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Effect of acid hydrolysis conditions on the degradation properties of cellulose from *Imperata brasiliensis* fibers

Kelly C. C. de Carvalho Benini[a]*, Paulo H. F. Pereira[a], Maria Odila H. Cioffi[a], Herman Jacobus Cornelis Voorwald[a]

[a]*Departament of Materials and Technology, Unesp – São Paulo State University, Ariberto Pereira da Cunha, 333, Gauaratinguetá, São Paulo, Brazil*

Abstract

The thermal properties of Imperata brasiliensis fibers and cellulose nanofibrils (CNFs), obtained at different conditions of sulfuric acid hydrolysis, were studied in the present work. Imperata Brasiliensis fibers were chemically treated by alkaline solution followed by bleaching treatment and both, untreated and treated fibers were characterized. Using a design of experiments (DOE), CNFs were obtained at nine different conditions, considering four factors (acid concentration, pulp/solution ratio, temperature and reaction time), at three levels. From results of thermogravimetric analysis (TGA), it was possible to determine some degradation properties and kinetic parameters such as activation energy (Ea) and understand how this parameter changes as a function of chemical treatments and acid hydrolysis conditions. Considering obtained results, it was possible to stablished that chemical treatments, carried out before acid hydrolysis, were effective since some amorphous components were removed, which was confirmed by the increase of thermal stability and Ea values. The best conditions of acid hydrolysis to obtain CNFs from Imperata brasiliensis fibers was also determined, being H_2SO_4 64 (wt%) at 35°C for 75 min with pulp/solution ratio of 1/20 (g/mL). The suspension obtained at these conditions presented initial degradation temperature of 117 °C and, Ea for the main stage of cellulose degradation of about 64 kJ/mol.

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Keywords: Thermal analysis; Activation energy; Imperata brasiliensis fibers

* Corresponding author. Tel.: 55-12 3123 2865.
E-mail address: kcccarvalho@hotmail.com

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1. Introduction

In the last years, cellulose nanofibers have been extensively studied for many scientific and technological applications, because of its unique characteristics such as thermal stability, biodegradability, abundance, renewability, mechanical resistance and optical properties [1, 2].

The use of different plants to extract cellulose nanofibers have been presented in the literature by many researchers, such as, Oun and Rhim [1], Mariano et. al [2] and Henrique et. al [3]. The exploration of different resources is important considering that cellulosic materials characteristics can be changed according to plant age and location, climatic seasonal conditions and processes of impurities extraction (chemical reagents, temperature) [4-6].

Cellulose degradation processes involve different mechanisms that occur simultaneously in a complex process. However, the investigation of cellulose degradation, before and after chemical treatments, is extremely important, since these processes, due to the presence of chemical reagents and temperature, can interfere in the cellulose crystalline structure, changing, consequently, its thermal and physical behavior [7]. During hydrolysis reactions for cellulose nanofibrils (CNFs) obtaining, for example, formations of carbonyl groups in cellulose chains, can be responsible for the cellulose degradation [8].

Thermogravimetric analysis is the most common technique used to study thermal stability of cellulose fibers and nanofibers. These cellulosic materials present distinct stages of degradation that involves loss of absorbed water, dehydration (180-280°), depolymerization of glucoside unions, decomposition of α-cellulose, volatilization, and char formation [7].

Imperata brasiliensis *Trin.* (Brazilian Satintail), a kind of grass which did not present a commercial used, is a plant that grown in different regions of Brazil. Considered as a weed, its exploration as a resource for cellulose obtaning has the main objective of to add value for this agricultural residue [9].

In the present work, Imperata brasiliensis fibers were alkali treated and bleached with hydrogen peroxide, subsequently being treated by sulfuric acid hydrolysis in order to have the nanocellulose. Cellulose nanofibrils (CNFs), at different acid hydrolysis conditions following a Design of Experiments (DOE) using Taguchi method were obtained, in order to varying a large number of conditions with a small number of experiments.

The thermal stability and thermal kinetic parameters studies for untreated fibers, bleached fibers and CNFs were performed in order to understand the effect of chemical treatments and hydrolysis conditions in the thermal degradation properties of these cellulosic materials.

2. Methodology

2.1. Materials

Imperata brasiliensis fibers used in this work were gathered at Guaratinguetá (São Paulo State, Brazil). The chemical reagents used were sulfuric acid (H_2SO_4, 98%) and sodium hydroxide (NaOH) purchased from Sigma-Aldrich, hydrogen peroxide (H_2O_2, 30%) from Vetec and cellulose membrane dialysis tubing (MWCO 12000-14000) from Servapor®.

2.2. Preparation of cellulose nanofibrils

CNFs were obtained from Imperata brasiliensis (IB) fibers by pre-chemical treatments. Initially, untreated Imperata brasiliensis fibers (IBU), were grinded into powder, sieved under 25 mesh, and dried in an oven for 48h at 60°C as described before by Benini et. al [9]. Afterwards it were treated with an alkaline solution 5% (w/w) at 75°C for 1h under mechanical stirring. Fibers were then bleached for 3 times with a 1:1 solution of H_2O_2 24% (v/v) and NaOH 4% (w/w) at 50°C for 2h under mechanical stirring. After each treatment, fibers were filtered, washed with distilled water until neutral pH and, dried in an oven for 48h at 60°C. Bleached fibers (IBB) were treated with sulfuric acid solution according to Design of Experiments (DOE), using Taguchi method with a matrix L9 (3^4), with four parameters at three levels as described at Table 1, in order to obtain cellulose nanofibrils (CNFs).