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Physiochemical properties of differently pretreated cellulosic fibers

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ABSTRACT

Surface characteristics of differently pretreated flax fibers have been studied using electrokinetic analysis (EKA) and inverse gas chromatography (IGC). Semi-retted and retted flax fibers were scoured and bleached conventionally. All pretreated flax fibers showed negative zeta-potential at all pH values, indicating an acidic fiber surface. The isoelectric point was not reached at pH 3 and can be estimated to be near a pH of 2 or even below, a value where the fibers will be damaged. Inverse gas chromatography measurements showed differences in the surface energy among the differently pretreated flax fibers irrespective of the relative humidity. The group of retted flax fibers in general was found to have higher surface energies than the corresponding semi-retted group. On the other hand, within the same flax fibers group (retted or semi-retted), it was found that the surface energy decreases in the order bleached fibers > scoured fibers > raw fibers.

1. Introduction

Cellulosic fibers are treated to become more absorbent and easily wetted with water or other aqueous solutions, in a process known as scouring. The success of the subsequent wet processing operations like bleaching and dyeing depends on the efficiency of the scouring process (Abdel-Halim & Al-Deyab, 2011a, 2011b; Abdel-Halim, Fahmy, & Fouda, 2008; Abdel-Halim, Emam, & El-Rafie, 2008a; Abdel-Halim, Konczewicz, Zimniewska, Al-Deyab, & El-Newehy, 2010; Abdel-Mohdy, Abdel-Halim, Abu-Ayana, & El-Sawy, 2009; Fahmy & Abdel-Halim, 2010; Fouda & Fahmy, 2011; Hashem, Elshakankery, Abd El-Aziz, Fouda, & Fahmy, 2011). The constituents of cellulosic fibers mainly responsible for their hydrophobicity are localized in the cuticle of the primary wall, where the pectin acts as cementing material including waxes (Abdel-Halim & Al-Deyab, 2011c, 2011d; Abdel-Halim, Emam, & El-Rafie, 2008b; Abdel-Halim, Abdel-Mohdy, Al-Deyab, & El-Newehy, 2010; Abdel-Halim, Fouda, Hamdy, Abdel-Mohdy, & El-Sawy, 2010; Abdel-Halim et al., 2011; Hashem, Sokkar, Abdel-Halim, & Gamal, 2005; Hebeish, El-Rafie, Abdel-Mohdy, Abdel-Halim, & Emam, 2010; Sokkar, Abdel-Halim, Aly, & Hashem, 2004). The major goal of any scouring process is to improve the water absorbency of cellulosic fibers by removing such water repellent components from the fibers, which facilitates uniform dyeing and finishing. Efficient scouring process should result in considerable removal of both pectic and waxy substances.

The physicochemical properties of the fiber surface are very important because they govern the degree of adhesion of the reinforcing fiber to the polymer matrix (Abdel-Halim, El-Rafie, & Kohler, 2008; Asten, Veenendaal, & Koster, 2000; Jokinen, Mikkola, Matisons, & Rosenholm, 1997; Mukhopadhyay & Schreiber, 1995; Nardin, Balard, & Papirer, 1990).

The zeta potential of fiber materials can be determined with the help of the Helmholtz–Smoluchowski equation (Alvarez & Vázquez, 2006; Buschle-Diller, Inglesby, & Wu, 2005). Bismarck, Springer, Mohanty, Hinrichsen, and Khan (2000) investigated the change in time and pH dependence of zeta potentials of modified sisal, coir and of jute fibers.

The principle of IGC consists of characterizing the fiber material as stationary phase in a chromatography column with known probes at infinite dilution. The nature of probe's interaction with the fiber is solely dispersive. Thus, they yield a reference line when plotted according to the following equation (Gadhe, Gupta, & Elder, 2006; Santos & Guthrie, 2005):

$$RT \ln V_n = 2N(\gamma_S^d)^{1/2} a(\gamma_L^d)^{1/2} + C$$

where R is the gas constant, T is the temperature, N is the Avogadro's number, a is the surface area of adsorbate molecule, C is a constant, and γ_S^d, γ_L^d are the dispersive components of the surface energy of solid and liquid, respectively.

Natural fibers, especially bast fibers are considered as good candidate for replacing synthetic fibers in reinforcing plastics. This is due to the very good tensile strength of such fibers, their economic

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price in addition to their availability as renewable resources. The work presented in this paper aims at evaluating and comparing the surface energy of differently pretreated retted and semi-retted flax fibers and showing to what extent the chemical pretreatments (scouring and bleaching) improve the surface properties of such fibers. This evaluation is to be done using the streaming potential technique (zeta potential) and inverse gas chromatography (IGC).

2. Experimental

2.1. Flax fiber pretreatment

2.1.1. Materials

Semi-retted and retted flax fibers were taken from standard stocks of Institute of Applied Research (IAF) FH-Reutlingen. Rongal HT (reducing agent) and Alboron MBG 100 (non-ionic wetting agent) were supplied by Albon-Chemie Germany; Lavotan DSU (non-ionic wetting agent) and Contavan (H_2O_2-stabilizer) were supplied by CHTR. Beitlich GmbH Germany; sodium hydroxide, sodium carbonate and hydrogen peroxide were all laboratory grade reagents.

2.1.2. Scouring of flax fiber

Retted or semi-retted flax fiber was scoured in an aqueous solution containing 5 g/l NaOH, 3 g/l Na_2CO_3, 2 g/l Regonal HT (reducing agent) and 1.5 ml/l Alboron MBG 100 (wetting agent) using a material to liquor ratio of 1:10 (Tanapongpipat, Khamman, Pruksathorm, & Hunsom, 2008). The scouring was done using Ahiba Turbocolor Apparatus equipped with Ahiba Multiprocess controller mpc 600. The temperature was raised to 98 °C in 10 min and kept at this limit for 60 min. At the end of the scouring process, the fiber was given two boiling washings (5 min each) followed by one hot wash (5 min) and finally one cold wash (5 min).

2.1.3. Bleaching of flax fiber

Scoured (retted or semi-retted) flax fiber was bleached in an aqueous solution containing 6 ml/l hydrogen peroxide (35%), 1.25 g/l NaOH, 1.5 ml/l Contavan TIG (H_2O_2-stabilizer) and 1 ml/l Lavotan DSU (wetting agent) using a material to liquor ratio of 1:10 (Fillat, Pepió, Vidal, & Roncero, 2010). The bleaching was also done using the same Ahiba Turbocolor Apparatus. The temperature was raised to 90 °C in 30 min and kept at this limit for 60 min. At the end of the bleaching process, the fiber was given one boiling washings (5 min) followed by one hot wash (5 min), one cold wash (5 min), cold souring by acetic acid (5 min), one cold rinse (5 min) and finally air dried.

2.2. Zeta potential measurement

The zeta-potential was measured using the commercial Electrokinetic Analyzer EKA from Anton Paar, Austria. The Ag/AgCl-electrodes are perforated to allow the liquid to be pumped through the plug. Using the standard measurement method, the fibers are introduced into the cell, generally a glass tube. Before the fibers are put into the measuring cell, they are wetted and equilibrated in demineralized water. The fibers are then tightly compressed forming a plug between the two electrodes so that the required pressure difference across the cell (typically 350 mbar) is obtained. With each specimen the pH was varied in the range of 3–10. A reversible flow of electrolyte solution is pumped through the fiber-plug between two porous Ag/AgCl-electrodes.

Test parameters:

Electrolyte:	KCI solution 10^{-4} M
Repetitions:	4 measurements for each pH
pH control:	0.1 M HCl or 0.1 M KOH
Pressure:	350 mbar
Sampling time:	120 s

2.3. Inverse gas chromatography measurements

Gadgets: Inverse gas chromatography experiments were carried out on an SMS-IGC 2000 with FID & TCD Detectors. Columns used were SMS standard Glass columns 4 mm in diameter and 300 mm in length.

Chemicals: Measurements were undertaken with various non-polar and polar probe molecules, supplied by Aldrich, namely *n*-Hexane, *n*-Heptane, *n*-Octane, *n*-Nonane, *n*-Decane, Ethanol, Ethyl acetate and Acetone.

Test parameters:

Helium gas flow:	25 ml/min
Conditioning temperature:	34 °C

2.3.1. Procedure of analysis

The column was weighed before packing. The fibers were introduced into the column and well packed using a thin smooth-surface metal rod. The fibers ends outside the column were cut off and the column with the fibers inside was weighed to get the weight of the fiber sample. The column was then connected to the inverse gas chromatograph and the experiment parameters were set to condition the column for varying time intervals according to the desired relative humidity and then to inject the probes subsequently in the order of increasing vapor pressure. The probes were taken from the gas phase of each solute and the gas, not the liquid was injected. All surface energy experiments were carried out at 34 °C at 25 ml/min carrier gas flow rate. Calculations were performed using the SMS-IGC analysis software version 1.1. The retention time of nitrogen sets the systems dead time and after the measurement, the dead time was corrected, because the solutes were measured with FID detector while nitrogen was measured with TCD detector.

3. Results and discussion

3.1. Electrokinetic measurements

It has been accepted in literature that cellulosic surfaces generally show bipolar character with prevalent acidic contribution due to the proton of the hydroxyl functional group as well as of present carboxyl groups. The increase of pH lowers the zeta-potential indicating the gradual loss of protonated surface groups (Pothan, Simon, Spange, & Thomas, 2006). It has been further stated that the observed plateau region is the result of complete dissociation of accessible surface groups within a particular pH range. In the case of fibers consisting of pure cellulose to the most part as in scoured and bleached cotton, the plateau was approached by increasing negative potentials, indicating the dissociation of mostly acidic groups (Buschle-Diller et al., 2005). The zeta-potential versus pH curve has a shape that is typical for surfaces with hydrophilic character. All flax fibers (Fig. 1) show negative zeta-potential at all pH values. The negative zeta-potential values suggest the dissociation of Brønsted acid surface sites. The isoelectric point is not reached at pH 3 and can be estimated to be near a pH of 2 or even below, a value where the fibers will be damaged.

Regarding the untreated fibers, the retted material is more negatively charged than the semi-retted fibers, which have a very low charge. This suggests that the raw retted material exhibits more cellulosic surface than the raw semi-retted fibers. The zeta-potential of the retted fibers shows a rather constant value between −9 and