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Crystalline properties and decomposition kinetics of cellulose fibers in wood pulp obtained by two pulping processes

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In this study two cellulose fibers, *Eucalyptus grandis* (CEG) and *Pinus taeda* (CPT), obtained through the kraft and sulfite pulping processes, respectively, were characterized. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were carried out. From the XRD analysis the interplanar distance, crystallite size and crystallinity index were calculated and the degradation kinetics parameters were determined by TGA at heating rates of 5, 10, 20 and 40 °C min^{-1} using the Avrami, Flynn-Wall-Ozawa (FWO) and Criado methods. The results obtained by FTIR showed that the composition of the fibers is similar, while from the XRD analysis slight differences in the crystallinity were observed. The thermogravimetric analysis showed higher thermal stability for CPT than CEG while the values for the activation energy (E_a) were higher for CEG than CPT. The results obtained by Avrami and Criado methods showed that the degradation mechanism in the CEG samples involves a diffusion process while in the case of CPT the degradation process is a phase boundary controlled reaction. The degradation mechanisms demonstrated that the difference between thermal stability and E_a may be due to differences in the type of crystalline structure of the samples obtained through the two pulping processes.

1. Introduction

Cellulose is a polymer which contains crystallites and thus it has a paracrystalline morphology [1,2]. The linear cellulose molecules are linked laterally by hydrogen bonds to form linear bundles, leading to a crystalline structure [1]. Native cellulose is known to be a composite of two distinct crystalline modifications, namely I_α and I_β, whose fractions vary depending on the origin of the cellulose sample [2–4]. The I_α and I_β structures are assigned to one-chain triclinic and two-chain monoclinic unit cells, respectively [3]. These allomorphs are believed to coexist in the fibril in different ratios [4]. In addition, I_α cellulose is reported to be the dominant polymorph in bacterial and alga celluloses, while I_β cellulose is predominant in higher plants such as cotton and wood [5]. Therefore, the crystalline structure of cellulose affects the physical and mechanical properties of the cellulose fibers. The degree of crystallinity of cellulose is one of the most important crystalline structure parameters, and the rigidity of cellulose fibers increases and the flexibility decreases with an increasing ratio of crystalline to amorphous regions [1,6].

Changes occurring in the cellulose structure during pulping have been investigated in several studies [1,3,4,7]. Gümüskaya et al. [1] concluded that not only chemical agents but also the temperature and pressure in a cooking digester had major effects on the crystalline structure of cellulose in cotton linters during cooking. Hult et al. [4] investigated the organization of cellulose microfibrils in holocellulose, sulfite pulp and kraft pulp and revealed that in kraft pulp the microfibrils are more closely associated than in the sulfite pulp and holocellulose.

Due to the complexity of cellulose thermal decomposition reactions, extensive research has been carried out in this area. Wu and Dollimore [8] investigated the thermal degradation behavior of natural cellulosic materials and demonstrated that the rate-controlling mechanism involved mainly the phase boundary and probably diffusion processes. Nada and Hassan [9] investigated cellulose and some cellulose derivatives and reported activation energy values of 53–182 kJ/mol. Antal et al. [10] using dynamic thermogravimetric analysis found activation energy values of between 190 and 250 kJ/mol, depending on the type of cellulose, the heating rate and the mass of sample. Capart et al. [11] calculated kinetics parameters of microgranular cellulose using dynamic and isothermal methods in a nitrogen atmosphere and described two reactions with activation energies of 202 and 255 kJ/mol, respectively. The aim of this study was to investigate the effects of

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chemical treatments on the crystalline properties and decomposition kinetics of cellulose fibers in wood pulp during two pulping processes.

2. Materials and methods

2.1. Materials

Bleached sulfite cellulose fibers from *Pinus taeda* (CPT) were supplied by Cambará S.A (Cambará do Sul, Brazil). Bleached kraft cellulose fibers from *Eucalyptus grandis* (CEG) were supplied by CMPC S.A. (Guaíba, Brazil). The samples were dried at 70 °C for 24 h in a vacuum oven before the tests. The average fiber particle length for CTP and CEG is around 150 μm.

2.2. Fourier transform infrared (FTIR) spectroscopy

The Fourier transform infrared (FTIR—Nicolet IS10-Thermo Scientific) spectroscopy analysis was carried out with 32 scans, in the range of 4000 cm^{-1} to 400 cm^{-1}, at a resolution of 4 cm^{-1} using attenuated total reflectance (ATR), on cellulose powder under pressure on ATR crystal.

2.3. Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA50—Shimadzu) was carried out under N_2 atmosphere, from 25 up to 610 °C. Approximately 20 mg of each sample was used. The analysis was carried out at four different heating rates (5, 10, 20 and 40 °C min^{-1}). The results obtained were used to calculate the kinetics parameters.

2.4. X-ray diffraction (XRD)

X-ray diffractograms were collected using a sample holder mounted on a Shimadzu diffractometer (XRD-6000), with monochromatic Cu Kα radiation ($\lambda = 0.15418$ nm) and the generator working at 40 kV and 30 mA. Intensities were measured in the range of $5 < 2\theta < 30°$, typically with scan steps of 0.05° and 2 s/step (1.5° min^{-1}). Peak separations were carried out using Gaussian deconvolution. The determination coefficients (r^2) were close to unity (0.9972 and 0.9947 for CEG and CPT, respectively). The *d*-spacings were calculated using the Bragg equation [3,12], the crystallite sizes (L) were calculated using the Scherrer equation [3,12] and the crystallinity index (CrI) using the Segal method [1,3].

2.5. Theoretical Considerations

The fundamental equation used in all kinetic studies is generally described as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where k is the rate constant and $f(\alpha)$ is the reaction model, a function dependent on the reaction mechanism. Eq (1) expresses the rate of conversion, $d\alpha/dt$, at a constant temperature as a function of the reduction in reactant concentration and the rate constant. In this study, the conversion α rate is defined as [13–16]:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{2}$$

where m_0, m_f and m_t are the initial and final weights of the sample and its weight at time (t), respectively. The rate constant k is generally given by the Arrhenius equation:

$$k(T) = Ae^{\frac{-Ea}{RT}} \tag{3}$$

where E_a is the apparent activation energy (kJ mol^{-1}), R is the gas constant (8.314 kJ mol^{-1}), A is the pre-exponential factor (min^{-1}), and T is the absolute temperature (K). The combination of Eqs. (1) and (3) gives the following relationship:

$$\frac{d\alpha}{dt} = Ae^{E_a/RT}f(\alpha) \tag{4}$$

For a dynamic TGA process in a non-isothermal experiment, introducing the heating rate, $\beta = dT/dt$, into Eq. (4), Eq. (5) is obtained as:

$$\frac{d\alpha}{dt} = \left(\frac{A}{\beta}\right)e^{E_a/RT}f(\alpha) \tag{5}$$

Equations (4) and (5) are the fundamental expressions of analytical methods used to calculate kinetic parameters on the basis of TGA data.

2.6. Flynn-Wall-Ozawa method

In the FWO method [13,14], it is proposed that through the integration of Equation (5) and substituting (E_a/RT) with x, the following relationship can be obtained:

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{AE}{\beta R}P(x) \tag{6}$$

were $P(x)$ is a function known as the Arrhenius integral that has no analytical solution but can be solved by numerical methods or using different approaches. The test method is based on integral approaches proposed by Doyle [17], in a range of $\log P(x)/x=(E_a/RT)$ to $20 < x < 60$. The integral of $P(x)$ can be expressed simplistically as:

$$\ln\beta = \ln\frac{AE}{g(\alpha)R} - 5.330 - 1.052\frac{E}{RT} \tag{7}$$

In Eq. (7) $g(\alpha)$ is a function of the conversion. According to the principles of the isoconversional FWO method, it is assumed that the reaction rate at a given conversion is a function only of the temperature. Therefore, for different heating rates (β) and a given degree of conversion (α), a linear relationship is observed through a plot of $\log\beta$ vs. $1/T$, and the apparent activation energy (E_a) is obtained from the slope of the straight line obtained [13–15].

2.7. Criado method

The degradation reaction mechanism can be determined using the Criado method [18–20] which can accurately determine the reaction mechanism in a solid reaction process, defined by a $Z(\alpha)$-type function:

$$Z(\alpha) = \frac{\left(d\alpha/dt\right)}{\beta}\pi(x)T \tag{8}$$

where $x = E/RT$ and $\pi(x)$ is an approximation of the temperature integral which cannot be expressed in a simple analytical form. Paterson [19] proposed a reasonable relationship between $\pi(x)$ and $P(x)$ as shown in Eq. (9):

$$\pi(x) = xe^{x}P(x) \tag{9}$$