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Effect of particle size on the surface properties and morphology of ground flax

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ABSTRACT

Flax fibers were ground with a ball-mill and four fractions with different size ranges were collected by sieving. These were tested for water sorption, degree of polymerization (DP), copper number, hydroxyl number and analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and inverse gas chromatography (IGC). Significant differences were found between the properties of the flax fiber and those of the ground versions, including fragmentation of fibers, increase of water sorption, copper number, hydroxyl number and surface O/C ratio, and decrease of DP, crystallite size and dispersive component of surface energy (γ_s^d). Some parameters depended on the particle size: O/C ratio and hydroxyl number had local maxima at 315–630 μm, while γ_s^d increased steadily with the decrease of particle size. These relationships were explained by fiber disintegration, destruction of waxy surface layer, exposure of cellulosic components, increase of surface area and crystalline imperfections.

1. Introduction

Recently, apart from the conventional textile and apparel industrial applications, flax has increasingly been used as a filler or amplifier in manufacturing of composite materials, because of its high stiffness and strength. The interaction between the natural filler and the matrix polymer depends largely on the surface properties of the fiber and the matrix (Bagdi, Müller, & Pukánszky 2000; John & Thomas, 2008; Pallesen & Andersen, 2002; Scott, 2000). Fibers are usually used in ground form in polymer composites and the grinding process may have significant effect on both the surface and bulk properties of the fibers. To optimize the interaction at the fiber–matrix interface, it is necessary to get detailed information about the effect of grinding on the surface properties of the natural fibers.

Flax itself can be considered a natural composite: it consists of long elementary fibers (approx. 2–5 cm) with a diameter of 10–25 μm, 'glued' together by pectins into bundles with a diameter of 50–100 μm. Pectins are accumulated in the primary wall and the cell junctions. The epidermal region is rich in waxes as well. The secondary wall is mainly made up of cellulose and non-cellulosic polysaccharides. Raw flax contains about 70% cellulose, 18% hemicelluloses, 2% pectic substances, 2% lignin, 4% water soluble materials, some fats and waxes (1.7%) and minute amounts of coloring matters (Astley & Donald, 2001; Focher, Marzetti, & Sharma, 1992; Morvan, Andème-Onzighi, & Girault, 2003).

Cutting, milling and freeze-grinding of the multicellular and multicomponent flax were found to have significant effect on particle size, surface characteristics, fiber ends of the samples and pyrolysis properties (Sharma, Faughey, & McCall, 1996). Flax is susceptible also to ambient grinding (Csiszár & Fekete, 2011). In spite of this, no detailed publications have been found on the effect of particle size on the surface and bulk properties of the ground cellulosic fibers.

Microstructure and surface properties of fibrous and ground cotton and flax were studied to some extent in our previous work (Csiszár & Fekete, 2011). Analysis of a fraction of the particles with a length 200–315 μm revealed that flax was much more susceptible to grinding than cotton. The flax fibers were degraded in length and disintegrated into elementary fibers before being destroyed into units with sheet-like structure. The size reduction by grinding was accompanied by several physical and chemical changes in the flax fibers: the degree of polymerization was reduced by about 30% with a simultaneous increase in copper number; the crystallites were reduced in size and contained more imperfections; the concentration of oxygen atoms on the ground surface increased significantly.

To extend our previous research, the present work was undertaken with the aim of studying the effect of particle size on the surface and bulk properties as well as on the morphology of the

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ground flax. Flax fibers from linen roving were ground with a ball-mill and four fractions of the particles with different size ranges were collected by sieving and subsequently analyzed by various techniques, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), inverse gas chromatography (IGC), as well as by simple, widely applied tests like water sorption capacity, degree of polymerization (DP), copper number and hydroxyl number (OH-number). As a result, particle size–surface property relationships were found and interpreted.

2. Experimental

2.1. Materials

The flax, which was grown and dew retted in France, was supplied by Hungarolen Kft, Komárom, Hungary. Raw linen roving made from long and fine flax fibers was used for the experiments. The analytical grade chemicals for classical tests and the chromatography grade probes (n-alkanes: heptane, octane, nonane, decane) used for IGC were purchased from Sigma–Aldrich Chemicals.

2.2. Grinding

Flax fibers were cut into lengths of 1–3 mm and ground in a Mixer Mill MM400 (Retsch GmBH, Germany) at a frequency of 30 1/s, with 11 stainless steel balls for 2.5 min. The mass ground was kept constant at 1.5 g. The fractions studied in this work were composed of particles with length enclosed between 200 and 315, 315 and 630, 630 and 800 and 800 and 1000 μm, collected by sieving.

2.3. Classical analytical methods

Water sorption capacity of the samples was determined by exposing the triplicate samples, previously dried over P_2O_5 for 5 days, to an atmosphere of 65% RH at 25 °C for 5 days. Measure of water sorption is a routine characterization of cellulose accessibility. It estimates the less ordered regions in the fiber, since water vapor cannot penetrate into the highly ordered regions of the substrate (Krässig, 1993). The average viscometric degree of polymerization was measured according to the ASTM standard D4243-99 (ASTM, 1999). The test method measures the mean efflux time of the solvent, i.e. cupri-ethylenediamine (T_0) and that of the solution of the cellulosic sample in cupri-ethylenediamine (T_s). The specific viscosity (η_s) is given by the equation: $\eta_s = (T_s - T_0)/T_0$. From the specific viscosity and the concentration of the cellulose solution the intrinsic viscosity of the solution is deduced, and from this the degree of polymerization is calculated as described in the test method. Copper number was determined by Braidy's method (Ester, Gerber, & Edgar, 1963). Copper number is defined as the weight of copper reduced by 100 g of a sample of cellulose fiber, from cupric to the cuprous state. It is determined by a quantitative modification of Fehling's test. The reduction is due to the activity of the aldehyde (—CHO) group present in oxycellulose and hydrocellulose. The method serves to detect cellulose damage and estimate the quantity of reducing groups. Hydroxyl number was determined by using the acylation method by acetic anhydride (ASTM, 2000). The OH number expressed in mg KOH/g substrate characterizes the amount of the accessible primary and secondary hydroxyl groups in the flax samples.

2.4. Instrumental methods

X-ray diffraction patterns were obtained in a Philips model PW 3710 based PW 1050 Bragg-Brentano parafocusing goniometer, using CuK radiation ($\lambda = 0.15418$ nm), graphite monochromator and proportional counter. The XRD scans were digitally recorded with a step of 0.04° and evaluated with profile fitting methods.

XPS studies were done by a Kratos XSAM 800 spectrometer using Mg $K_{1,2}$ radiation and fixed analyzer transmission mode (80 and 40 eV pass energies for survey and detailed spectra, respectively). The diameter of the analyzed spot was about 2 mm. The spectra were referenced to the C 1s line (binding energy, BE = 285.0 eV) of the hydrocarbon type carbon. Data acquisition and processing were performed with the Kratos Vision 2 program. The conditions of the measurements and the spectrum elaboration were kept constant, and thus the intensities measured on parallel samples were repeatable with good precision (within ±5%).

Surface morphological investigations were made by a JEOL 5500 LV electron microscope in low vacuum (30 Pa) mode with a backscattered electron detector. The accelerating voltage was 20 kV and the working distance 20–21 mm. The samples were fastened to the copper sample holder by adhesive carbon tape and measured without any coating.

In IGC the solid substrate with unknown surface is packed into the column and the known materials are the vapor probes that are injected into the column. The fibrous and powder flax was packed into the stainless steel column having an inner diameter of 5 mm and a length of 50 cm. Approximately 1.5 g of the samples were filled into the column. Vapor samples of 5–20 μL were injected into the column and retention peaks were recorded by a FID detector. Each reported value is the result of at least three parallel measurements. High-purity nitrogen was used as carrier gas and its flow rate changed between 5 and 20 mL/min depending on the type of adsorbent. IGC measurements were carried out using a Perkin Elmer Autosystem XL apparatus, after conditioning the samples at 105 °C for 16 h under a constant flow of nitrogen, at 40 °C. A new column was prepared for each set of experiments. By using IGC, the surface characteristics can be derived from retention times or volumes. Besides numerous parameters, the dispersion component of the surface tension of the adsorbent (γ_s^d) was determined with this technique (Csiszár & Fekete, 2010; Csiszár & Fekete, 2011; Dorris & Gray, 1980).

3. Results and discussion

3.1. Morphological structure

Flax fibers were ground in a ball mill at a frequency of 30 1/s, for 2.5 min. Four fractions of the particles with different lengths (200–315, 315–630, 630–800 and 800–100 μm) were collected by intensive sieving and morphological examination of the ground fiber fractions was made using SEM.

In Fig. 1 the original flax fibers are illustrated in longitudinal view. The photomicrograph shows parts of some bundles made up of ultimate fibers. These elementary fibers are cemented together by the middle lamella, which is rich in pectin and other non-cellulosic materials. During the applied short grinding process, these bundles are completely disintegrated into elementary fibers and degraded in length (Fig. 2). Most of the units of the ground samples possess a recognizable structure of the elementary fibers, but do not show similarity to the external form of the original flax fiber. Many of the elementary fibers separated from the fiber bundles are further destroyed into units with sheet-like structure and with a diameter of 15–25 μm, as can be seen mainly in the photomicrograph of the fraction with a length range of 200–315 μm (Fig. 2a). A comparison of micrographs a–d in Fig. 2 does not show pronounced qualitative differences, since the morphological structures are similar for the various fractions.