Carbohydrate Polymers 94 (2013) 927–933

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

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

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ARTICLE INFO

Article history:
Received 12 December 2012
Received in revised form 11 February 2013
Accepted 13 February 2013
Available online 26 February 2013

Keywords:
Flax
Grinding
Surface composition
Morphology
Crystallite size
Inverse gas chromatography

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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0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.02.026

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.

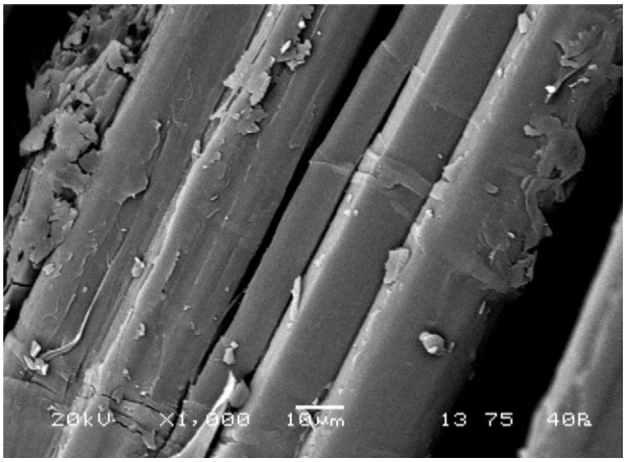

Fig. 1. Scanning electron micrograph of flax fiber (1000×).

3.2. Bulk properties

Fragmentation of the cellulosic fibers during grinding is accompanied by chemical alteration of the macromolecules and physical changes in the pore structure of the fibrous substrate. This is reflected by the changes in the measured data in Table 1, which clearly show significant effect of the short grinding process on the bulk properties of flax. The degree of polymerization decreased and the copper number increased, implying that the applied mechanical action is intense enough to reduce the molecular mass of cellulose and other polysaccharides present in the multicomponent flax fiber. The rupture of bonds in the polysaccharide macromolecules leads to a slight increase in the carbonyl groups expressed by the higher copper number values. Comparing the values of DP for the fibrous and ground substrates, a decrease of about 30% can be seen after grinding, while there is no significant difference between the DP values of the different ground fractions.

Results in Table 1 also prove that the applied grinding modifies the accessibility of the original flax and modifies the adsorption properties characterized by the water-substrate interaction. Clearly, there is a significant difference between the water sorption capacity of the fibrous sample and the respective values measured for the ground substrates. At 65% relative humidity and 25 °C, the water sorption capacity of the flax fiber was 9.32%, which increased to about 9.6% for the fractions with larger particle size, and a further increase to 9.9% was measured for the fraction with the smallest particles (200–315 μm). Adsorption properties of the fibers are expected to be influenced by the crystalline structure. In particular, a low water sorption can indicate a compact crystal structure of the substrates, since the crystalline regions do not contribute to the water sorption. Oppositely, the increase in water sorption capacity indicates a considerable enlargement of the accessible internal surfaces of the flax (Krässig, 1993), achieved in our case by grinding. These values are in a good agreement with the X-ray results (Fig. 3),

Table 1
Bulk properties and characteristics for morphology of flax fiber and ground fractions of flax.

Substrates	Degree of polymerization	Copper number	Water sorption capacity (%)
Flax fiber	2460 ± 50	2.08 ± 0.14	9.32 ± 0.01
Ground 1000–800 μm	1680 ± 60	2.49 ± 0.31	9.68 ± 0.00
Ground 800–630 μm	1770 ± 90	2.36 ± 0.11	9.66 ± 0.02
Ground 630–315 μm	1740 ± 30	2.12 ± 0.20	9.63 ± 0.05
Ground 315–200 μm	1790 ± 40	n.d.[a]	9.91 ± 0.09

[a] Not determined.

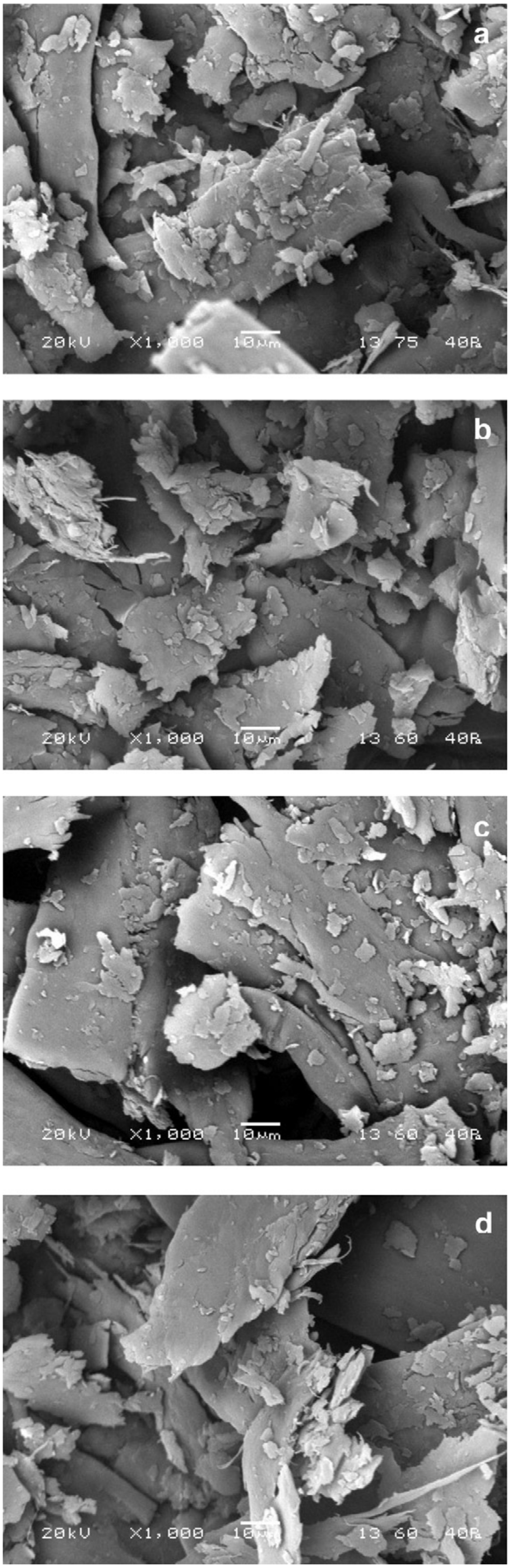

Fig. 2. Scanning electron micrographs of ground flax fiber (1000×). Fractions with a length of 200–315 μm (a), 315–630 μm (b), 630–800 μm (c) and 800–1000 μm (d).

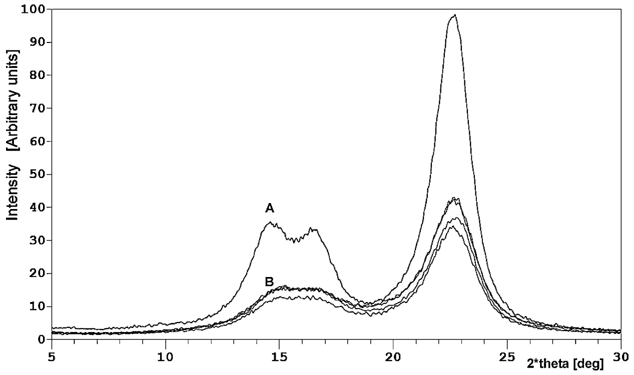

Fig. 3. X-ray spectra of flax fiber (A) and ground flax fractions (B).

which confirm the alterations in the supramolecular structure of the flax fiber upon grinding.

Thus, for all ground samples, a broadening of the Cellulose I reflections at 2Θ of 14.7; 16.5° and 22.7°, as well as their reduction in intensity can be observed (Fig. 3). Furthermore, the crystallites in all of the ground samples are reduced in size from 5.8 nm up to 4.6 nm and contain more imperfections. It means that the applied grinding process slightly destroys the crystalline structure of the flax fibers, producing less perfect cellulose crystals with more defects. Basically, there is a significant difference between the spectra of the flax fiber and the ground samples, nevertheless, the difference between the values of the ground fractions cannot be detected clearly by this method.

On the other hand, water sorption values reveal differences between the ground samples. Mihranyan et al. found an inverse correlation between the crystallinity and the water sorption of cellulose powders, since a monotonic decrease in water sorption was observed with increasing crystallinity (Mihranyan, Llagostera, Karmhag, Strømme, & Ek, 2004). The differences in water sorption of the ground fractions indicate that the fraction with the smallest particles (200–315 μm) adsorbed the highest amount of water, which suggests a lower crystallinity. Furthermore, it has to be underlined that grinding increases the specific surface area and surface energy of the substrates, which can also affect the water sorption capacity of the cellulosic substrates.

3.3. Surface chemical composition and bonding

Besides alteration of morphological and bulk properties, grinding modifies the chemical composition of the fiber surface as well. XPS method was chosen to characterize these changes taking place upon grinding of the flax fiber. The surface of cellulosic fibers consists mainly of carbon and oxygen atoms, but the O/C ratio is different for the different components (such as cellulose, waxy materials, lignin, pectin) of the outer layer of the fiber. XPS provides quantitative information on the chemical composition of the surface and the differently bonded carbon and oxygen atoms as well.

The O/C atomic ratio and the results of decomposition of the C 1s and O 1s peaks for the surfaces of flax fiber and ground flax substrates are shown in Table 2. Before discussing these results, we remember that the sampling depth of XPS for these samples can be estimated to be about 10 nm under the conditions applied (Andrade, 1985). On the other hand, cellulosic fibrous materials are known to be covered by a layer called cuticle, characterized by a thickness of about 12 nm for cotton (Ryser & Holloway, 1985). Cuticle is composed mainly of non-cellulosic lipophilic components such as waxes, sterol esters and triglycerides, and also less ordered cellulose and pectin (Akin, Morrison, Rigsby, & Dodd, 2001; Peters, 1963). The amount of lipids in flax fibers is about 1.8%. The main constituents of lipids in flax are waxes, which contain long-chain saturated n-fatty acids (ranged from C_{16} to C_{30}) esterified with long-chain n-fatty alcohols (ranged from C_{20} to C_{38}) (Gutiérrez & Del Rio, 2003).

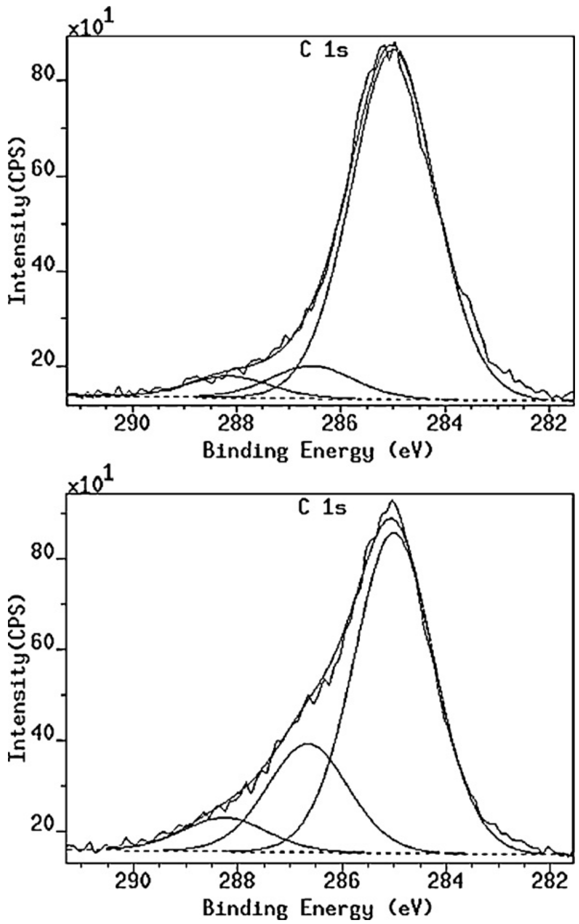

Fig. 4. Decomposition of the C 1s peak. Top: flax fiber, bottom: fraction with size range of 315–630 μm.

The O/C ratio found for flax fiber is 0.156 (Table 2), while those for pure wax and cellulose are 0.11 and 0.83, respectively (Buchert, Carlsson, Viikari, & Ström, 1996; Laine, Stenius, Carlsson, & Ström, 1994; Toth, Faix, Rachor, Bertoti, & Szekely, 1993). A comparison of the latter O/C values with that measured for flax fiber suggests that the layer analyzed by XPS is composed mainly of cuticle, rich in wax. This is consistent with the high percentage of carbon in C—C and C—H type bonds (75.5%) in the surface layer of flax fiber.

As seen in Table 2, the O/C ratio for the ground flax samples is always higher than that of the fiber. Upon grinding, mainly components C2 and O2 increase, which can be attributed essentially to C and O present in C—O type bonds (see Figs. 4 and 5 and also Table 2). The increase of the surface concentration of C atoms in C—O type bonds is compensated mainly by the decrease of the C1 component, attributable to the hydrocarbon type C atom. The significant increase of the O/C ratio and of the concentrations of the various oxidized states of carbon (mainly C—O, but also C=O and/or O—C—O) suggests the appearance of cellulose on the surface upon grinding. The predominant presence of O atom in C—O type bond on the surface of the ground samples corroborates the appearance of cellulose upon grinding.

As seen in Fig. 6, the dependence of the O/C ratio on the particle size of the ground flax is not monotonous, since it has a local maximum at values ranging between 315 and 630 μm. It is remarkable

Table 2
O/C atomic ratio and results of decomposition of the C 1s and O 1s peaks for the surfaces of flax fiber and ground fractions of flax.

Sample	O/C	C1%	C2%	C3%	O1%	O2%
		285.0 eV	286.6 eV	288.2 eV	532.1 eV	533.2 eV
		C—C, C—H	C—O	C=O, O—C—O	C=O	C—O
Flax fiber	0.156	75.5	7.0	4.6	6.3	6.6
Ground 1000–800 μm	0.237	61.9	13.7	5.1	8.7	11.0
Ground 800–630 μm	0.288	55.7	16.4	5.7	8.3	13.8
Ground 630–315 μm	0.303	53.1	18.1	5.9	7.9	15.0
Ground 315–200 μm	0.264	60.6	14.0	5.0	8.4	12.0

that the local maxima seen in this figure for the O/C ratio and in Table 2 for the portions of C2 and O2 components (concentrations of C and O in C—O type bond) coincide with the local maximum observed for the OH-number in Fig. 7.

OH-number, which reveals the accessible primary and secondary hydroxyl groups of the substrate, was determined in a heterogeneous chemical reaction by ester formation. Results in Fig. 7 show that the OH-number of the flax fiber is 162 and that of the ground factions is about two times higher, implying that the accessibility of the hydroxyl groups is greatly affected by grinding. The relatively small accessibility of the flax fiber caused by the waxy surface layer and the intact crystalline structure limits the attack of the reagent on and into the fiber. However, changes in crystalline structure and surface composition of the fiber by grinding impart favorable conditions for the heterogeneous esterification reaction.

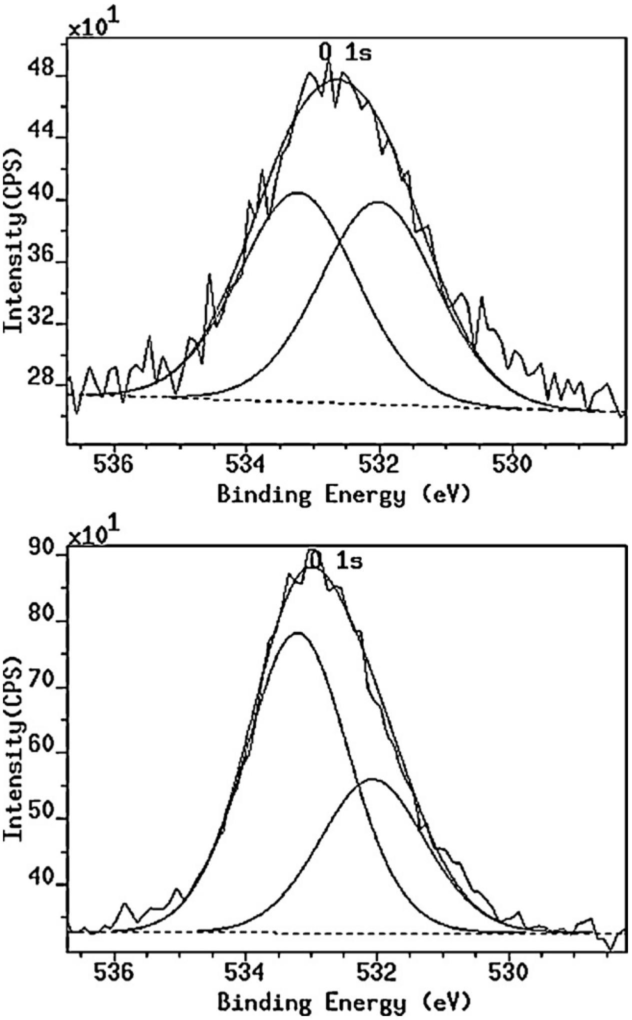

Fig. 5. Decomposition of the O 1s peak. Top: flax fiber, bottom: fraction with size range of 315–630 μm.

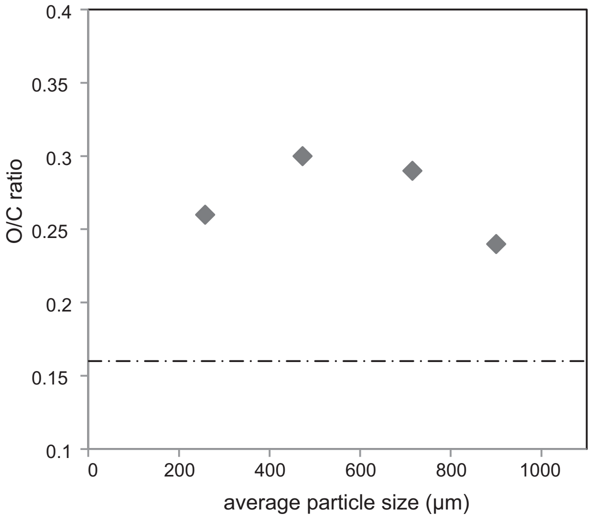

Fig. 6. Oxygen-to-carbon ratio from XPS survey spectra for the flax fiber (–·–·–) and for the ground fiber fractions (♦) as a function of average particle size.

A possible explanation for the local maximum on the O/C ratio vs. size can be given in terms of competition of two processes taking place upon grinding: (a) gradual disintegration of flax fibers, leading to opening of the internal cellulosic part, characterized by an O/C ratio higher than that of the waxy overlayer, as explained above in detail, and (b) a gradual distribution of wax present in the system, spreading also onto the newly opened surfaces. The latter can be

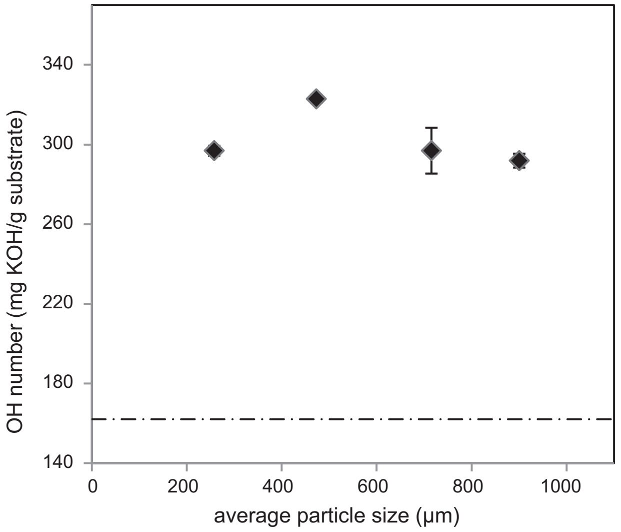

Fig. 7. Hydroxyl number of the flax fiber (–·–·–) and the ground fiber fractions (♦) as a function of average particle size. Standard deviation on symbols.

facilitated by the temperature increase caused by the thermal effect of grinding. Process (a) may dominate at the first stage of grinding (apparently up to about 315 μm), while the influence of process (b) may prevail upon further grinding, reaching a second stage at sizes lower than about 315 μm.

The proposed explanation is in agreement also with the local maximum observed for the dependence of OH number vs. size, because cellulose contains OH groups, which is not characteristic for the waxy material. At this point it should be noted that OH number is a property characteristic essentially for the bulk, but the presence of a waxy overlayer decreases the accessibility of OH groups both at the outer surface and in the pores of the internal regions.

Furthermore, it should also be mentioned here that grinding increases the specific surface area of the substrates, which can lead to aggregation of the particles with the smallest size (200–315 μm) and as a consequence, it can also contribute to a slight decrease in the O/C ratio and OH number.

3.4. Surface energetics

Inverse gas chromatography at infinite dilution is an objective method to obtain quantitative information on the surface properties of solids. Based on the data of the retention volume, the dispersive component of the surface free energy (γ_s^d) can be determined by this method and the surface energetics can be characterized accurately.

In our previous work (Csiszár & Fekete, 2011) it was demonstrated that the dispersion component of surface tension of ground samples measured by IGC was significantly lower than that of the fibers (i.e. cotton and flax), in spite of that the new surfaces created by grinding were rich in oxygen atoms. Thus, the probable higher energy of the ground surface could not be measured by inverse gas chromatography. This surprising observation was explained with the changes in crystal structure occurred during grinding. Grinding decreases the crystalline perfection and crystallite size, and on the less perfect crystalline surfaces the adsorption of the n-alkane probes is limited, since on a molecular scale rough surface, the retention time is shorter due to the hindered access (Belgacem, Blayo, & Gardini, 1996; Papirer, Brendle, Balard, & Vergelati, 2000). On the flat cellulose surface of a highly crystalline substrate such as flax fiber, the n-alkane probes can adopt a particular conformation which leads to an optimal interaction between the probe and the surface, and consequently results in a longer retention time and a higher surface energy.

The γ_s^d values of the flax fiber and the ground fractions in Fig. 8 are in accordance with the results mentioned above and reveal that the dispersion component of surface tension of the flax fiber ($40.04 \pm 0.04\,\mathrm{mJ/m^2}$ at 40 °C) is significantly higher than the surface energy of the ground samples ($36.3 \pm 0.03\,\mathrm{mJ/m^2}$–$38.0 \pm 0.03\,\mathrm{mJ/m^2}$ at 40 °C).

Another important observation from the data in Fig. 8 is that the γ_s^d value of the ground fractions depends largely on the particle size and increases continuously with decreasing the size of particles. Dependence of γ_s^d on the particle size correlates well with the data of O/C ratio and OH numbers, implying that the higher γ_s^d values may be attributed to the higher oxygen content of the surface. Furthermore, it is worth pointing out that there is no significant difference in crystallinity of the ground fractions (Fig. 3), thus the crystallinity does not probably influence the adsorption of the n-alkane probes on the surface. Consequently, the differences measured between the γ_s^d values of the ground fractions (Fig. 8) do not originate in the crystallinity, but in the real surface properties of the ground particles. As expected, the fraction with smaller particles, which can probably be characterized by higher accessibility of the surface functional groups, exhibits higher surface energy, and the γ_s^d values increase steadily with decreasing particle size.

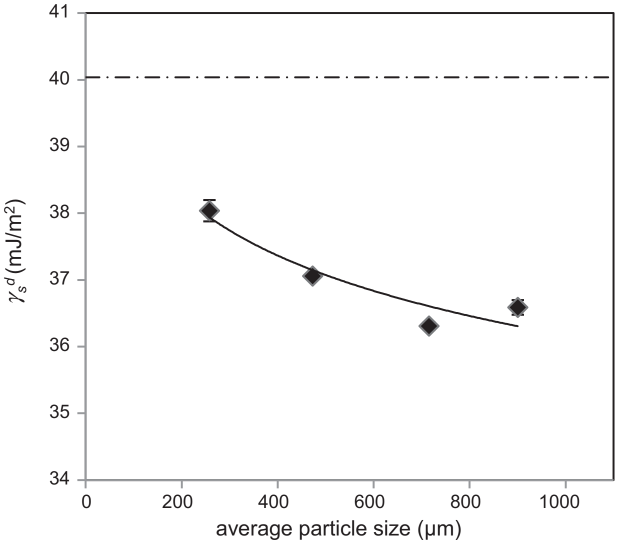

Fig. 8. Dispersion component of surface tension (γ_s^d) for the flax fiber (–·–·–) and the ground flax fractions (♦) as a function of particle size. Standard deviation on symbols.

It has to be underlined that the parameters measured by IGC depend largely on the adsorption of the probes on the solid surface. Since this interaction is strongly influenced by the sample preparation (i.e. grinding) and the measurement conditions, the determined surface characteristics are not material constants (Fekete, Móczó, & Pukánszky, 2004). However, under standard conditions, the surface modifying effect of the different treatments on a certain sample can be determined reliably by IGC (Belgacem et al., 1996). Our results prove that IGC is an appropriate measurement for characterizing the surface energy of the ground cellulosic samples with equal crystallinity but varying surface composition (O/C ratio).

4. Conclusions

Flax fibers were ground in a ball-mill and four fractions were collected by sieving and analyzed to determine the effect of particle size on the microstructure and surface properties of the fibers. The results confirm our previous statement that the multicellular and multicomponent flax is very susceptible to grinding and undergoes complex chemical and physical changes. All of the applied analytical methods revealed differences in properties of the flax fiber and the ground flax, and except for X-ray analysis and DP measurement, they all can measure also the differences in properties of the ground fractions.

In general, grinding of the flax fibers leads to a serious decrease in the degree of polymerization and an increase in water sorption capacity. Furthermore, grinding slightly destroys the crystalline structure of flax and the ground fractions contain smaller cellulose crystals with more imperfections.

Grinding creates new surfaces where the O/C ratio is significantly higher than that of the original fiber. This can be explained by the destruction of the waxy surface layer. The surface of the ground samples contains carbon and oxygen present mainly in C—O type bonds (but also C═O and O—C—O), showing the appearance of cellulose and other polysaccharides on the surface upon grinding. The O/C ratio and the hydroxyl number depend on the particle size, and both have a local maximum at the fraction of 630–315 μm. These can be rationalized in terms of competition of two processes: disintegration of flax fibers, leading to opening of the internal cellulosic part and the gradual distribution of wax, spreading also onto the newly opened surfaces. Furthermore, aggregation of the smallest particles can also be considered.

The dispersion component of surface tension of ground samples measured by IGC was significantly lower than that of the flax fibers, in spite of that the new surfaces created by grinding were rich in oxygen atoms. This finding can be explained with the less perfect crystalline surfaces of the ground samples where the adsorption of the n-alkane probes is limited. On the other hand, for the ground fractions with similar crystal structure, the higher accessibility of the surface functional groups does exhibit higher surface energy. This means that the γ_s^d values exhibit the real surface properties and reveal the effect of particle size.

Acknowledgement

Research was partially financed by grant from the Hungarian National Science Foundation (grant numbers OTKA K82044 and K67936). This work is connected to the scientific program of the "Development of quality-oriented and harmonized R + D + I strategy and functional model at BME" project supported by the New Hungary Development Plan (Project ID: TAMOP-4.2.1/B-09/1/KMR-2010-0002). The skillful technical assistance of technician Ramona Bende is gratefully acknowledged.

References

Akin, D. E., Morrison, W. H., III, Rigsby, L. L., & Dodd, R. B. (2001). Plant factors influencing enzyme retting of fiber and seed flax. *Journal of Agricultural and Food Chemistry*, *49*, 5778–5784.

Andrade, J. D. (1985). X-ray photoelectron spectroscopy. In J. D. Andrade (Ed.), *Surface Chemistry and Physics Surface and interfacial aspects of biomedical polymers* (pp. 105–195). New York: Plenum.

Astley, O. M., & Donald, A. M. (2001). A small-angle x-ray scattering study of the effect of hydration on the microstructure of flax fibers. *Biomacromolecules*, *2*, 672–680.

ASTM (1999). *Standard test method for measurement of average viscometric degree of polymerization of new and aged electrical papers and boards*. ASTM D4243–99. Published in June 1999.

ASTM (2000). *Standard test methods for hydroxyl groups using acetic anhydride acetylation*. ASTM E222–00. Published in November 2000.

Bagdi, K., Müller, P., & Pukánszky, B. (2000). Thermoplastic starch/layered silicate composites: Structure, interaction properties. *Composite Interfaces*, *13*, 1–17.

Belgacem, M. N., Blayo, A., & Gardini, A. (1996). Surface characterization of polysaccharides, lignin, printing ink pigments and ink fillers by inverse gas chromatography. *Journal of Colloid and Interface Science*, *182*, 431–436.

Buchert, J., Carlsson, G., Viikari, L., & Ström, G. (1996). Surface characterization of unbleached kraft pulps by enzymatic peeling by ESCA. *Holzforschung*, *50*, 69–74.

Csiszár, E., & Fekete, E. (2010). Characterization of the surface properties of differently scoured cotton by inverse gas chromatography at infinite dilution. *Textile Research Journal*, *80*, 1307–1316.

Csiszár, E., & Fekete, E. (2011). Microstructure and surface properties of fibrous and ground cellulosic substrates. *Langmuir*, *27*, 8444–8450.

Dorris, G. M., & Gray, G. (1980). Adsorption of n-alkanes at zero coverage on cellulose paper and wood fibres. *Journal of Colloid and Interface Science*, *77*, 353–362.

Ester, V. C., Gerber, R., & Edgar, R. (1963). Change in cotton, linen, rayon and cellulose secondary acetate with temperature of steaming. *Textile Research Journal*, *33*, 357–370.

Fekete, E., Móczó, J., & Pukánszky, B. (2004). Determination of the surface characteristics of particulate fillers by inverse gas chromatography at infinite dilution: A critical approach. *Journal of Colloid Science*, *269*, 143–154.

Focher, B., Marzetti, A., & Sharma, H. S. S. (1992). Changes in the structure and properties of flax fibre during processing. In H. S. S. Sharma, & C. F. Van Sumere (Eds.), *The biology and processing of flax* (pp. 329–342). Belfast: M Publications.

Gutiérrez, A., & Del Rio, J. C. (2003). Lipids from flax fibers and their fate in alkaline pulping. *Journal of Agricultural and Food Chemistry*, *51*, 4965–4971.

John, J. M., & Thomas, S. (2008). Biofibres and biocomposites. *Carbohydrate Polymers*, *71*, 343–364.

Krässig, H. A. (1993). *Cellulose, structure, accessibility and reactivity* (1st ed.). The Netherlands: Gordon and Breach Science Publishers., pp. 167–187.

Laine, J., Stenius, P., Carlsson, G., & Ström, G. (1994). Surface characterization of unbleached kraft pulps by means of ESCA. *Cellulose*, *1*, 145–160.

Mihranyan, A., Llagostera, A. P., Karmhag, R., Strømme, M., & Ek, R. (2004). Moisture sorption by cellulose powders of varying crystallinity. *International Journal of Pharmaceutics*, *269*, 433–442.

Morvan, C., Andème-Onzighi, C., & Girault, G. (2003). Building flax fibres: More than one brick in the walls. *Plant Physiology and Biochemistry*, *41*, 935–944.

Pallesen, B. E., & Andersen, T. L. (2002). Reinforced biocomposites from flax and hemp. *Journal of Industrial Hemp*, *7*, 61–81.

Papirer, E., Brendle, E., Balard, H., & Vergelati, C. (2000). Inverse gas chromatography investigation of the surface properties of cellulose. *Journal of Adhesion Science and Technology*, *14*, 321–337.

Peters R. H. (1963). *Textile chemistry*, Vol. I. *The Chemistry of Fibres*. (Chapter 6). Amsterdam: Elsevier Publishing Company.

Ryser, U., & Holloway, P. J. (1985). Ultrastructure and chemistry of soluble and polymeric lipids in cell walls from seed coats and fibres of *gossypium* species. *Planta*, *163*, 151–163.

Scott, G. (2000). 'Green' polymers. *Polymer Degradation and Stability*, *68*, 1–7.

Sharma, H. S. S., Faughey, G., & McCall, D. (1996). Effect of sample preparation and heating rate on the differential thermogravimetric analysis of flax fibres. *Journal of the Textile Institute*, *87*, 249–257.

Toth, A., Faix, O., Rachor, G., Bertoti, I., & Szekely, T. (1993). ESCA (XPS) study on light-induced yellowing of thermomechanical and chemothermomechanical pulps. *Applied Surface Science*, *72*, 209–213.