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Effect of chitosan and cationic starch on the surface chemistry properties of bagasse paper

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ABSTRACT

The use of non-wood fibers in the paper industry has been an economical and environmental necessity. The application of dry–strength agents has been a successful method to enhance the strength properties of paper. The experimental results evidencing the potential of chitosan and cationic starch utilization in bagasse paper subjected to hot water pre-extraction has been presented in this paper. The research analyzes the surface properties alterations due to these dry–strength agents. Inverse gas chromatography was used to evaluate the properties of surface chemistry of the papers namely the surface energy, active sites, surface area as well as the acidic/basic character. The results of the study revealed that the handsheets process causes surface arrangement and orientation of chemical groups, which induce a more hydrophobic and basic surface. The acid–base surface characteristics after the addition of dry–strength agents were the same as the bagasse handsheets with and without hot water pre-extraction. The results showed that the dry–strength agent acts as a protecting film or glaze on the surfaces of bagasse paper handsheets.

1. Introduction

Continuous improvement in the variety and quality of paper grades is essential for the success of the pulp and paper industry. New demands due to economic and especially environmental reasons have changed papermaking dramatically, forcing papermakers to improve the quality and increase the added-value of their products [1,2]. The use of non-wood fibers or recycled fibers in the paper industry has been an economical and environmental necessity over the last two decades. However, papermakers usually need the application of specific substances to enhance the end-use performance of their products [3].

The importance of mechanical properties, regarding the end-uses of paper products, paper strength improvement has been a prime important consideration for papermakers when paper and paperboard products are not made exclusively from virgin wood fibers [4]. The application of dry–strength additive has been a successful method to enhance the strength properties of paper [5]. The wood fibers contain their own natural dry–strength additive in the form of hemicelluloses. The small amount of hemicelluloses removal from pulps makes it more difficult to develop their bonding characteristics. Various dry–strength agents have been used throughout the years but a tendency towards the application of bio-chemicals is observed. The bio-chemicals, obtained from renewable resources, are based on organic macromolecules of biological origin represented mainly by polysaccharides, such as starch and Chitosan [6]. These highly hydrophilic polymers have chemical structures similar to cellulose, enabling them to participate in extensive hydrogen bonding with fiber surfaces. Since the surface of fibers is negatively charged, the application of products with cationic groups attached to the main chain increases the attraction between the molecules of dry–strength agents and fibers. Because of this, unmodified starch has little affinity to cellulosic fibers; therefore, almost all starches strengths are cationic. Cationic starch gives better natural retention due to its positive charge, which makes it adhere to negatively charged fibers under normal papermaking conditions. Starch derivatives represent the most common and by far the largest amount of dry–strength agents [7].

Due to its biodegradability, biocompatibility, antimicrobial activity, nontoxicity, and versatile chemical and physical properties, chitosan has a great potential for a wide range of applications [8]. Chitosan is the main derivative of chitin, which is the second polysaccharide on earth, after cellulose. The unique structural feature of chitosan is the presence of primary amines at the C-2 position of the D-glucosamine residues. These amine groups, in the first place, allow specific chemical reactions, and secondly confer

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important functional properties to chitosan, which can be exploited for application in a variety of areas, included in the paper industry as a dry–strength additive, due to its abundance and comparative cost-effectiveness [9,10].

Chemical modification of the paper by dry–strength agent, changes the structural and chemical properties, including the surface energy of the paper and its hydrophilic/hydrophobic surface character. In the particular case of the printing paper, the surface characterization is one of the most important factors concerning consumers' evaluation. Thus, all the studies dealing with printing quality, paper surface properties and paper-ink interaction are of utmost importance. Inverse gas chromatography (*i*GC) is a very useful method to determine the surface properties of a solid. Unlike gas chromatography, this analytical chromatography method is used as stationary phase for samples whose properties are unknown, and as mobile phase for probe molecules with known properties. Through the passage of these probes, it is possible to determine the characteristics of the solid surface by the their retention times. The dispersive and specific components of the surface free energy, acid–base character, adsorption isotherm, monolayer capacity, surface area and heterogeneity are some of the properties obtained through *i*GC analysis.

1.1. Dispersive component of the surface energy

The dispersive component of the surface energy (γ_S^D) is determined using dispersive probes molecules namely homologous *n*-alkanes through the pulse technique. The retention time obtained from the interaction between the probes molecules and the solid surface allows us to determine the dispersive surface free energy, ΔG_{ads}, obtained by Eq. (1) [11]:

$$\Delta G_{ads} = RT \ln V_N = 2N_A(\gamma_S^d)^{1/2} a(\gamma_L^d)^{1/2} + K \quad (1)$$

where R is the gas constant, K is a constant depending on the chosen reference state, T is the column temperature, V_N is the net retention volume, γ_S^d denotes the dispersive component of surface free energy of the solid, γ_L^d denotes the dispersive component of the surface free energy of the test solute, a is the area occupied by probe molecule and N is the Avogadro's number. Component γ_S^d can be calculated from the slope of the obtained line in the plot of ΔG_{ads} versus $a(\gamma_L^d)^{1/2}$ of the series of *n*-alkanes.

1.2. Specific component of the surface energy (acid–base properties)

Specific component of the surface energy, ΔG_{ads}^{sp}, is one parameter of the surface energy giving the contribution of Lewis acid–base interactions with the solid surface through polar probes. The polar molecules and solid interactions involve two terms: dispersive, ΔG_{ads}^{d}, and specific, ΔG_{ads}^{sp}, interactions. ΔG_{ads} is determined by the Eq. (2).

$$\Delta G_{ads} = \Delta G_{ads}^{d} + \Delta G_{ads}^{sp} \quad (2)$$

ΔG_{ads}^{sp} can be determined using Fowkes plot with the following relation [12]:

$$\Delta G_{ads}^{sp} = RT \ln V_N - RT \ln V_{N(ref)} \quad (3)$$

where V_N is the net retention volume for the polar probe and $V_{N(ref)}$ is the net retention volume established by the *n*-alkane reference line for the same polar probe. Through specific enthalpy of adsorption, it is possible to quantify the Lewis acidity and Lewis basicity of the non-volatile material using with the following equation [13,14]:

$$\frac{\Delta H_{ads}^{sp}}{AN*} = \frac{DN}{AN^*} \times K_A + K_B \quad (4)$$

where AN^* and DN are Guttmann's modified acceptor and donor numbers, respectively; K_A is a Lewis acidity constant and K_B is a Lewis basicity constant.

1.3. Isotherm measurements

Using a wide variety of probe molecules at different temperatures, adsorption isotherm is obtained by applying BET equation as follows [15]:

$$\frac{p}{n(p_\circ - p)} = \frac{1}{n_m c} + \frac{c-1}{n_m c} \times \frac{p}{p_\circ} \quad (5)$$

where n_m is a monolayer capacity, n is the amount adsorbed, p is the partial pressure, $p_\circ$ is the saturation pressure and c is related to the heat of sorption. Knowing the monolayer capacity and the cross area, a_m, of a probe molecule, the surface area can be calculated by Eq. (6).

$$S_{BET} = a_m n_m N_A \quad (6)$$

where N_A is the Avogadro constant.

Through the adsorption isotherm, the heterogeneity of the surface can be deduced from the adsorption potential, A, by the following equation [16]:

$$A = RT \ln\left(\frac{p_\circ}{p}\right) \quad (7)$$

In this paper, the effects of addition of dry–strength agents, namely chitosan and cationic starch, on the surface properties were investigated.

2. Materials and methods

2.1. Materials

Bagasse stalks, obtained from the Khuzestan and Industry Co., Iran, were subjected to hot water pre-extraction as described by Cordeiro et al. [17].

Two dry–strength agents were used in this study: chitosan and cationic starch. High-molecular weight chitosan was a Sigma–Aldrich product (USA), a material with 85.4% desacetylation and molecular weight of 9×10^5 g/mol. The cationic starch used in this study was made from potato and was obtained from Lyckeby Amylex Co. It contained about 17% amylase and 83% amylopectin and had a degree of substitution of 0.065.

The non-polar and polar molecules used for the *i*GC measurements were all GC grade (>99% purity) supplied by Sigma–Aldrich. The methane gas (reference probe) and helium (carrier gas), of high purity (>99.99%), were supplied by Air Liquide Company. All the solutions used in this work were freshly prepared to avoid any possible degradation.

2.2. Pulp process

Pulps from raw and hot water pre-extracted bagasse fibers were obtained using the following pulping conditions: initial solid:liquid ratio of 1:5, temperature of 433 K and pulping time of 60 min. The amount of active alkali was 14%. After cooking, the pulps were thoroughly washed with fresh water on a fine filter, and then disintegrated in a hydropulper at 30,000 revolutions and 0.5% consistency for 5 min. Pulps from pre-extracted and un-extracted