane $10\bar{1}$) and 15º (plane 101) and cellulose II with diffraction at 2θ ≈ 20º (plane $10\bar{1}$), 2θ ≈ 22º (plane 002) and 2θ ≈ 13º (plane 101).[12] The calculation of Ic was made by considering the diffraction of the 002 plane (2θ ≈ 22º) as maximum intensity and the minimum intensity, related to non-crystalline regions (2θ ≈ 15º). Mercerization also leads to a decrease in the crystalline regions, as evidenced by the decrease in Ic of these celluloses. As observed for $\overline{DPv}$, after an initial drop, there is no detectable dependence of Ic on mercerization time. Considering the un-mercerized celluloses, linters has crystallites larger than those of sisal, which may be one of the reasons leading to the sluggish dissolution of un-mercerized linters in LiCl/DMAC. Alkali treatment leads to a decrease of *ca.* 25% in the average size of crystallites of sisal, and 30% for linters, see Table 1. These results are within the range found for the crystallite sizes of cellulose from other sources, *e.g.*, *Pinus densiflora* (2.02 nm), *Populus euramerican* (4.1 nm), and cotton (4.02 nm).[13,14]

In summary, the relatively easy dissolution of linters after mercerization may be related to a decrease in both Ic and the (average) crystallite size. Whereas the dissolution of sisal does not require this pretreatment, because the corresponding crystallites are smaller than those of linters, its derivatization improves, for the reasons discussed above.

Celluloses dissolution: Kinetics of cellulose decrystallization

As mentioned above, cellulose dissolution occurs if the solvent penetrates into the crystalline regions and disrupts the strong hydrogen-bonding network therein. Therefore, studying the dependence of the kinetics of dissolution on the structural characteristics of cellulose is a prerequisite for understanding, hence optimization of cellulose derivatization. We have calculated the rate constants and activation parameters for the decrystallization of the mercerized samples by measuring the dependence of Ic of the *undissolved cellulose* fraction on the time, t, and temperature, T; typical results are shown in Figures 1 and 2. The procedure that has been employed to calculate the observed rate constants, k_{obs}, and the activation parameters from the above-mentioned Figures is outlined in the Calculations section.

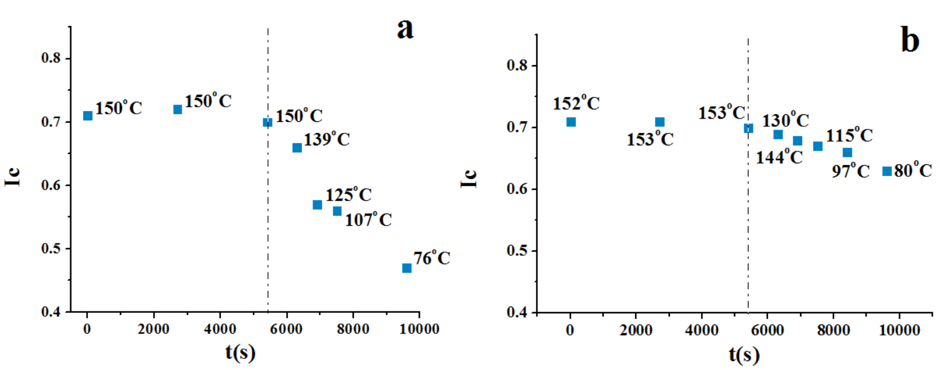
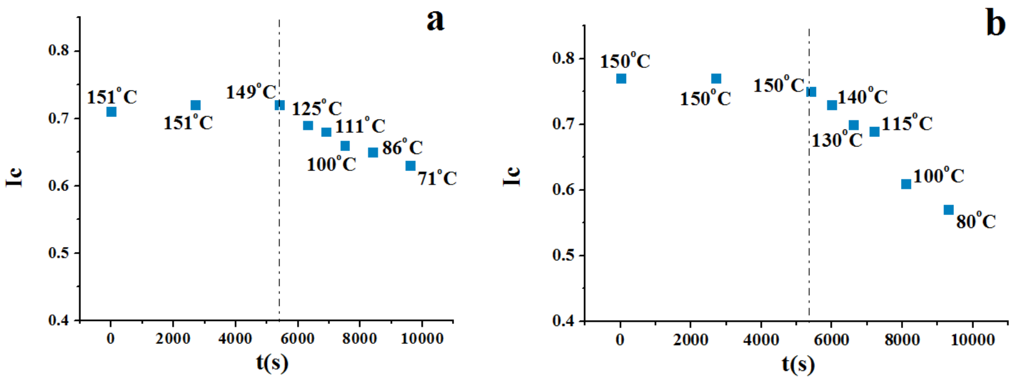


Figure 1. Dependence of Ic of undissolved cellulose on reaction time and temperature. Parts (a) and (b) are for sisal samples that were mercerized for 1 h, 3 h, respectively. In each part, the vertical dashed-line refers to the "zero" time of decrystallization.



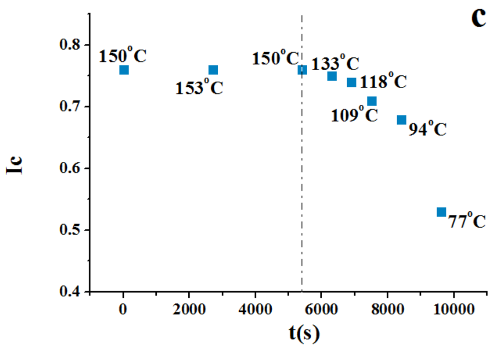


Figure 2. Dependence of Ic of undissolved cellulose on reaction time and temperature. Parts (a), (b), and (c) are for linter samples that were mercerized for 1 h, 3 h, and 4 h, respectively. In each part, the vertical dashed-line refers to the “zero” time of decrystallization.

As shown in Figures 1 and 2, the values of Ic of all cellulose samples were constant at 150 °C, and decreased as a function of decreasing T. The former result indicates that solvent penetration during polymer activation (at 150 °C) is limited to the amorphous regions, in agreement with previous interpretation.[11,15]

The decrystallization process can be treated as a pseudo-first-order reaction (*see supplementary material*). Rate constants and activation parameters obtained for cellulose decrystallization are listed in Tables 2 and 3, respectively.

Table 2. Rate constants and activation parameters for the decrystallization of sisal under non-isothermal conditions

Mercerized sisal 1h				Mercerized sisal 3h				Mercerized sisal 4h			
t(s)	Ic	10^5 k(t) (s^{-1})	10^3 1/T(t) (K^{-1})	t(s)	Ic	10^5 k(t) (s^{-1})	10^3 1/T(t) (K^{-1})	t(s)	Ic	10^5 k(t) (s^{-1})	10^3 1/T(t) (K^{-1})
0[a]	0.70	--	--	0	0.70	--	--	0	0.68	--	--
900	0.66	7.76	2.43	900	0.69	2.36	2.42	900	0.69	4.64	2.44
1500	0.57	8.98	2.51	1500	0.68	2.40	2.48	1500	0.68	4.71	2.51
2100	0.56	9.14	2.63	2100	0.67	2.43	2.56	2100	0.63	5.08	2.58
3000	-	-	-	3000	0.66	2.47	2.67	3000	0.61	5.25	2.70
4200	0.47	10.89	2.87	4200	0.63	2.59	2.83	4200	0.59	5.42	2.88
$\Delta S^{\neq}$= -85.17 (±0.97) cal K^{-1} mol^{-1} $\Delta H^{\neq}$= 2.96(±0.38) kcal mol^{-1} $\Delta G^{\neq}$ = 28.3 kcal mol^{-1}				$\Delta S^{\neq}$= -83.37 (±0.18) cal K^{-1} mol^{-1} $\Delta H^{\neq}$= 1.21(±0.06) kcal mol^{-1} $\Delta G^{\neq}$ = 26.1 kcal mol^{-1}				$\Delta S^{\neq}$= -82.34 (±0.32) cal K^{-1} mol^{-1} $\Delta H^{\neq}$= 1.39(±0.12) kcal mol^{-1} $\Delta G^{\neq}$ = 25.9 kcal mol^{-1}			

[a] Zero time refers to the start of cellulose decrystallization, *i.e.*, when T was lowered below 150 °C (corresponding to the vertical dashed-lines in Figures 1 and 2).

Table 3. Rate constants and activation parameters for decrystallization of mercerized linters under non-isothermal conditions

Mercerized linters 1 h				Mercerized linters 3 h				Mercerized linters 4 h			
t(s)	Ic	10^5 k(t) (s^{-1})	10^3 1/T(t) (K^{-1})	t(s)	Ic	10^5 k(t) (s^{-1})	10^3 1/T(t) (K^{-1})	t(s)	Ic	10^5 k(t) (s^{-1})	10^3 1/T(t) (K^{-1})
0[a]	0.72	--	--	0	0.75	--	--	0	0.76	--	--
900	0.69	2.63	2.50	900	0.73	7.11	2.42	900	0.75	8.65	2.47
1500	0.68	2.67	2.57	1500	0.70	7.41	2.49	1500	0.74	8.77	2.53
2100	0.66	2.75	2.65	2400	0.69	7.52	2.56	2100	0.71	9.14	2.60
3000	0.65	2.80	2.76	3000	0.61	8.51	2.67	3000	0.68	9.54	2.71
4200	0.63	2.89	2.94	4200	0.57	9.11	2.83	4200	0.53	12.58	2.86
$\Delta S^{\neq}$= -83.18 (±0.32) cal K^{-1} mol^{-1}				$\Delta S^{\neq}$= -83.03(±0.47) cal K^{-1} mol^{-1}				$\Delta S^{\neq}$= -83.64(±0.61) cal K^{-1} mol^{-1}			
$\Delta H^{\neq}$= 1.23(±0.12)kcal mol^{-1}				$\Delta H^{\neq}$= 2.01(±0.18) kcal mol^{-1}				$\Delta H^{\neq}$= 2.36(±0.24) kcal mol^{-1}			

[a] Zero time refers to the start of cellulose decrystallization (corresponding to the vertical dashed-lines in Figures 1 and 2)

The fact that calculation of Ic is a matter of debate has no bearing on our kinetic data, as long as these indices are calculated by the same procedure.[3] The reason is that the values of k(t) are based on *differences-, and not absolute values* of Ic. At first glance, the results obtained are surprising because the rate constants and activation parameters calculated are only slightly dependent on the physico-chemical properties (DPv and Ic) of the starting cellulose samples. Additionally, decrystallization is associated with a small $\Delta H^{\neq}$ and a large, negative $\Delta S^{\neq}$. Due to the chemical heterogeneity of the fiber wall the calculated activation parameters may be considered "apparent"; they refer to the sum of several interactions, whose enthalpy and/or entropy changes may have different signs. These include the following interactions: (i) within the biopolymer during decrystallization; (ii) between the two components of the solvent; (iii) between cellulose and LiCl/DMAc. With regard to point (i), cellulose decrystallization is not a single-step reaction; it can be divided into the following steps. a) Transition of the solid polymer into a hypothetical, highly elastic liquid state. This corresponds to disintegration of the crystalline regions (ΔH_{fusion}) and transition of the amorphous regions from vitreous to a highly elastic state ($\Delta H_{transition}$). b) Solvation of the polymer macromolecules ($\Delta H_{interaction}$). c) Mixing of solvated polymer molecules with solvent to give an infinitely diluted solution (ΔH_{mixing}).[16,17] The total enthalpy of cellulose dissolution is, therefore, given by:

$$\Delta H_{\mathbf{solution}} = \Delta H_{\mathbf{fusion}} + \Delta H_{\mathbf{transition}} + \Delta H_{\mathbf{interaction}} + \Delta H_{\mathbf{mixing}} \qquad \mathbf{(1)}$$

The only endothermic term of Eq. (1) is ΔH_{fusion}, which is associated with breaking the hydrogen-bonds in the crystalline regions. The other terms are exothermic and are related to interactions between cellulose hydroxyl groups and the components of the solvent. Therefore, the overall process of cellulose dissolution is exothermic and is favored at lower temperatures,[16,18] in agreement with the data of Figures 1 and 2.

With regard to point (ii), we may employ the extra-thermodynamic quantities of transfer of single ions from aprotic to protic solvents as a model for the reaction under consideration. This use is appropriate because recent measurements (using solvatochromic indicators) have indicated that the polarity at the surface of cellulose is akin to that of aliphatic alcohols.[19] Single-ion enthalpies of transfer indicate that Li^+ is more efficiently solvated by DMAc than by alcohols (hence by cellulose). That is, the equilibrium shown in Equation 2 is endothermic:

$$\text{Li-DMAC} + \text{cellulose} \leftrightarrows \text{DMAc} + \text{Li-cellulose} \qquad \mathbf{(2)}$$

The inverse holds for Cl^-, *i.e.*, the equilibrium depicted by Equation 3 is exothermic.[20]

$$\text{Cl}^-\text{-DMAC} + \text{cellulose} \leftrightarrows \text{DMAC} + \text{Cl}^-\text{-cellulose} \qquad \mathbf{(3)}$$

Considering point (iii), solvatochromic data for cellulose solutions in LiCl-DMAc have indicated that Cl^--HO-cellulose hydrogen bonding is more important for dissolution than Li-cellulose interactions.[21]

Points (i) to (iii) can now be employed to explain the results shown in Tables 2 and 3. If decrystallization were rate limiting, and considering that the equilibria shown in Equations 2 and 3 occur *prior to* decrystallization, then the activation parameters calculated represent the sum of the three reactions. That is, the endothermicity associated with breaking of the inter-molecular hydrogen bonding (between the cellulose chains) can be largely offset by the exothermicity of the hydrogen bonds formed between cellulose and the chloride ion. This cancellation explains the small values of $\Delta H^{\neq}$. Concerning $\Delta S^{\neq}$, the change (crystalline → dissolved polymer chains) is expected to have positive entropy, because the chain movements are largely restricted in the crystalline region. Some of this (expected) increase in the degree of freedom of the solvated cellulose chains may not contribute to $\Delta S^{\neq}$. The reason is that it is possible that only a part of the same chain lies in the crystalline region; the part in the non-crystalline counterpart makes only a small contribution. Additionally, light scattering measurements have indicated that in most cases, including the present one, the dissolved cellulose chains are not molecularly dispersed, but are present as relatively large aggregates,[10] this leads to smaller difference in entropy between the crystalline and dissolved biopolymer chains. Ion association with the polymer most certainly contributes to the overall $\Delta S^{\neq}$. That is, the change from crystalline cellulose to polymer-LiCl complex may be associated with an entropy decrease due to ion complexation by the polymer.[22]

The mobility may be further reduced due to attractive electrostatic interactions between polymer segments where the Li^+ and Cl^- ions are complexed.

Conclusions

Dissolution of celluloses of different physico-chemical properties in LiCl/DMAc has been studied with the aim of probing the structural factors that affect this process. Due to its highly organized crystalline structure, linters can be readily dissolved after mercerization. This pre-treatment reduces Ic and crystallite size considerably, these are important factors for dissolution in LiCl/DMAc. Sisal dissolves in LiCl/DMAc without mercerization, most probably because its Ic and crystallite size are smaller than those of cotton linters. Additionally, solvent penetration is easier because of the presence of macro-pores in its supra-molecular structure. Mercerization of this cellulose may be advantageous, however, because of elimination of hemicellulose and other non-cellulosic material. Use of purer starting cellulose is important from the application point of view, as it leads to a better control of product yield and reproducibility.

The rate constants and activation parameters of cellulose decrystallization, a required step for its dissolution, are negligibly dependent on the physico-chemical properties of cellulose. The reaction is associated with a small enthalpy and a large, negative entropy, probably due to compensations between the energetics of the interactions of LiCl with both the solvent and the polymer.

Experimental Section

General. The solvents and reagents were purchased from VETEC, Mallinckrodt, or Tiririca Química (DF) and were purified by standard procedures. The celluloses employed included sisal (isolated from the Kraft pulping of sisal lingo-cellulosic fiber, Lwarcel; Lençois Paulista; São Paulo) and low average molar weight linters (short fibers that cover the cotton seeds, obtained after the processing of these seeds, Indústria Fibra S/A, Americana, São Paulo). Before use, LiCl was dried by heating at 200 °C for 3 h, cooled under reduced pressure, and kept in a desiccator.

Cellulose characterization. Cellulose characteristics were determined as indicated elsewhere, for the viscosity-based degree of polymerization ($\overline{DPv}$),[23] index of crystallinity (Ic)[24], and α-cellulose content.[25]

Kinetics of cellulose dissolution. The dissolution step was similar to that reported by Marson and El Seoud[15] with some modifications. A 250 mL four-necked round-bottomed flask was equipped with a stopcock, addition funnel (without equilibration sidearm), mechanical stirrer, and condenser closed with a stopper. The appropriate amounts of cellulose (4 g) and LiCl (10 g) were introduced; the flask was connected to a vacuum pump through the stopcock and immersed in an oil bath, whose temperature was externally controlled (FE50RP controller, Flyever, São Carlos, SP, Brazil). The pressure was reduced to 2 mm Hg, and the system was heated from room temperature to 110 °C (3 °C min^{-1}) and kept under these conditions for 30 min. The vacuum pump was turned off, and dry DMAc (120 mL) was slowly added. The system was then brought to atmospheric pressure with dry, oxygen-free nitrogen, and the condenser was provided with a drying tube. The temperature was raised to 150 °C (4 °C min^{-1}), and the cellulose slurry was vigorously stirred for 90 min. The mixture was slowly cooled to 40 °C at a rate of 1 °C/min. During the cooling period, 10 mL aliquots of the cellulose slurry were withdrawn from the reactor; the bath temperature and time were recorded. The *undissolved* cellulose of each aliquot was quickly filtered by suction into a sintered-glass funnel, washed with methanol (50 mL), and dried first in air (110 °C) and then under reduced pressure (60 mm Hg, 60 °C) until constant weight (about 18 h). The indices of crystallinity, Ic, of these samples were determined by X ray diffraction (Zeiss-Jena URD-6 universal diffractometer operating at 40 kV, 20 mA and $\lambda(\text{Cuk}\alpha)$ = 0.154 nm).

Acknowledgements

E. Frollini and O. A. El Seoud thank the CNPq (National Council of Research) for research productivity fellowships, the FAPESP (State of São Paulo Research Foundation) for financial support, and a research fellowship for D. L. Morgado.

References

1. El Seoud, O. A.; Heinze, T. *Adv. Polym. Sci.* **2005**, *186*, 103.
2. El Seoud, O. A.; Koschella, A.; Fidale, L. C.; Dorn, S.; Heinze, T. *Biomacromolecules* **2007**, *8*, 2629.
3. Krässig, H. A. Cellulose: Structure, accessibility and reactivity, New York, Gordon and Breach, 1992, pp 167-258.
4. Ishii, D.; Kanazawa, Y.; Tatsumi, D.; Matsumoto, T. *J. Appl. Polym. Sci.* **2007**, *103*, 3976.
5. Ass, B. A. P.; Ciacco, G. T.; Frollini, E. *Bioresource Technol.* **2006**, *97*, 1696.
6. Ass, B. A. P.; Belgacem, M. N.; Frollini, E. *Carbohyd. Polym.* **2006**, *63*, 19.
7. Ratanakamnuan, U.; Atong, D.; Aht-Ong, D. *Adv. Mat. Res.* **2007**, *24-25*, 457.
8. Ciacco, G. T.; Ass, B. A. P.; Ramos, L. A.; Frollini, E. *E-Polymers* **2008**, *22*, 1.
9. Krouit, M.; Granet, R.; Krausz, P. *Bioorg. Med. Chem.* **2008**, *16*, 10091.
10. (a) Ciacco, G. T.; Morgado, D. L.; Frollini, E.; Possidonio, S.; El Seoud, O. A. *J. Braz. Chem. Soc.* **2010**, *21*, 71; (b) Ramos, L. A.; Morgado, D. L.; El Seoud, O. A.; da Silva, V. C.; Frollini, E. *Cellulose* **2011**, *18*, 385.
11. Ramos, L. A.; Assaf, J. M.; El Seoud, O. A.; Frollini, E. *Biomacromolecules* **2005**, *6*, 2638.

12. Tasker, S.; Badyal, J. P. S.; Backson, S. C. E.; Richards, R. W. *Polymer* **1994**, *50*, 4717.
13. Awadel-Karim, S.; Nazhad, M. M.; Paszner, L. *Holzforschung.* **1999**, *53*, 1.
14. Harada, H.; Goto, T. in *The structure of cellulose microfibrils in Valonia*; Brown, M. R., Jr., Ed.; Cellulose and other natural polymer systems: biogenesis, structure and degradation. New York: Plenum, **1988**; pp. 383-399.
15. Marson, G. A.; El Seoud, O. A. *J. Appl. Polym. Sci.* **1999**, *74*, 1355.
16. Myasoedova, V. V.; Pokrovskii, S. A.; Zav'yalov, N. A.; Krestov, G. A. *Russ. Chem. Rev.* **1991**, *60*, 954.
17. Basedow, A. M.; Ebert, K. H.; Feigenbutz, W. *Makromol. Chem.* **1980**, *181*, 1071.
18. Marson, G. A.; El Seoud, O. A. *J. Polym. Sci.: Part A: Polym. Chem.* **1999**, *37*, 3738.
19. Fidale, L. C.; Issbrucker, C.; Silva, P. L.; Lucheti, C. M.; Heinze, T.; El Seoud, O. A. *Cellulose* **2010**, *17*, 937.
20. Hefter, G.; Marcus, Y.; Waghorne, W. E. *Chem. Rev.* **2002**, *102*, 2773.
21. Spange, S.; Fischer, K.; Prause, S.; Heinze, T. *Cellulose* **2003**, *10*, 201.
22. (a) Mark, J. E.; Eisenberg, A.; Graessley, W. W.; Mandelkern, L.; Samulski, E. T.; Koenig, J. L.; Wignall, G. D. *Physical Properties of Polymers*; ACS: USA, **1992**; 2nd Edn, p 150; (b) Oestlund, A.; Lundberg, D.; Nordstierna, L.; Holmberg, K.; Nyden, M. *Biomacromolecules* **2009**, *10*, 2401.
23. TAPPI *Viscosity of pulp (capillary viscosimeter method)* T230 om –89 in TAPPI test methods 1991. Atlanta: TAPPI, 1990; Vol. 1, pp 1-6.
24. Buschle-Diller, G.; Zeronian, S. H. *J. Appl. Polym. Sci.* **1992**, *45*, 967.
25. Browning, B. L. *Methods of wood chemistry*; New York: Interscience, 1967; Vol. 2, p 499.