

Surface Characterization of Flax, Hemp and Cellulose Fibers; Surface Properties and the Water Uptake Behavior

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The surface characteristics of several natural fibers—flax, hemp and cellulose—were investigated using scanning electron microscopy, BET-surface area and zeta (ζ -) potential measurements. ζ -Potential measurements using the streaming potential method were performed in order to study the water uptake behavior as well as the surface properties of several natural fibers. The influence of different flax-fiber separation methods and several modifications, like industrial purification, and such a treatment followed by alkaline purification as well as polypropylene grafting on the fiber surface morphology, surface area and time- and pH-depending ζ -potentials were studied. The time-dependence of the ζ -potential, measured in 1 mM KCl solution, offers an alternative possibility to estimate the water uptake behavior for nearly all investigated natural fibers. The water uptake data derived from the ζ -potential measurements ($\zeta = f(t)$) were compared with data from conventional water adsorption studies for some chosen examples.

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INTRODUCTION

State of the art is to increase the strength and the stiffness of polymer components using reinforced compound structures. As an alternative to the use of established reinforcing fibers (glass- or carbon fibers) growing raw materials are inserted increasingly as a strengthening component for innovative products for lots of applications in the field of lower mechanical loads (1), like for instance automobile interior linings (roof, rear wall, side panel lining), shipping pallets, construction products (i.e. composite roof tiles), furniture and household products (i.e. storage containers, window and picture frames as well as food service trays, toys and flower pots) as well as fan houses and blades (2). Flax (on account of its strength) and hemp (because of its high amount of straw and fibers) are presently predominantly applied in Germany. Suitable matrix materials for natural fiber reinforced polymers are resin systems, thermoplastic starch and polyolefins, like polyethylene (PE) and polypropylene (PP), where PP provides most of the advantages with regards to economic (price), ecological (recycling behavior) and technical requirements (higher thermal stability as PE). Injection molding and consolidating of hybrid non-wovens are suitable procedures to process natural fiber reinforced polymers into sophisticated 3-dimensional parts. However, the use of lignocellulosic fibers as reinforcements in such thermoplastics is limited because of difficulties associated with their highly polar character, making them less compatible with non-polar plastics, like polyolefins (3). Therefore, the inherent polar and hydrophilic nature of natural fibers and the non-polar characteristics of polyolefins result in difficulties when compounding these materials, exhibiting poor stress transfer efficiencies. Physical and chemical methods have been used to optimize the interfacial characteristics and improve the properties of lignocellulosic fiber polymer composites (4). The use of annual growing lignocellulosic natural fibers as reinforcements is appealing because of the properties of the resultant composites and from an environmental point of view. Agro-based natural fibers with their favorable aspect ratios and high specific properties at low costs have the potential to be outstanding reinforcements in thermoplastics (2, 5). The nonabrasive nature of these fibers allows the use of high fiber loading without the extensive damage to compounding and molding equipment that can occur with much harder mineral based fibers/platelets such as glass or mica. The high moisture absorption of the natural fibers and their low microbial resistance are disadvantages (Table 1) that need to be considered, particularly during shipment and long-term storage as well as during processing of the composites. In addition, their hydrophilic behavior affects the properties of the fibers themselves as well as the properties of their composites (4, 6, 7).

As shown in Figs. 1a and 1b the microstructure of natural fibers is extremely complicated, in that it comprises different hierarchical microstructures (8, 9). The

Table 1. Main Advantages and Disadvantages of Lignocellulosic Fibers.

Advantages	Disadvantages
Low cost	High moisture adsorption
Renewable	Poor microbial resistance
Low density	Low thermal resistance
Nonabrasive	Local and seasonal quality variations
Low energy consumption	Demand and supply cycles
High specific properties	
High strength and elasticity modulus	
No skin irritations	
No residues when incinerated	
Fast absorption/desorption of water (\pm)	
Good thermal conductivity (\pm)	
Biodegradability (\pm)	

single fibers (elongated cell) consist of a primary wall and three other secondary walls. In the center there is a lumen. The primary cell wall consists of pectin that can be stiffened and dehydrated by the addition of lignin. It then becomes part of the adhesive system holding cells together. In the secondary cell wall, the cellulose molecules are synthesized by enzymes that float around in the cell membrane, spinning off primary fibrils of about 5 nm in diameter, each containing about 40 molecules. These primary fibrils are assembled into microfibrils of about 20–40 nm in diameter, which have hemicelluloses decorating the outside. These hemicelluloses act as the connection between the microfibrils, creating the primary structural network. Lignin can be deposited within this network in two ways: either as isolated lumps (when it acts to limit the movement of the microfibrils, thus increasing stiffness by steric hindrance) or (later) as a continuous matrix, which then supplements and presumably replaces the hemicellulose in importance as a linker of the cellulose microfibrils.

For several applications flax and hemp fibers should be prepared or modified (4):

- Homogenization of the properties of the fibers,
- Degree of elementarization and degumming,
- Degree of polymerization and crystallization,
- Good adhesion between fiber and matrix,
- Moisture repellence,
- Flame-retardant properties.

These properties can be partly influenced by different fiber separation procedures as well as by subsequent fiber treatment processes.

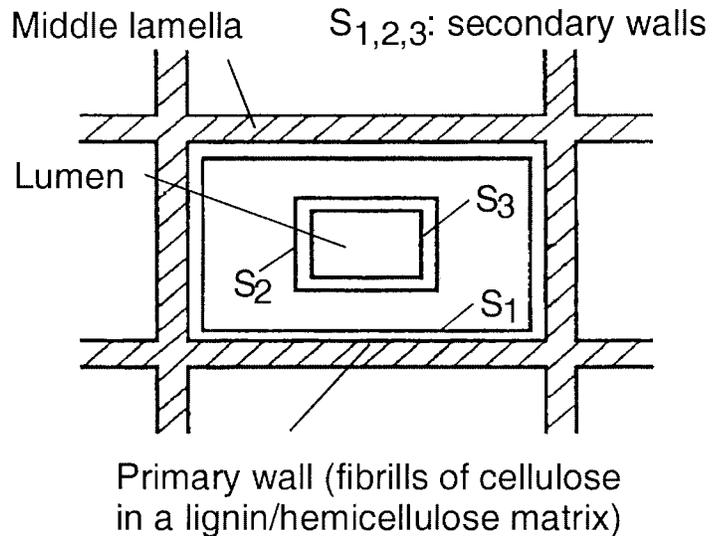


Fig. 1a. Cross-section of a flax fiber (schematic) [4].

It is well known that the performance of composites, for example, the mechanical properties, depends on the properties of the individual components and their interfacial compatibility. Cellulose, which is the main structural element of flax and hemp fibers, is strongly polar due to hydroxyl groups, acetal and ether linkages (C-O-C) in its structure. This renders cellulose more compatible with polar, acidic or basic groups, compared to non-polar polymers like polypropylene (10).

Several noncellulose components (for the composition (11, 12) of flax fibers see Table 2) have to be removed to assure the compatibility of the reinforcing fibers and the surrounding polymer matrix. The primary wall of the fiber contains almost all of the non-cellulose compounds, except proteins, inorganic salts and coloring matter, which have been found in the fiber lumen (13), and it is this section that creates

problems—poor absorbency, poor wettability and other undesirable textile properties (14). In general, a minimum concentration of 3% NaOH is necessary for scouring natural fibers to account for alkali consumption for neutralizing various substances, like acidic hydroxyl groups of cellulose, carboxyl groups of pectins and also amino acids generated by protein hydrolysis (13).

Composite interfaces can be characterized by analyzing the surfaces of the composite constituents before they are combined, since the composite performance, i.e. the mechanical properties, depends on the properties of the single components as well as on the interfacial compatibility between the materials. The structure and the composition of local surfaces differ from the bulk material and this can provide useful information to predict the properties and performance of the composite.

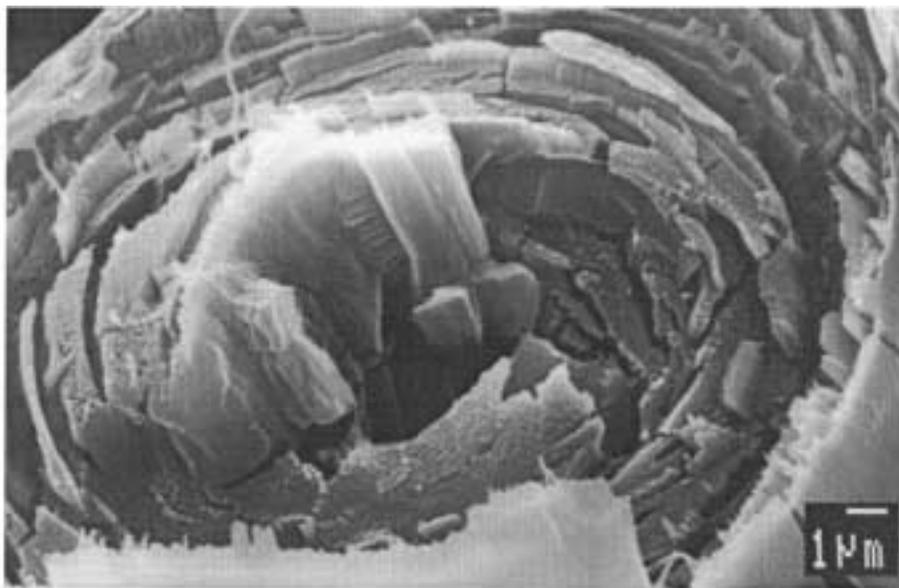


Fig. 1b. Cross-section of a flax fiber (SEM) [9].

Table 2. Chemical Composition of Hemp and Flax Fibers According to Ref. 9.

Component	Hemp [%]	Flax [%]
Cellulose	~67	~65
Hemicellulose	~16	~16
Pectin	0.8	3
Lignin	3.3	2.5
Proteins, ash and minerals	2.1	3 (proteins only)
Fats and Waxes	0.7	1.5
Ash (Minerals)	As above	1
Water	10	8

Because of the known hydrophilic character of cellulose-based materials, suitable methods, which allow characterization of the 'wet-state' of these materials, are used to study their surface properties. For this aim, in particular ζ -potential measurements have become established (15). ζ -Potential measurements on natural fibers (bleached cotton) were mainly used to characterize their dyeing behavior (16, 17) but also for natural fibers for composite applications (18, 19). By means of ζ -potential measurements, it was attempted to prove changes in the surface composition and in the water uptake behavior due to the fiber separation procedure and subsequent treatment of investigated natural fibers. It is known that flax in particular shows inhomogeneous properties within the stalk length, which is dependent on the growing conditions (20).

The study of the water uptake behavior (e.g. the swelling) of the investigated natural fibers, which have been used as reinforcements for polymers, is necessary for the construction of composite materials, since the adhesive strength is influenced by absorption layers (in particular of water) at the common interface between the adhesive and the adherent component (21). A major restriction in the successful use of natural fibers in durable composite applications is their high moisture absorption and poor dimensional stability (swelling), as well as their susceptibility to rotting (22). Swelling of fibers can lead to micro-cracking of the composite and, therefore, to deteriorated mechanical properties.

A deeper understanding of the complex nature of natural fibers and their surface properties is still needed in order to optimize natural fiber surface modification processes, which might help to increase the usefulness of those fibers as reinforcing material for polymers and to gain insights about the interaction between these materials (3, 23).

EXPERIMENTAL

Materials: Fibers and Fiber Treatment

Rough green flax (GFA) and rough green hemp were obtained from the ECCO Gleittechnik GmbH (Germany). They separated the fibers by means of an ultrasound technique and purchase the natural fiber materials in Germany and other European countries. Rough flax and rough hemp are fiber materials that

are neither subjected to dew or to water retting. After the mow the stems were broken and washed. Therefore, the intensification of the subsequent ultrasound procedure increases. Through the use of ultrasound supported by a low concentrated sodium hydroxide solution it is possible to separate the fibers to a degree sufficient for technical, non-textile applications.

Dew retting is a natural retting procedure that is used for the fiber separation of the flax straw. It leads to a partly removal of the center lamella, and after the treatment the fibers can easily be separated from the stem using a subsequent mechanical routine. A major disadvantage of this flax fiber extraction method is the high risk of crop failure due to the weather dependency during dew retting.

Flax fibers were purified by boiling them in 2–10% sodium hydroxide solutions. Unwanted fiber components dissolve during the boiling process, which was carried out for 30 min in a 5% and 10% NaOH solution. After repeated thoroughly washing with distilled water and following drying, it is possible to discover changes with respect to the basic material.

- Hurds can be removed more easily,
- Fibers are purified,
- Unwanted fiber ingredients are largely removed,
- Fiber separation ability is increased.

The dew-retted fibers (RFA) (Schürer, Germany) come from Polish cultivation and are destined for textile application. In a first processing step, the fibers were purified with surfactants. In order to carry out favorable color absorption, a treatment in a slightly alkaline washing bath (approx. 3% NaOH) follows.

The steam explosion method (STEX) represents a suitable alternative to a complete retting procedure. Under pressure and increased temperature, steam and additives penetrate the fiber interspaces of the bast fiber bundles. The center lamella will thus be removed at optimum conditions of reaction. The following sudden relaxation of the steam leads to an effective breaking up of the bast fiber composite that results in an extensive decomposition into individual fibers (DDA).

Three other types flax fibers, green (GFB), dew-retted (RFB) and Duralin, have been supplied by CERES B.V. (The Netherlands). The upgrading process in order

to obtain Duralin flax as developed by CERES B.V. uses full rippled (deseeded) straw-flax. The use of straw-flax turned out to be beneficial for both strength and reproducibility (no dew-retting required) of the treated fibers. In addition, a valuable by-product, the treated flax-shives, is produced from which e.g. water-resistant chipboards could be made (4). The Duralin treatment consists of a steam or water-heating step of the rippled straw-flax at temperatures above 160°C during approx. 30 min in an autoclave. A drying step and a heating (curing) step above 150°C during approx. 2 h follows the first step. During this treatment, the hemi-cellulose and lignin are depolymerized into lower molecular weight aldehyde- and phenolic functionalities, which are combined by the subsequent curing reaction into a water resistant resin, which cements the cellulose microfibrils together. After the treatment the fibers can easily be separated from the stem by a simple breaking and scutching operation. The fibers obtained by these procedures are fiber bundles rather than individual fibers.

Pure cellulose (Buckeye (Linters), Germany), extracted from cotton, was used for reference measurements. The Type 4410/030 has a degree of polymerization (DP) of 2000 and Type 4403/020 of 1470.

The maleic anhydride modified polypropylene (MAH-graft PP) was produced by combining Novolen PPN 1060 F (Targor GmbH, Germany) with a low molecular coupling agent AR 504 (Clariant GmbH, Germany). The effectiveness of the coupling agent is based on (24, 25):

- 1) the formation of chemical bonds by esterification between the anhydride groups of the coupling agent and the -OH groups of the cellulose (main structural element in all natural fibers) and
- 2) the interlacing of the PP chains of the basal body of the coupling agent with the matrix material.

Currently, MAH-graft PP is the most effective coupling agent between PP and natural fibers (24, 26). A similar procedure that has been described by Felix and Gatenholm (27) was used to graft MAH-graft PP onto the flax fiber surfaces. Before performing PP-grafting onto the retted RFA-flax fiber surfaces, the fibers were Soxhlet-extracted with toluene for 24 h and then dried at 60°C under vacuum (1 mbar) for 24 h and their weight measured. The purified fibers were then immersed in a solution of (3% and 5%) MAH-graft PP (concentration: 5 wt% on the fibers) in hot (100°C) toluene for 5 min. After grafting the fibers were again Soxhlet-extracted for 48 h in order to remove all components, which were not covalently attached to the fibers. Finally, the fibers were dried again at 60°C under vacuum (1 mbar) for 24 h and the weight gain again measured in order to determine the grafting density.

In order to remove most absorbed water, all natural fibers were dried in a vacuum oven at 60°C and 1 mbar of vacuum over phosphorus pentoxide (Sikkapent) for 24 h prior to the ζ -potential measurements.

Scanning Electron Microscopy and BET-Adsorption Measurements

In order to evaluate changes in the fiber surface morphology, fibers (cellulose as well as flax and hemp) were analyzed by scanning electron microscopy (SEM) using a Jeol JSM 840 scanning electron microscope (Japan). The excitation energy used was 5 keV. To achieve good electric conductivity all fibers were first carbon sputtered followed by sputtering a gold palladium mixture before examination.

The total specific surface areas of natural fibers were determined with nitrogen as adsorbate applying the Brunauer-Emmett-Teller (BET) technique (28, 29) using a Sorptomatic 1990 (FISONS).

Regarding the structure of natural fibers like flax or hemp, they can be considered as non-porous solid, and therefore, one should expect according to Brunauer *et al.* (28) an adsorption isotherm type II (for non-porous solids) out of the 5 classes. Because of the small surface area of 'dried' natural fibers complete adsorption isotherm were measured using 9–11 g fiber material, which was dried in vacuum at 100°C in order to remove 'all' adsorbed water. Before the actual measurement the measuring system was evacuated till a constant pressure of < 0.9 Pa was reached. The measured nitrogen adsorption isotherms were evaluated using a three-parameter non-linear fitting procedure as suggested by Schneider (30), which makes it possible to obtain simultaneously the adsorbed monolayer volume V_m , the BET constant C and the net volume of micropores V_{mi}^0 . Measured data points in the range of $0.05 < p/p^0 < 0.45$ were used for the fitting procedure.

$$V_{ads} = \frac{V_m \cdot C \cdot p/p^0}{(1 - p/p^0) \cdot [1 + (C - 1)p/p^0]} + V_{mi}^0 \quad (1)$$

The specific surface area A_s of the fibers is calculated from the adsorbed volume V_{ads} , the molar gas volume $V_{mol} = 22.414$ l/mol using the known surface area, which one nitrogen molecule covers on the absorbent surface ($a_{N_2} = 16 \text{ \AA}^2$).

$$A_s = \frac{N_A \cdot V_m}{V_{mol}} \cdot a_{N_2} \quad (2)$$

Water Absorption Measurements (Conventional Method)

Humidity chambers (desiccators) were set up at 100% humidity using distilled water. The specimens were prepared from bundles of single fibers bound together. The specimens (GFB, RFB and Duralin flax fibers) were dried at an air oven at 60°C for 24 h,

weighed at a balance accurate to 4 decimal places (± 0.1 mg) and were then placed in the humidity chamber. The humidity chamber was held at room temperature. The weight difference was measured at different time intervals (according to the DIN standard 53495) and then the total water uptake was calculated using the following equation:

$$MC = \frac{(m - m_d)}{m} \cdot 100\% \quad (3)$$

where MC = moisture content, m = mass of the sample after exposing it in humidity and m_d = mass of the dried sample. The total number of samples used for each type of fibers was three.

Zeta (ζ)-Potential Measurements

The electrokinetic analyzer EKA (Anton Paar KG, Graz, Austria) based on the streaming potential method (31) was used to measure the electrokinetic or ζ -potential of different natural fibers. The streaming potential is measured as function of the pressure decay (in the range of 30–150 mbar) in a fiber bundle (capillary system) while the electrolyte solution (1 mM KCl, pH = 5.6) is pumped through. The streaming potential, which arises due to the shear-off of the diffuse part of the electrochemical double layer, was measured as a function of time and the pH at 20°C using two Ag/AgCl electrodes (Sensortechnik Meinsberg GmbH). In order to minimize the asymmetric potential, the used electrodes were short circuited after each measurement in 0.1 mM KCl-solution. All theoretical and experimental details about this technique have been reported in the literature (32).

According to Kanamaru (33) the quotient $\Delta\zeta = (\zeta_0 - \zeta_\infty)/\zeta_0$ should correspond to the water uptake at 100% relative humidity (RH) (the sorption capacity) of the investigated solid. The decrease of the ζ -potential as a function of time due to the water uptake can be described as follows:

$$-\frac{d\zeta}{dt} = k \cdot (\zeta - \zeta_\infty) \quad (4)$$

which leads to

$$-\ln \frac{\zeta - \zeta_\infty}{\zeta_0 - \zeta_\infty} = k \cdot t, \quad (5)$$

where ζ is the measured ζ -potential value at a certain time, ζ_∞ the ζ -potential value which reaches the function $\zeta = f(t)$ asymptotically and k a constant depending on the structure of the investigated polymer (34).

Investigating the kinetics of the water uptake, the swelling-process using electrokinetic methods can be problematic. Since the first step of a steaming potential measurement is always a rinsing process of the fiber plug (because one has to remove all air included), then the time dependent ζ -potential measurement will be started and the streaming potential and also the asymmetric potential of the used Ag/AgCl-electrodes changes. But during this time the swelling process already started. Therefore, it will be a problem to locate

the initial starting point ζ_0 . However, the starting value ζ_0 , which should be measurable immediately after the 'dry' fiber sample contacts the electrolyte solution, was in analogy to Kanamaru (33), obtained by fitting an exponential first order decay function to the measured ζ -potential time curve and subtracting ζ_∞ . The ζ_0 -value obtained using this procedure agrees within the experimental error (rinsing and removing all included air takes approx. 1.5 min and equilibrating problems of the entire system) with the actual measured values.

As stated already in the literature (32), the asymmetric potential U_{asym} (the potential which exists between the two measuring electrodes in dormancy, without applying a liquid stream and which is quantified as intersection point of the ordinate) will not affect the measured ζ -potential as long as it remains constant during a single measurement of the streaming potential $U = f(\Delta p)$. The streaming potential is only obtained from the slope ($dU/d(\Delta p)$) of the function $U = f(\Delta p)$, and since we measured a line graph (correlation coefficient $R \geq 99.5\%$) over the whole applied pressure range ($30 \leq \Delta p \leq 150$ mbar) a deviation of the observed line from the zero-point will not affect the obtained ζ -potential. However, the asymmetric potential is a function of the electrolyte concentration (the higher the concentration the smaller U_{asym}) and of time. In the case of the natural fibers U_{asym} was, at the beginning of a measurement, in the range of -5 mV and disappeared asymptotically after approx. 30 min (Fig. 2).

The acidity and basicity of solid surfaces can be determined qualitatively by measuring the ζ -potential as a function of the pH, if the dissociation of functional groups is the predominant mechanism forming the double-layer.

NMR Measurements

All NMR measurements were performed using a Bruker -300 instrument. The $\{^1\text{H}\}$ - ^{15}N -CP/MAS NMR with the cross polarization contact time of 5 ms were applied for the low-temperature measurements at 170 K. The chemical shifts have been referenced to solid $^{15}\text{NH}_4\text{Cl}$.

For the NMR-experiments industrial purified RFA-flax fibers were chosen. The purified RFA-flax sample (a) has been dried in vacuum (pumped at ca. 20 mbar for 24 h at room temperature) in order to remove weakly adsorbed water. After that a small amount of ^{15}N -enriched 2,4,6-trimethylpyridine (collidine) has been added to the sample and the closed flask has been left for one day to ensure a homogeneous collidine distribution. Another purified RFA-flax sample (b) was first stored in 10% aqua. HCl-solution for a night and later treated in the same way.

RESULTS AND DISCUSSION

Fiber Morphology and Surface Area

The scanning electron micrographs (SEM) clearly show differences in the surface morphology of the flax fibers depending on the used fiber separation process

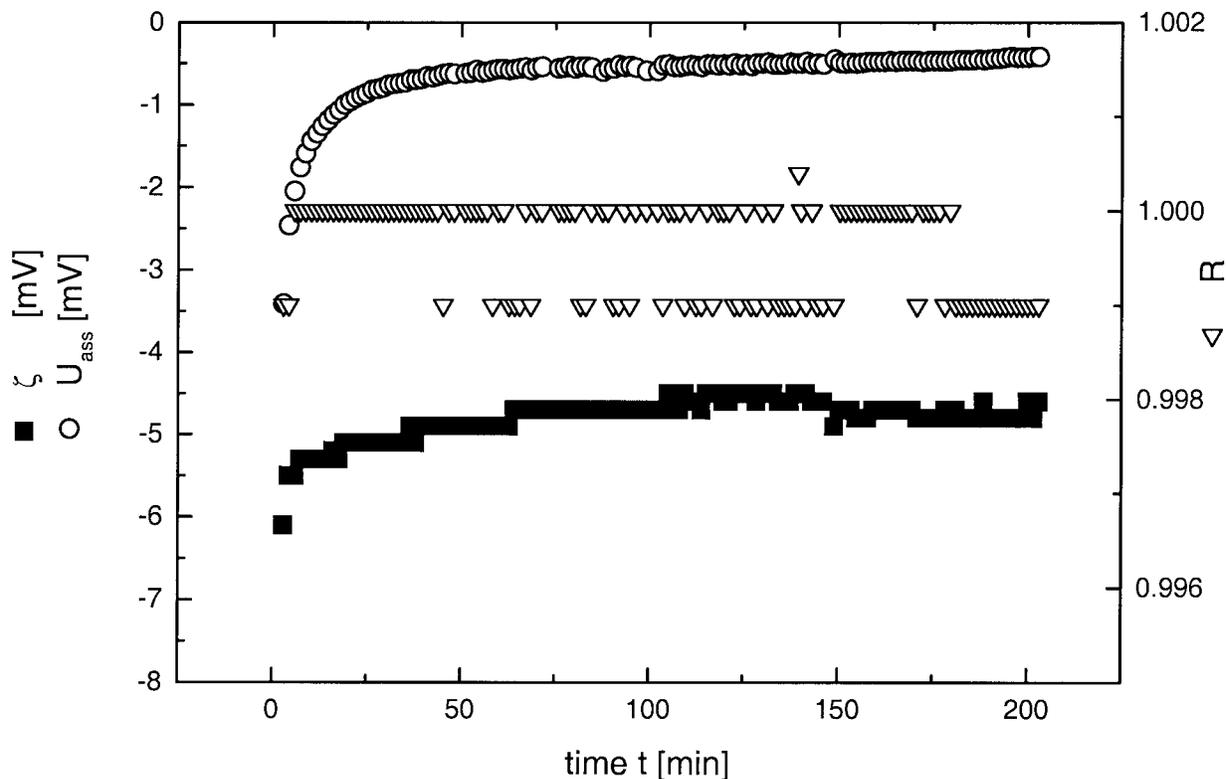


Fig. 2. Time dependence of the measured ζ -Potential, asymmetry-potential (U_{ass}) and the correlation coefficient R for GFA-green flax.

and as well on the applied fiber surface modifications (Figs. 3, 4). Fiber properties, like the degree of disintegration, the fineness and the amount of non-cellulose components, can be adjusted within a broad range due to fiber retting, applied fiber separation processes as well as further treatment and modification steps. The Figs. 3 show the different 'original' but differently separated natural fibers. The non-retted green flax (Fig. 3a) as well as hemp fibers (Fig. 3b) were separated from the raw fibers using ultrasonification. During the separation procedure the fiber bundles will be partially penetrated, however even though a weak alkaline solution is used the fibers will not become totally separated. The SEM-pictures show partially uncovered structures, comparable to those of the pure cellulose (Fig. 3c), beside areas that are still covered by non-cellulose compounds (like waxes or fats). The steam explosion method, in contrast, leads to relatively smooth fibers (Fig. 3d). However, the fiber structure is still not completely laid open, e.g. fiber waxes and fats are still attached to the surface.

A very effective procedure in order to remove most waxy substances from the fiber surfaces is washing them in hot toluene. Figure 4a shows fibers that were washed in hot toluene, compared to the native retted flax fibers (Fig. 3e) it can be seen that noncellulose components were removed during toluene washing. After grafting 3%-MAH graft-PP to toluene washed

fibers the fibers were again extracted with hot toluene in order to remove all components, which were not covalently attached to the fibers. Performed IR measurements on MAH-graft PP cellulose- and flax fibers give evidence for covalent bonding of the modified PP to the natural fibers (9). The measured weight gain after grafting 3% MAH-graft PP on a flax sample of 1.1 g was 87 mg. The PP-grafting leads to an estimated grafting density of around $6.6 \mu\text{mol}/\text{m}^2$ (or $6.6 \mu\text{mol}/\text{g}$) considering the specific surface (approx. $A_s \approx 1 \text{ m}^2/\text{g}$) of the fibers and the molecular mass of the MAH-graft PP ($M_w = 12000 \text{ g/mol}$). As can be seen in Fig. 4b, this modification will result in a patch-like PP-grafted fiber surface which still leads to improved macromechanical properties of the resulting composite (9).

Applied (industrial) purification processes of the retted flax fibers (Fig. 3e) lead to an extensive separation of fiber bundles into single fibers (Fig. 4c). The alkalization results in uncovering the fiber fibrils, however, there are still natural fiber additives sticking on the surfaces. After an alkalization using higher NaOH concentrations (5%) the fiber surfaces become more structured (the cell wall structure is loosened). The fiber fibrils are now ordered in lamellas, which are obvious as striations parallel to the fiber axis (Fig. 4d) and almost all waxes and other 'additives' are removed. However, the knuckle-swells and disclination as present in the raw-fibers can still be found after the

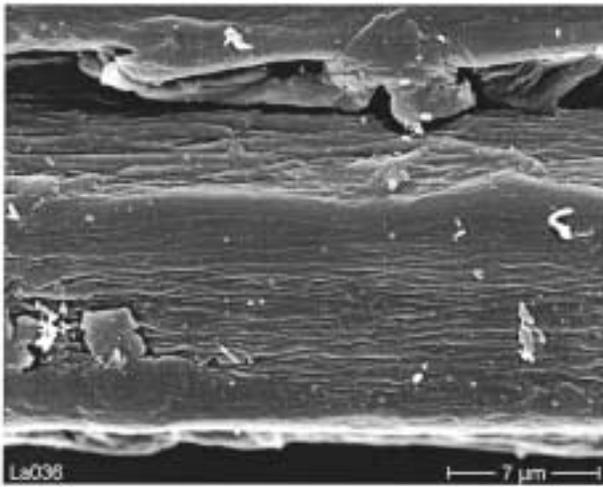


Figure 3a: Green flax (GFA), separated using ultrasonification

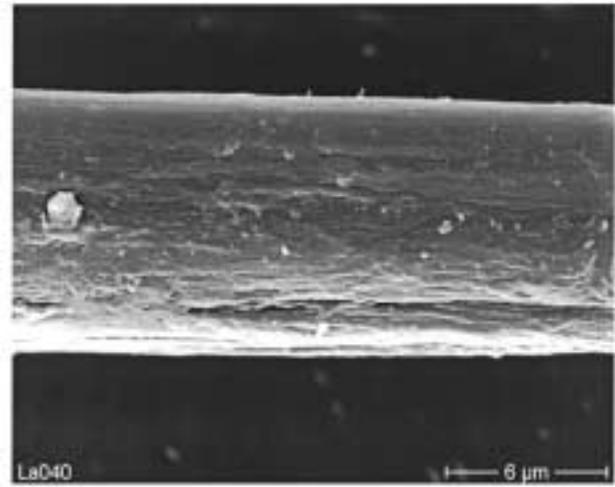


Figure 3d: DDA-flax

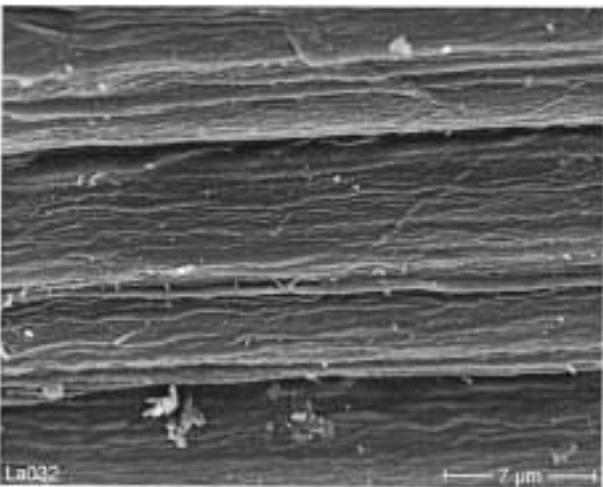


Figure 3b: Green hemp, separated using ultrasonification

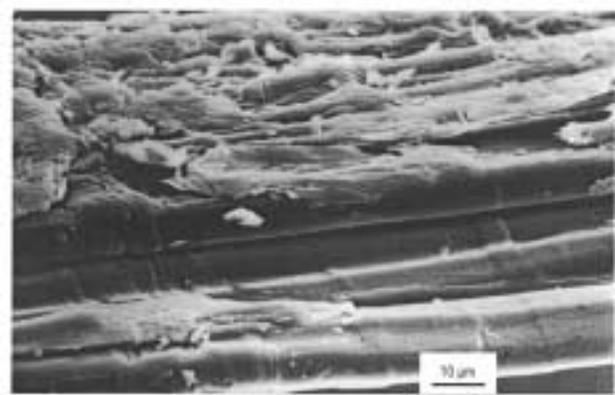


Figure 3e: Retted flax fibers (RFA), native (raw) state

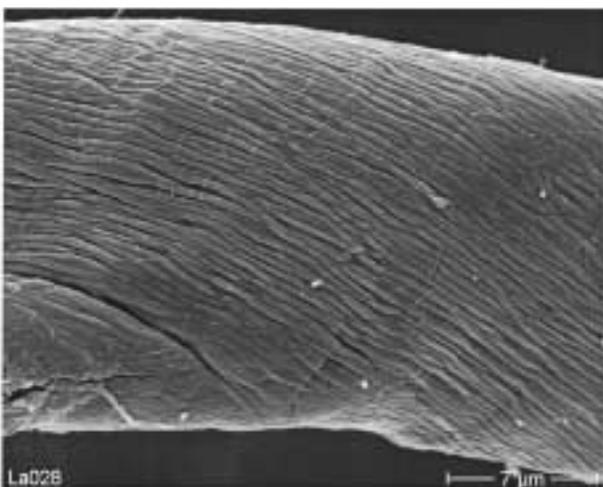


Figure 3c: Cellulose fiber

Fig. 3a-e. SEM-micrographs of the 'original' natural fibers.

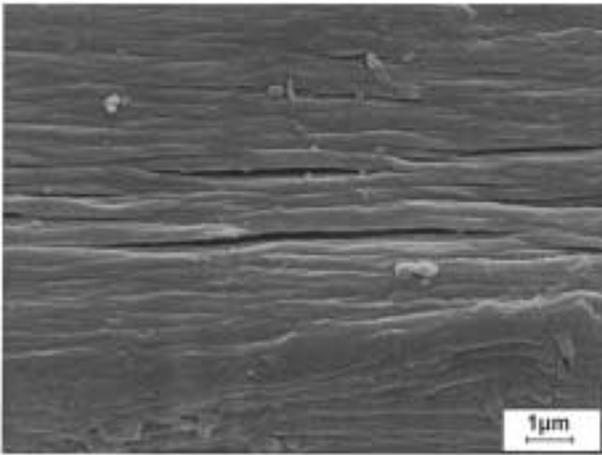


Figure 4a: RFA-flax, toluene extracted

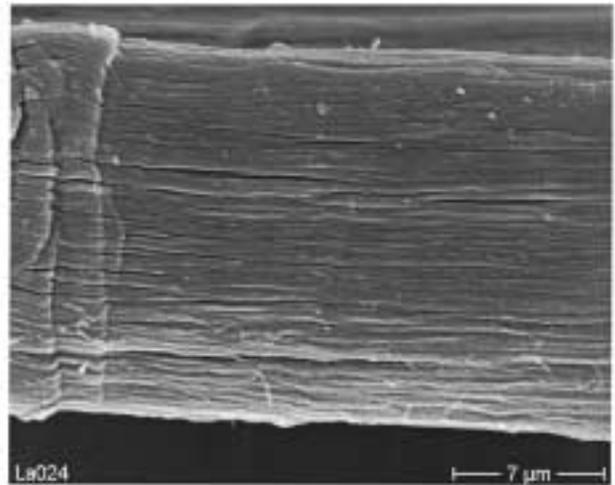


Figure 4d: RFA-flax, alkalinized in 5% NaOH

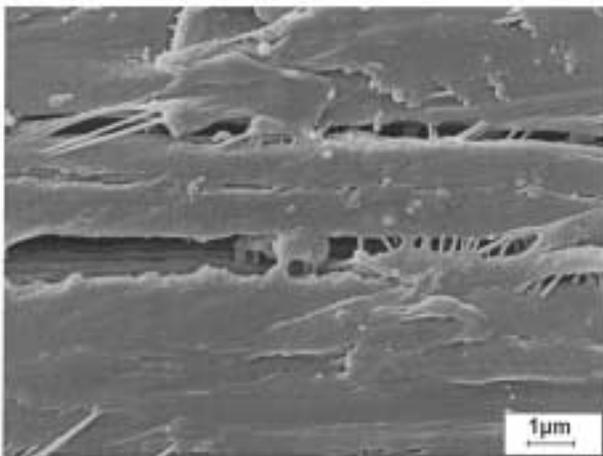


Figure 4b: RFA-flax, toluene extracted, 3% MAH grafted PP modified and again toluene extracted (only chemically bonded MAH-graft PP should remain on the flax fiber surfaces)

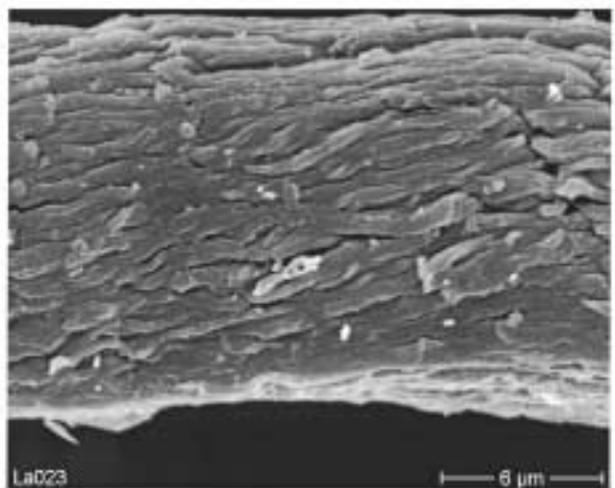


Figure 4e: RFA-flax, alkalinized in 10% NaOH

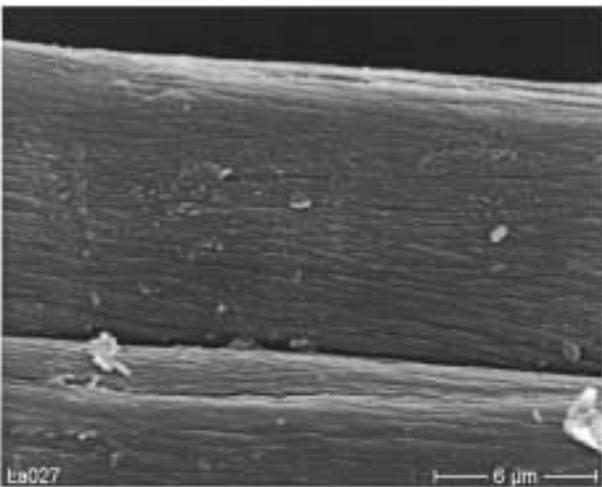


Figure 4c: RFA-flax fibers, industrial purified and alkalinized

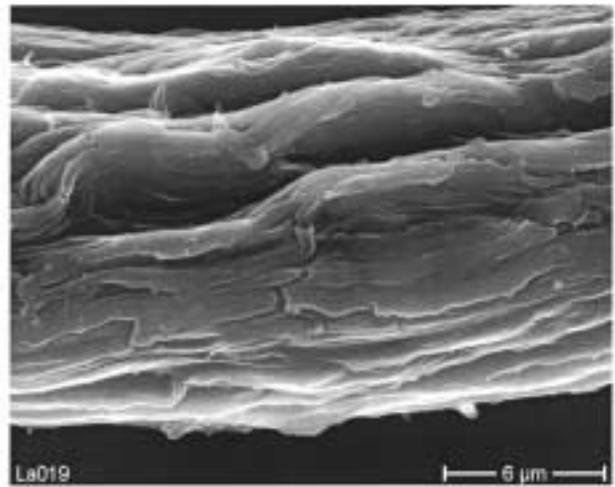


Figure 4f: RFA-flax, alkalinized in 10% NaOH – collapsed structure

Fig. 4a-f. SEM-micrographs of the treated natural fibers.

NaOH-treatment. A further increase in the NaOH-concentration to 10% results in a broadening of the lamellar structure (Fig. 4e), and partially starting conversion from cellulose I to cellulose II, which causes a collapsing of the fiber structure (Fig. 4f), resulting in increased roughness (deeper and broader striations).

As result we should expect an enlarged specific surface.

As seen above the applied fiber surface treatments result in changes of the surface morphology, in order to quantify the changes it was decided to determine the total specific surface area of the fibers. Figure 5 shows exemplary the measured BET-adsorption isotherms and theoretical fits to the experimental data according to the method introduced by Schneider. The results are summarized in Table 3. In general, all natural fibers studied have very small specific surface areas ($A_s \approx 0.5 \text{ m}^2/\text{g}$), which is just slightly bigger than the calculated geometric surface area ($A_{s,geo} = 0.38 \text{ m}^2/\text{g}$ at a fiber diameter $\bar{d}_f \approx 14 \text{ }\mu\text{m}$ (compare SEM-micrographs) and a density of flax fibers (35) of $\bar{\rho} = 1.47 \text{ g/cm}^3$).

For a chosen sample (industrial purified RFA) the complete adsorption/desorption curve was measured (Fig. 5b), and it was found that both curves were nearly completely identical; i.e. almost no hysteresis was observed. Natural fibers exhibit adsorption isotherms close to that of BET-type II (assumption $C \gg 1$). Since the natural fibers dried from water have only single lamellae (36), it was found that they are indeed

non-porous exhibiting only very small (micro)-pore volumes ranging from 20 to 50 mm^3/g . Comparing the results obtained for the investigated dried natural fibers (Table 3) with literature data for cellulose fibers (see 36, and references therein) show good agreement. It was stated that the specific surface area for native cellulose dried from water ranges from 0.6 to 1 m^2/g having only pore volumes of about 2 mm^3/g . However, swollen fibers dried by solvent exchange will exhibit very much greater specific surface areas ranging up to 200 m^2/g . The cell wall of swollen fibers, natural fibers consist of several hundreds of lamellae, and the large increase in the surface area is caused by small pores with a most common pore size of 16 to 38 Å (36).

Even though the investigated natural fibers have in general very small specific surface areas, they are affected by the used fiber separation process. As can be seen in Fig. 5a. two groups of natural fibers can be distinguished: one having 'larger' surface areas but smaller C-values and the other ones with lower surface areas and bigger C-values. The C-value is a measure of the difference of the adsorption free enthalpies of the first adsorbed gas layer to the subsequent (multi)-layers. A comparison of the retted flax fibers (RFA) shows the dependency of surface area and the C-value. An alkalization using NaOH-concentrations $\leq 5\%$ causes surface area to increase but simultaneously the C-value to decrease. However, unexpectedly (compare SEM-micrographs Figs. 4c, d; the

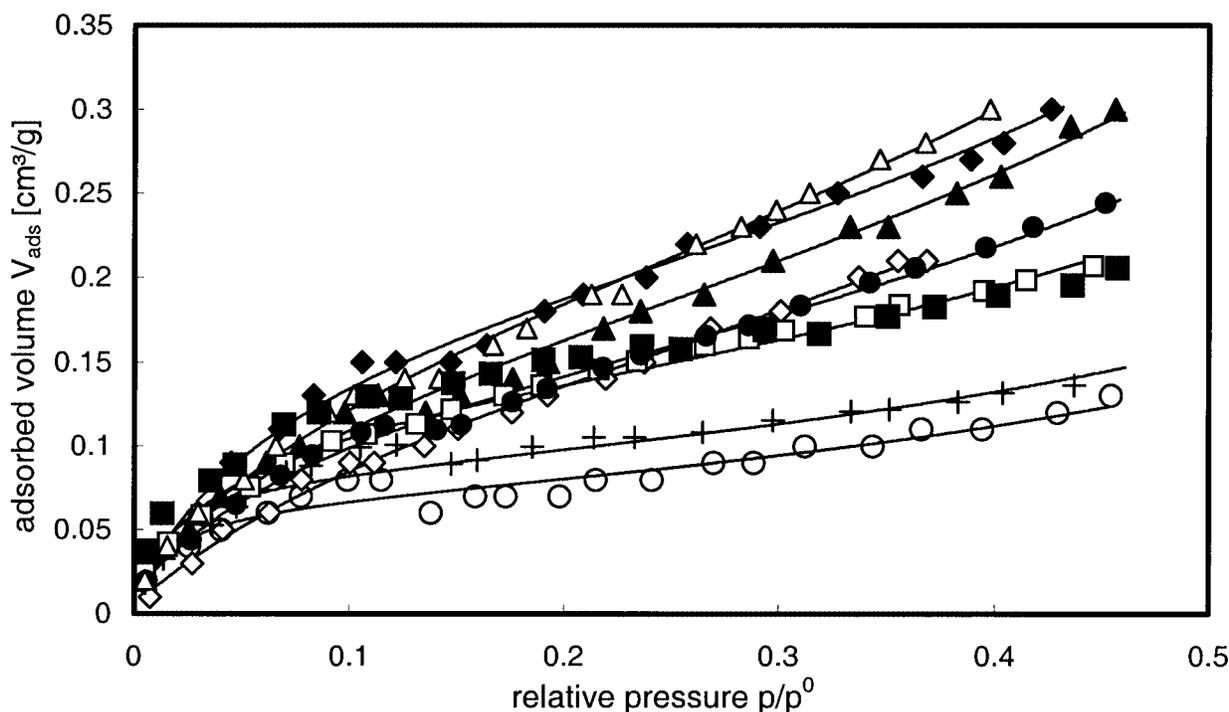


Fig. 5. BET-adsorption isotherms of various natural fibers; 'pure' cellulose (■) and flax fibers RFA (□), RFA 5% NaOH (●), RFA 10% NaOH (+), RFA industrial purified (◇), RFA industrial purified and alkalized (◆), DDA (△), green flax (○) and green hemp (▲).

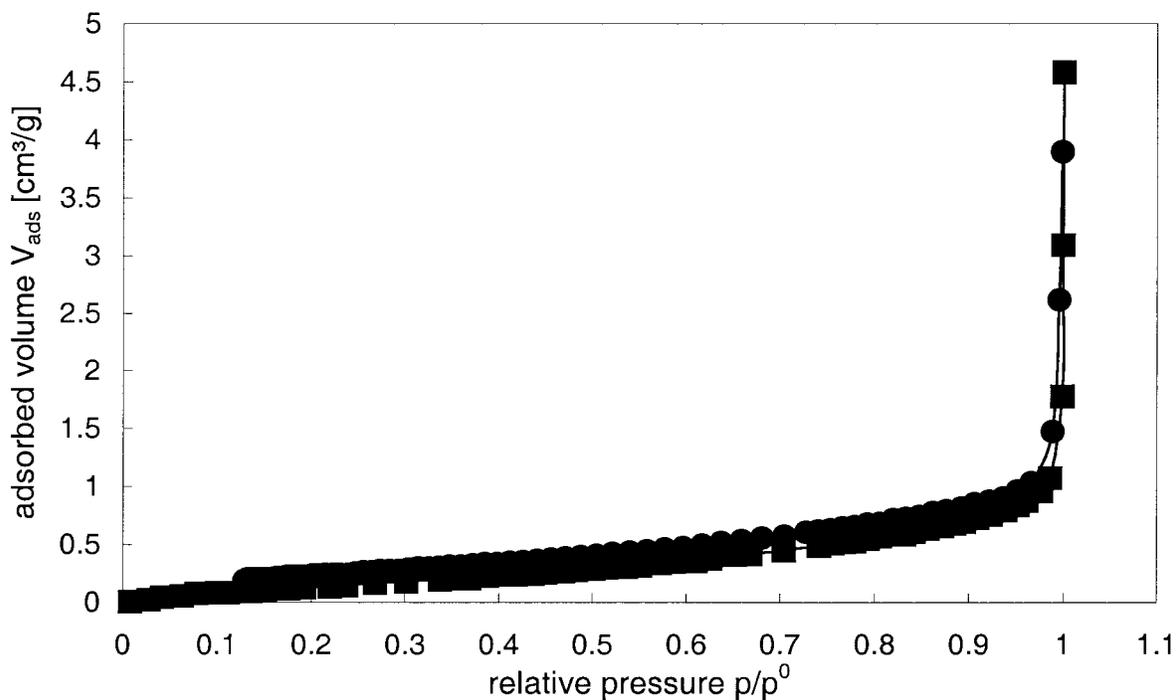


Fig. 5a. Adsorption/desorption BET-isotherms for the industrial purified RFA-flax fibers, adsorption (■) and desorption (●).

fine-lamellar structure changes in to rougher, bigger structures) increasing the NaOH concentration (10%) for the alkalization process results in a diminished surface area but increased C-value.

In general, it can be stated that the fibers, which are well or better separated from the raw fiber material (either by the original separation process, by STEX, or by following treatment steps) have bigger surface areas.

Time Dependence of ζ -Potential Measurements

The ζ -potential of the 'extremely' hydrophilic natural fibers is strongly influenced by the water uptake and, therefore, by the swelling of the investigated fibers. In order to evaluate the swelling behavior of natural fibers in aqueous solutions the time dependence of the ζ -potential in 1 mM KCl-electrolyte solution (pH = 5.6) of the 'dried' fibers was measured (Figs. 6a and b show the different behavior for different flax fibers: decrease

of negative ζ -potential as a function of time). The strong initial decrease of the negative ζ -potential of natural fibers with time is caused by water adsorption. This effect depends on the degree of hydrophilicity of the investigated fibers. More precisely, it is due to the swelling of the solid, which causes a transfer of the shear plane into the liquid that excludes the diffuse part of the electric double layer from the mechanical or electrical interaction (37). Another reason is the slow removal of water-soluble components (38) from the fibers (for flax 3.9% (4), e.g. ashes, alkali and earth metal salts (14)), since these constituents need to migrate from the fiber bulk to the surface, which might also cause a decrease of the ζ -potential.

As it can be seen from Fig. 6 (and Table 4, stressing the main results), the ζ -potential decreases for nearly all natural fibers from a measurable value $\zeta_{0,m}$ on different time scales more or less asymptotically to a constant but smaller value ζ_{∞} . However, in some cases

Table 3. Total Specific Surface Area A_s , BET C-Value and Micropore Volume V_{mi}^0 .

Natural fiber	A_s [m ² /g]	C	V_{mi}^0 [mm ³ /g]
GFA	0.31	72	34
RFA	0.51	22	25
RFA, industrial purified	0.71	7	21
RFA, industrial purified and alkalized	0.79	15	52
RFA, 5% NaOH	0.61	11	20
RFA, 10% NaOH	0.32	46	30
green hemp	0.75	8	52
DDA	0.88	8	20
Cellulose	0.45	36	50

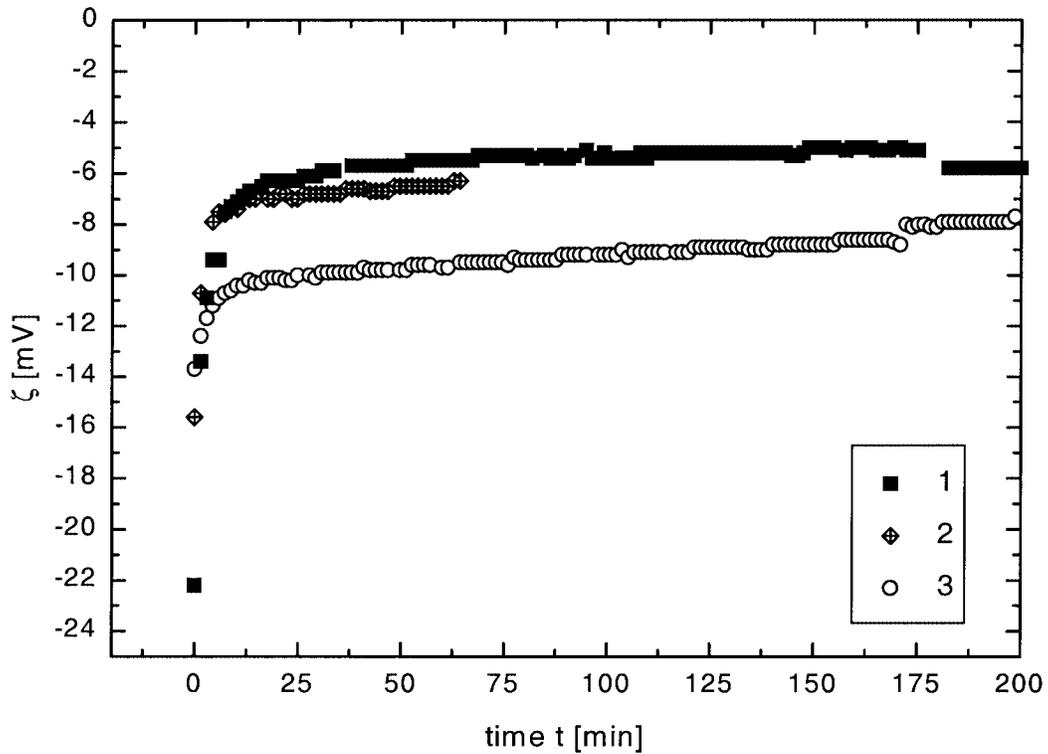


Fig. 6a. ζ -Potential-time dependence of unmodified and several modified flax fibers 1: RFA-pure retted flax; 2: industrial purified; 3: industrial purified followed by alkalization measured in 1 mM KCl at pH = 5.6.

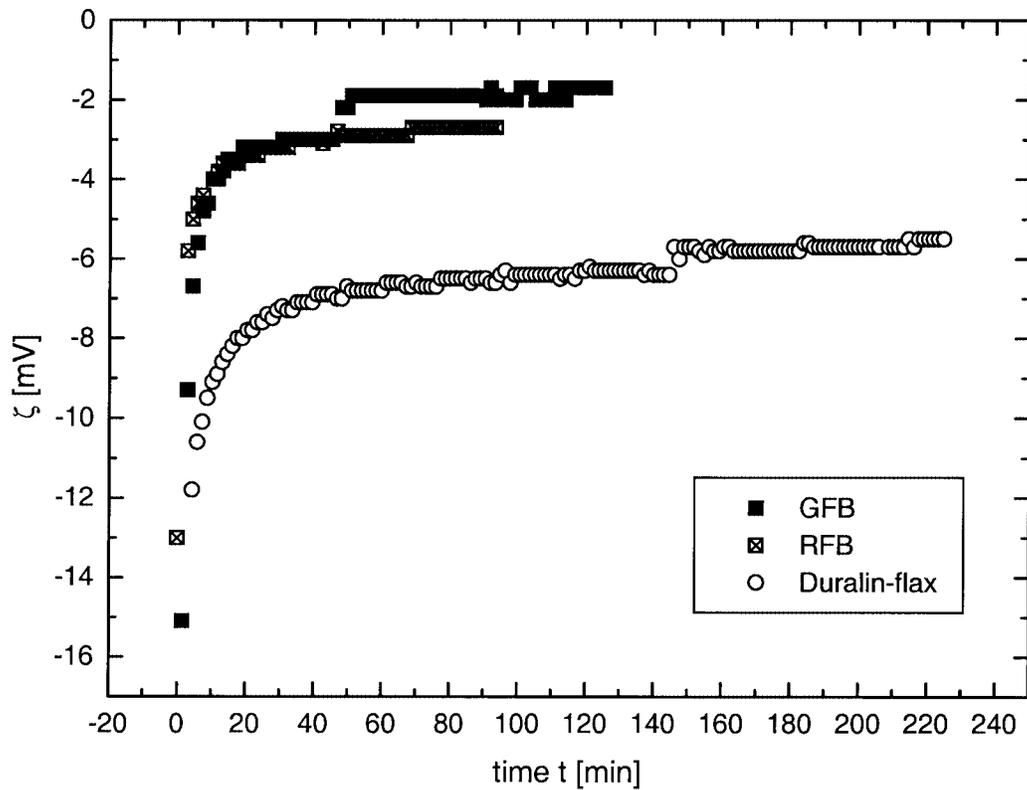


Fig. 6b. ζ -Potential-time dependence of unmodified GFB-green, RFB-dew-retted and modified Duralin-flax fibers in 1 mM KCl at pH = 5.6.

Table 4. Main Results of the Time Dependence of the ζ -Potential Measured in 1 mM KCl Supporting Electrolyte at pH = 5.6: ζ_0 = ζ -Potential Value Measured Immediately After Starting the Measurement (However, Due to the Delay Because the Rinsing Process the ζ_0 -Value Was Obtained By Fitting a First Order Exponential Decay Function to the Experimental Curve), ζ_∞ = ζ -Potential Value After Established Equilibrium, $\Delta\zeta = (\zeta_0 - \zeta_\infty)/\zeta_0$ -Value Which Should Correspond to the Water Uptake at 100% RH and Moisture Absorption Results for GFB-Green, RFB-Dew-Retted and Duralin Flax Fibers: Maximum Moisture Content MC and Average Maximum Moisture Content MC.

Natural fiber	ζ_0 [mV]	ζ_∞ [mV]	$\Delta\zeta = (\zeta_0 - \zeta_\infty)/\zeta_0$	Moisture Content MC [%]	Average Maximum Moisture Content MC [%]
GFA-green flax	-10.6	-4.4	0.58		
RFA-retted flax	-15.4 ± 1.5	-6.1 ± 1.2	0.60		
RFA-retted flax, purified	-14.2	-6.5	0.54		
RFA-retted flax, purified and industrial alkalized	-19.3	-8.7	0.55		
DDA	-15.9	-13.5	0.15		
GFB-green flax	-20.6	-1.7	0.92	37.19 40.85 49.69	42.58
RFB-retted flax	-8.8	-2.7	0.69	25.93 26.04 27.75	26.57
Duralin flax	-13.8	-5.5	0.60	19.34 19.72 18.60	19.22
RFA-retted flax washed in toluene	-13.9	-4.2	0.70		
PP grafted (3% MAH)	-7.0	-0.2	0.97		
PP grafted (5% MAH)	-10.0	-3.3	0.67		

no time dependence of the ζ -potential could be measured—e.g. not for the industrial purified RFA-flax fibers which were later alkalized in our laboratory in 5% and 10% NaOH and for the cellulose fibers—the ζ -potential remained constant over time at small negative values. This means (assuming that a 'non-swelling' behavior is excluded) that the swelling process is too fast (faster than the required preparation of the measuring cell takes to rinse the measuring cell unit and to remove all included air) to measure the decrease of the ζ -potential with time. All investigated fibers display a different ζ -potential-time dependence, which should be correlated with the different swelling or water uptake behavior of the materials.

The results of the ζ -potential-time dependence show that all fibers absorb quite a large amount of water. The original but 'untreated' GFA-green and RFA-retted absorb nearly the same amount of water, whereas DDA-flax fibers absorb much less water. This might be due to different types and amount of waxes (different types of fatty alcohols (4), hydrocarbons, fatty acids and various esters (14)), which will 'stick' on the fiber surfaces after the various separation processes. Any treatment of the fibers afterwards, like an industrial purification process and purification followed by alkalization in approx. 3% NaOH (shown for example for RFA-retted flax fibers) will affect the chemical fiber composition and increases the accessibility of dissociable 'surface'

groups as becomes obvious in the increased negative ζ -potentials. On the other hand however, a slight decrease (by about 10% in $\Delta\zeta = (\zeta_0 - \zeta_\infty)/\zeta_0$) in the amount of water absorbed could be detected for the industrial treated RFA-flax fibers. As stated in the literature an alkali treatment results in the partial dissolution of hemicellulose (39). Hemicellulose, however, is responsible for the biodegradation, moisture absorption and the thermal degradation of the fiber (40). Contrary, as observed for an alkalization in 5% and 10% NaOH solutions leading to the removal of all other hydrophobic compounds from the fibers (14) no ζ -potential-time dependence could be measured. This means that the swelling process is getting much faster leading to higher water uptake rates (which, therefore, cannot be detected using ζ -potential measurements).

The extraction of the retted RFA-flax fibers in hot toluene increases the amount of absorbed water as compared to the 'original' RFA fibers, because all remaining waxy substances are removed from the fiber surfaces (40), whereas grafting of MAH *graft*- (3% and 5%) PP onto the retted flax fiber surfaces that had been washed afterwards in hot toluene in order to remove the not covalently attached PP will not further influence the 'estimated' water uptake significantly. As already described above, even though the grafting leads to significant coverage of the flax fiber surfaces still 'original' unmodified fiber (also interior) surfaces are

visible (see also Fig. 4b) and, therefore, it is not expected that the amount of water absorbed will be reduced.

Felix and Gatenholm (27), however, observed using contact angle measurements, that grafted cellulose fibers turned totally hydrophobic (water contact angle $\theta \approx 140^\circ$), but in contrast to their results, in our case, it can be seen clearly that the swelling process in water is not inhibited. Even after PP-grafting on the toluene washed flax surfaces the amount of absorbed water is higher as compared to the original retted flax fibers, possibly because the fibers were twice exposed to the hot toluene extraction. Similarly, Joly *et al.* (41) also did not observe any reduction in hydrophilicity after PP-grafting onto cellulose-like fibers (flax, pure cellulose powder and Ramie).

The water absorption of flax fibers supplied from CERES B.V. under different relative humidities has also been studied (7). The data obtained using time-dependent ζ -potential measurements (Fig. 6b and Table 4) are to compare with conventional water absorption measurements (Fig. 7 and Table 4). GFB-green flax fibers absorb more water (maximum MC = 42%) than RFB-dew-retted (MC = 26%) whereas Duralin-fibers absorb much less water (MC = 19%). The saturation point for all fibers occurred almost at the same time (approx. 4500 min). The slope of the moisture content versus time curves is higher for green and dew-retted fibers (with green having higher slope) compared to the upgraded Duralin-fibers.

The above-mentioned results of the average maximum moisture content (\overline{MC}) are in good agreement

with the $\Delta\zeta$ -values obtained by time-dependent ζ -potential measurements (Fig. 8), despite the questionable explanation of the ζ -potential decrease by Kanamaru. He explained the lowering of the ζ -potential by water uptake hypothetically by a decrease of the dielectric constant of the fibers (33). However, the different water uptake behavior becomes obvious from the functions $\zeta = f(t)$. The GFB-green flax absorbs more water, followed by RFB-dew-retted flax and the upgraded Duralin flax displays the 'lowest' degree of hydrophilicity. This confirms the potential of ζ -potential measurements to allow the fast estimation of the swelling behavior of solids in water.

Even though some of the investigated fiber materials seem to absorb the same high amounts of water, i.e. they have similar $\Delta\zeta$ -values, even after subsequent fiber treatments there is an overall trend obvious (as shown in Fig. 8). The investigated fibers can be classified into groups, those very hydrophilic fibers which absorb very high amounts of water in really short time, so that the $\zeta = f(t)$ can not be measured (at least with the process we used) and those which water uptake can just be followed like the toluene washed fibers, those with medium water adsorption (the 'original' untreated fibers and industrially purified fibers) and low absorption, like the DDA-flax.

A reason for similar $\Delta\zeta$ -values even after applied fiber treatments might be the increased accessibility of weak Brønsted acidic functions that lignocellulosic fibers contain (like e.g. carboxylic groups), which are almost completely dissociated in water (42) those will result in an increase of the negative ζ -potential. On the

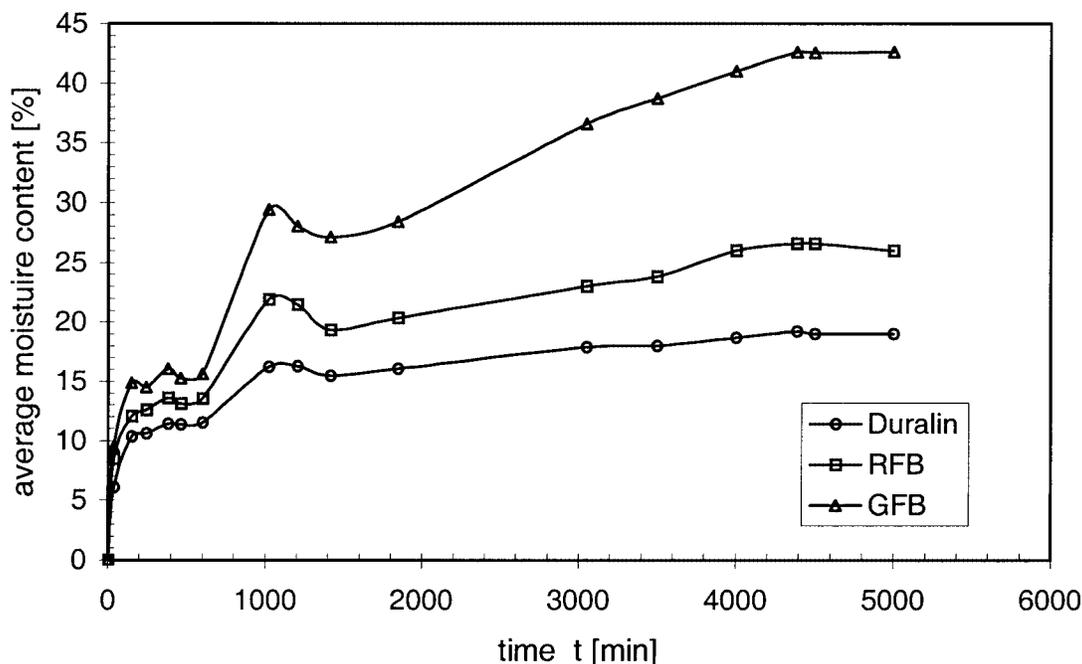


Fig. 7. Average moisture content \overline{MC} for GFB-green, RFB-(dew)-retted and upgraded Duralin-fibers at RH = 100%.

other hand, the adsorption of ions determining the ζ -potential occurs in competition with water adsorption and, therefore, the amount of absorbed water seems to stay nearly constant (34).

pH-Dependence of ζ -Potential Measurements

In order to determine the pH-dependence of ζ -potential the superimposed effects due to the swelling of the fibers have to be excluded. The starting point for these measurements was fixed by a time dependent ζ -potential measurement ($\zeta = f(t)$) in 1 mM KCl-supporting electrolyte solution.

The inhomogeneous character of the natural fibers (20) becomes clear from the measured ζ -potential pH dependencies (RFA-retted flax Fig. 9, cellulose Fig. 11; measurements were repeated on different parts of the samples taken from the same fiber charge). The overall trend of the function $\zeta = f(\text{pH})$ is almost the same, but the characteristic ζ -potential plateau-values (ζ_{plateau}) at $\text{pH} \geq 7$ differ significantly. Nearly for all studied natural fibers the isoelectrical point (i.e.p.), where $\zeta = 0$, could not be determined either due to the increase of the negative ζ -potential at low pH-values or due to the fact that the expected i.e.p. is situated in the very low pH region. From the chemical composition of the natural fibers (for flax, cellulose content > 64% (4)) a negative ζ_{plateau} -value should be expected due to the presence of weakly acidic carboxyl and hydroxyl groups (14). However, for some of the natural fibers, original and modified, only very small ζ_{plateau} -values, a zero ζ -potential within the error range, could be measured (see Table 5 including the main results). These small ζ_{plateau} -values show again clearly the high hydrophilic character of natural fibers. The swelling of

the hydrophilic fibers results in a reduction of the ζ -potential, because of the shift of the shear plane into the liquid phase (43).

For nearly all investigated fibers, except for green hemp and the flax fibers obtained from the steam explosion method (STEX, see also (44)) (DDA and Duralin) (see Figs. 10 and 13), the measured ζ -potential-pH course changes rapidly towards more negative ζ -potential values in the higher acidic range. A speculative hypothesis what causes this rapid change of the ζ -potential at low pH-values for the natural fibers [The same or an analogous behavior, the increase of the negative ζ -potential at low pH-values either in peak form or just a steep increase, was also found for other natural fibers, like jute (18), coir and sisal (19). It turned out that this process was as reproducible as possible for natural fibers, even over a period of several months and several repeated measurements. However, a similar observation was made with CP-MAS NMR.] might be the protonation of acetal or ether bonds that exist in either the cellulose (for flax, around 64.1% (4)) or lignin (about 2% (4)) present in the flax fibers. If such protonated bonds are present in the fiber surfaces, they may then induce excess counter-ion absorption (chloride ions), which then lead to a rapid increase of the negative ζ -potential at low pH-values. However, other explanations (but also tentative) might be possible, so it might be that due to the interaction of protons with surface functional groups the acidity constants $\text{p}K_a$ of the interacting groups changes, and therefore the $\zeta = f(\text{pH})$ course. It can also be possible that pH-depending swelling processes lead to a change in the surface composition and, therefore, the actual number of surface groups increases (in analogy to

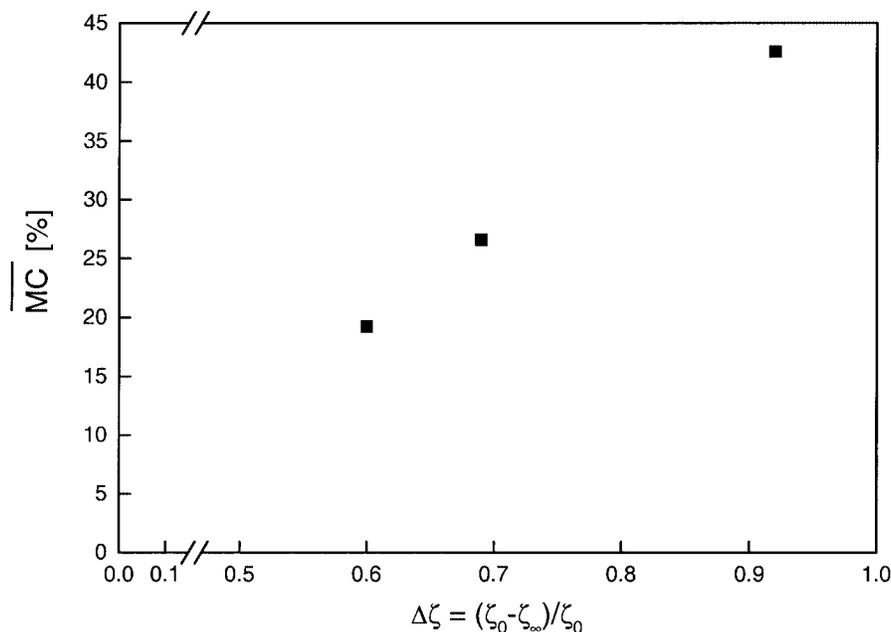


Fig. 8. Average moisture content \overline{MC} as function $\Delta\zeta = (\zeta_0 - \zeta_\infty) / \zeta_0$ -value that should correspond to the water uptake at 100% RH of the for GFB-green, RFB-(dew)-retted and upgraded Duralin-fibers at $\text{RH} = 100\%$.

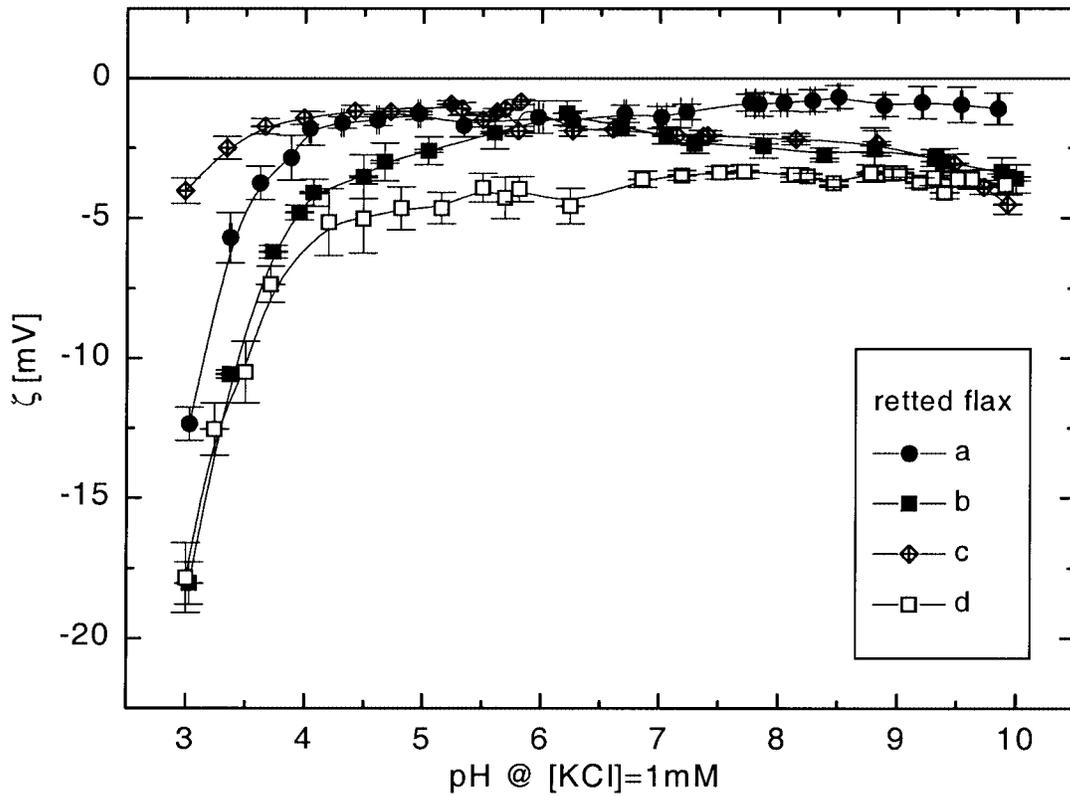


Fig. 9. ζ -Potential pH-dependence of untreated, RFA-flax fibers. The measurements were repeated four times (a-d) with fresh samples of the same fiber charge.

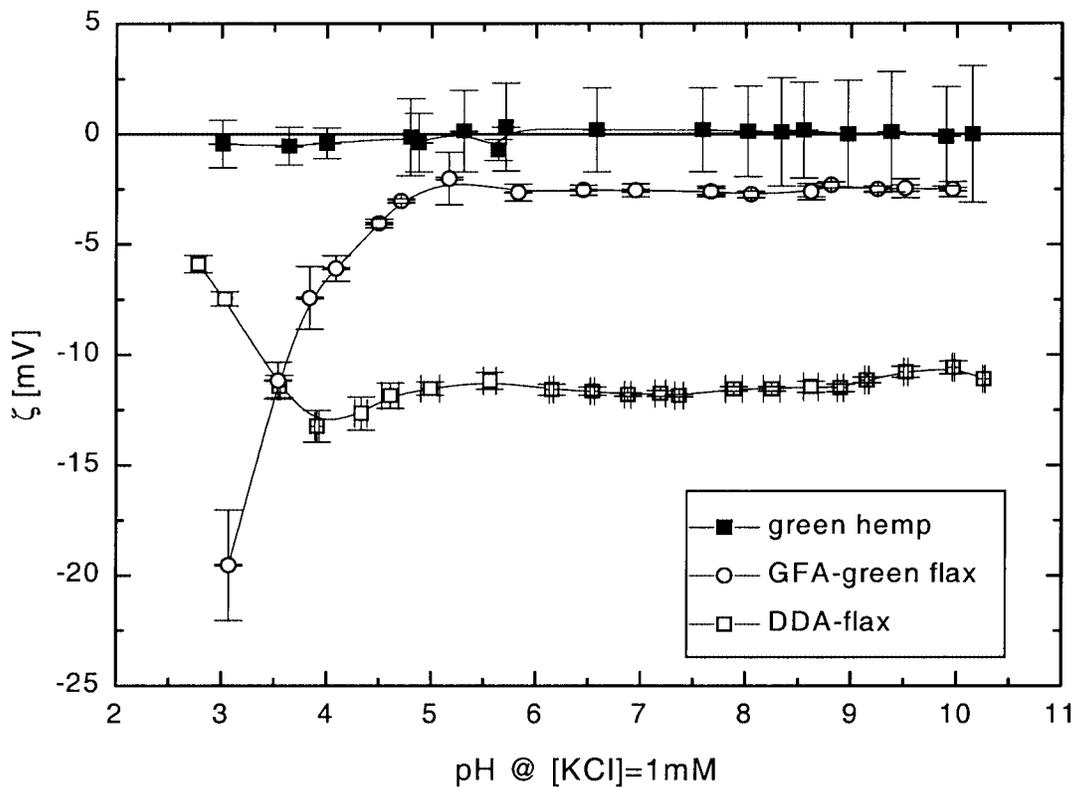


Fig. 10. ζ -Potential pH-dependence of GFA-green flax and hemp fibers, as well as flax fibers obtained using a DDA separation process.

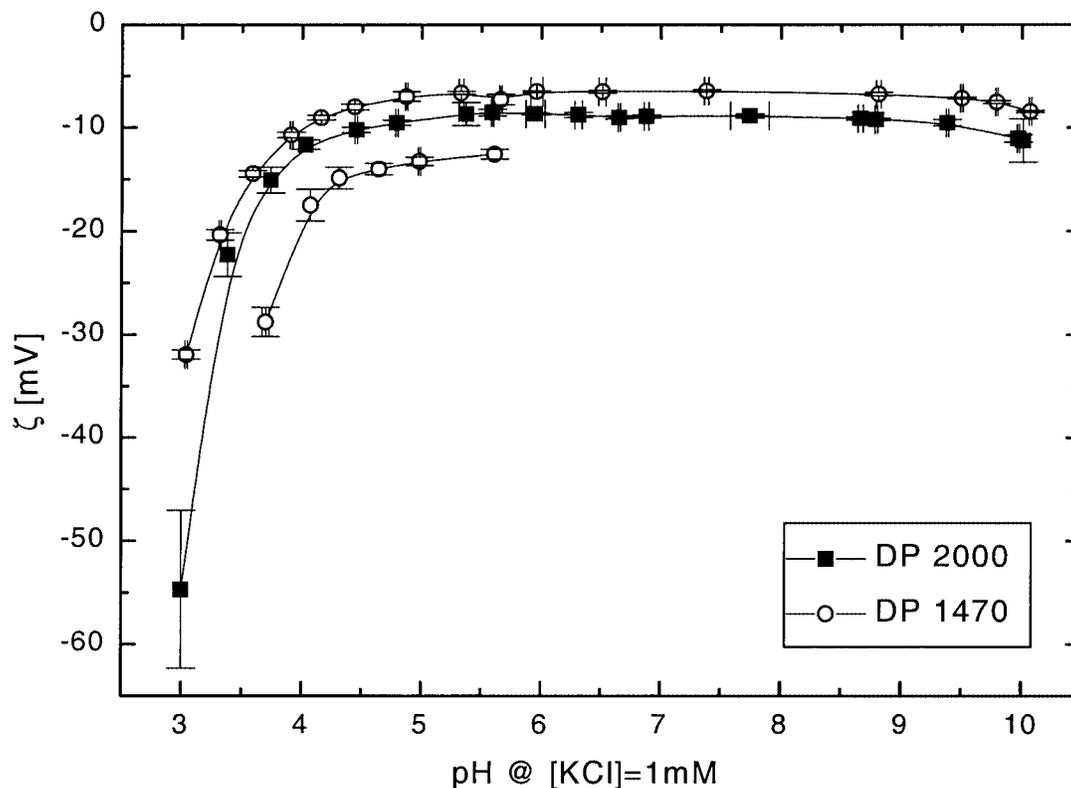


Fig. 11. ζ -Potential pH-dependence of untreated cellulose fibers (Buckeye Linters) with different degrees of polymerization (DP).

polymer surface dynamics (near-surface molecules have a higher mobility as compared to those in the material bulk), where reorientation of surface groups occur as function of the adjacent environment).

Exceptions to this observed behavior were green hemp fibers and the flax fibers obtained from the STEX-processes. In the case of the hemp fibers the

measured ζ -potential values remain constant (but 0 mV) over the whole pH-range ($3 < \text{pH} < 11$) due to the extremely hydrophilic character.

In contrast to previously published results (14, 45), even for 'pure' cellulose fibers (cellulose content between 88% and 96% (14)) a rapid increase of the negative ζ -potential (Fig. 11) was measured. In addition, the

Table 5. Results of the ζ -Potential pH-Dependence Measured in 1 mM KCl Supporting Electrolyte: ζ_{plateau} = ζ -Potential Plateau Value at $\text{pH} \geq 7$, $\text{pH}_{\zeta, \text{changes rapid}}$ Equals the Characteristic pH-Values Were Rapid Changes of the Measured ζ -Potential Occur in the Acidic Range.

Natural fiber	$\zeta_{\text{plateau}} (\text{pH} \geq 7)$ [mV]	$\text{pH}_{\zeta, \text{changes rapid}}$
GFA-green flax	-2.6	5.0
RFA-retted flax	-3.5 ± 2.4	4.3 ± 0.8
RFA-retted flax, purified	-5.0	5.4
RFA-retted flax, purified and industrial alkalinized	-6.1	4.8
RFA-retted flax, purified and alkalinized in 5% NaOH	-3.9	3.9
RFA-retted flax, purified and alkalinized in 10% NaOH	-10.3	4.6
DDA	-11.5	(i.e. $\text{p}_{\text{extrapolated}} = 1.9$)
GFB-green flax	-2.1	5.2
RFB-(dew)-retted	-3.3	6.3
Duralin	-8.2	(i.e. $\text{p}_{\text{extrapolated}} = 1.6 - 2.2$)
RFA-retted flax washed in toluene	-2.6	4.9
PP grafted (3% MAH)	-0.9	4.8
PP grafted (5% MAH)	-0.9	4.0
green hemp	0	—
cellulose DP1470	-8.8 (-5.9)	4.8
cellulose DP2000	-6.5	4.9

ζ -potential-pH dependence of the pure cellulose fibers shows that there is almost no difference in the surface properties of cellulose fibers depending on the degree of polymerization [A reason for the observed discrepancy might be that the fibers are coming from different sources, where separated differently from the plant and/or subjected to different treatments. As stated in the literature, there is an enormous amount of variability in natural fiber properties depending upon whether the fibers are taken from which part of the plants, the quality of plant and location etc. (25)]. The inhomogeneous character of the natural material is clearly predominant (Fig. 11) leading to different ζ_{plateau} -values. In spite of the inhomogeneous character of the natural fibers (compare with Fig. 9), the observed increase in the negative ζ -potential was reproducible for all investigated natural fibers (18, 19). The pH-value at which the rapid increase of the negative ζ -potential occurs, shifts for different fiber types (separation processes and applied surface treatments), and might be a measure for the accessibility as well as the amount of 'surface' groups, which can be protonated. If such a protonation process of acetal/ether-type linkages present on the fiber surfaces is possible, it should be a function of the temperature and therefore it was decided to measure the ζ -potential at low pH-values as a function of temperature. Cellulose fibers were chosen for this purpose. The 'normal' pH-dependence was measured starting from the pH 5.6 of

1 mM KCl-solution at 20°C down to pH 3.7, following by a continuous increase of the temperature up to 47°C.

From Fig. 12 it can be seen, that after an increase in temperature of only 4.5°C, the negative ζ -potential increases rapidly from -28 mV to -8 mV. A further increase on temperature results again in an increase of the negative ζ -potential. Measuring again the ζ -potential during the cooling process produces a hysteresis loop. The negative ζ -potential goes through a minimum value at 29°C and increases further. However, the initially measured high negative ζ -potential value will not be obtained again after coming back to 20°C even after measuring for a longer period of time. This indicates an irreversible character of this process.

Comparing the ζ -potential-pH-dependence measured for both green flax samples studied a slightly different function $\zeta = f(\text{pH})$ was measured for the second GFB-green flax sample (CERES B.V.), both fibers have a small negative ζ_{plateau} -value and both samples have a rapid increase of the negative ζ -potential in common. However, in the acidic range the ζ -potential goes through a minimum for the GFB fibers, but decrease further in case of GFA fibers. Such a behavior was also observed for different jute-fibers (18). Such differences between the green flax samples (GFA, separated using ultrasonic) supplied from different manufacturers are explainable by different surface compositions of natural fiber products.

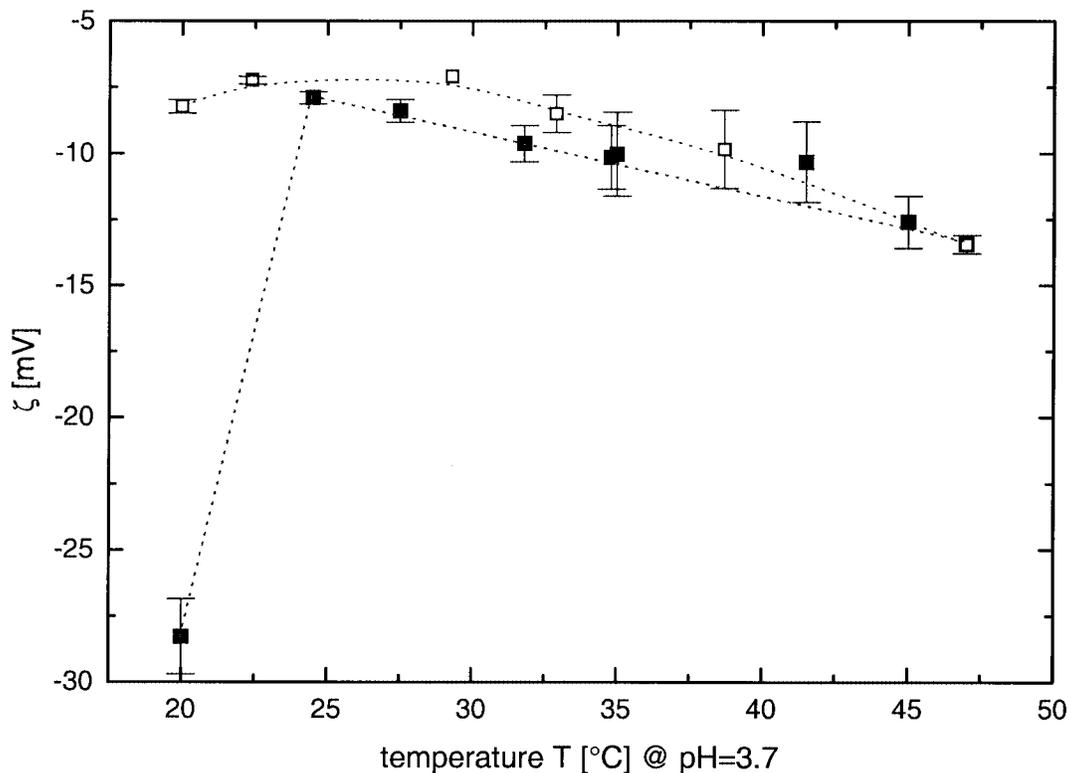


Fig. 12. ζ -Potential as function of temperature, measured at pH 3.7 in 1 mM KCl solution of cellulose fibers (Buckeye Linters DP1470).

For dew-retted RFB-flax fibers the same overall pH-dependent ζ -potential, slightly shifted to more negative ζ -potentials, was measured indicating a diminished hydrophilicity as compared to the GFB-green flax sample. However, the industrial separation process leading to Duralin (hemicellulose and lignin are depolymerized into lower molecular weight aldehyde- and phenolic functionalities, which combined by curing reaction into a water resistant resin) flax fibers changes the flax fiber surface composition, which becomes obvious in an altered ζ -potential curve. This $\zeta = f(\text{pH})$ curve (Fig. 13) corresponds to the usually expected pH-dependent ζ -potentials for solids, which contain acidic dissociable surface functional groups. The extrapolated i.e.p. is in the pH-range of 1.6 to 2.2. A very similar $\zeta = f(\text{pH})$ curve was measured for the DDA-flax (Fig. 10), these fibers were also obtained from STEX. The ζ_{plateau} -value is the same within the error and the extrapolated i.e.p. equals 1.9. These values are in good agreement with published values for purified cellulose fibers (38), indicating the presence of acidic surface functional groups. For these fibers, the higher ζ_{plateau} -value indicates the increased hydrophobicity of the fibers, which is in good agreement with the ζ -potential-time dependence and the water uptake studies (7).

Effect of Surface Modifications on Retted Flax Fibers on the pH-Depending ζ -Potential

Additionally to the different fiber separation processes, the influence of some exemplary performed fiber surface modifications were studied using the

retted RFA-flax sample (Figs. 14 and 15). The original RFA-retted flax has a ζ_{plateau} -value of around -3.5 mV. After an applied industrial purification process this negative ζ -potential value increases and it becomes even bigger after this purification process followed by (industrial) alkalization in approx. 3% NaOH (Fig. 14). Using higher NaOH concentrations (10%) for the alkalization process (as performed in our labs) will further increase the negative ζ_{plateau} -value. All these applied purification processes result to a certain degree in a removal of waxes from the natural fiber surfaces, therefore, the accessibility of acidic dissociable functional groups in the fiber surface increases and accordingly the ζ -potential. During the alkalization processes the wax-components will be saponified and, thereby removed from the fiber surface (14). It can again (14) be seen that the waxes 'sticking' on the fibers influence strongly the surface properties of cellulose-like materials. Since, as shown above, the raw-natural fibers are covered with noncellulose compounds (like waxes) it becomes necessary to treat 'original' flax fibers to remove all hydrophobic noncellulose components. Such a treatment increases the accessibility of surface groups (but not necessary the specific fiber surface), which can be used in further chemical modification steps to increase the compatibility of natural fibers to non-polar polymers. These further modification processes can be reactions with compatibilizing agents, like carboxylic anhydrides, isocyanates, vinylsulfone, chlorotriazine systems (41), organo silanes, and compounds that contain methylol groups or grafting of MAH-graft PP (4).

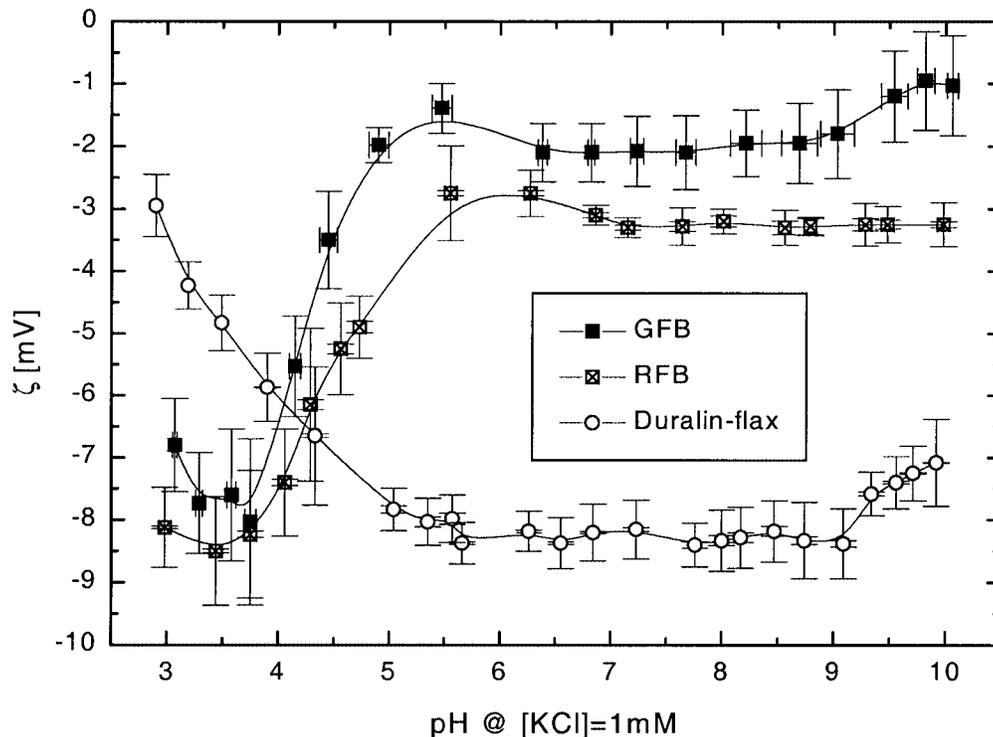


Fig. 13. ζ -Potential pH-dependence of unmodified GFB-green, RFB-dew-retted and modified Duralin-flax fibers.

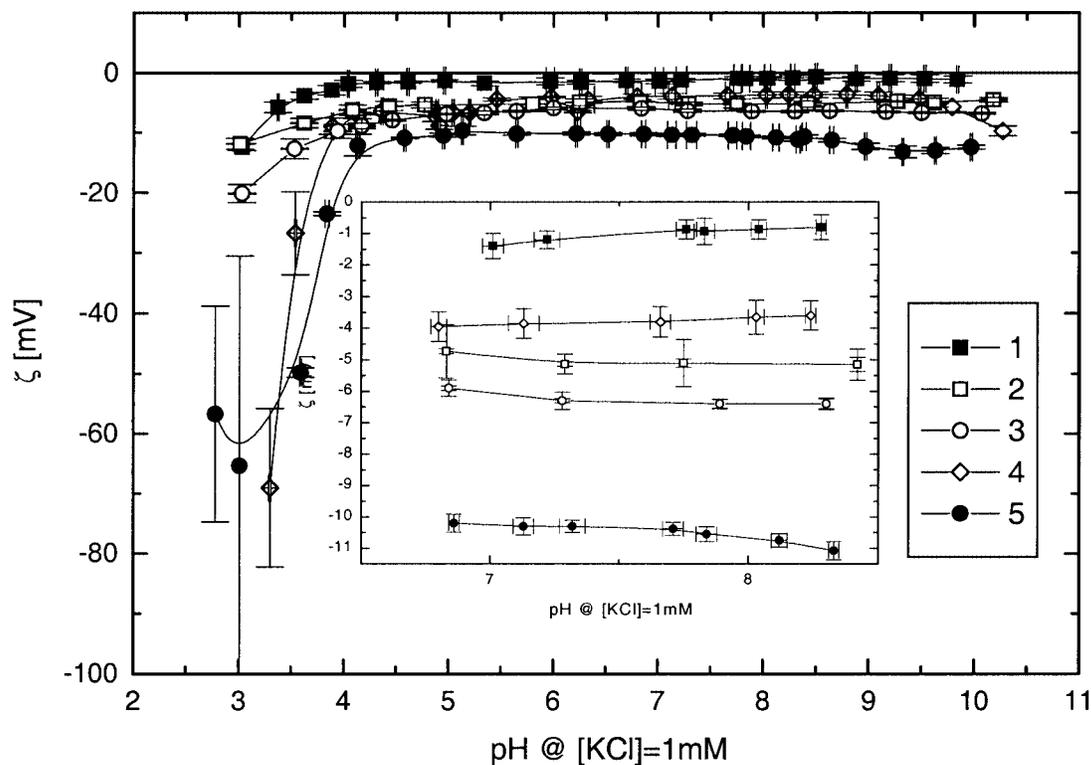


Fig. 14. ζ -Potential pH-dependence of untreated (1: pure retted flax (RFA)) and different modified flax fibers (2: industrial purified; 3: industrial purified followed by alkalization; 4: alkalized in 5% NaOH; 5: alkalized in 10% NaOH).

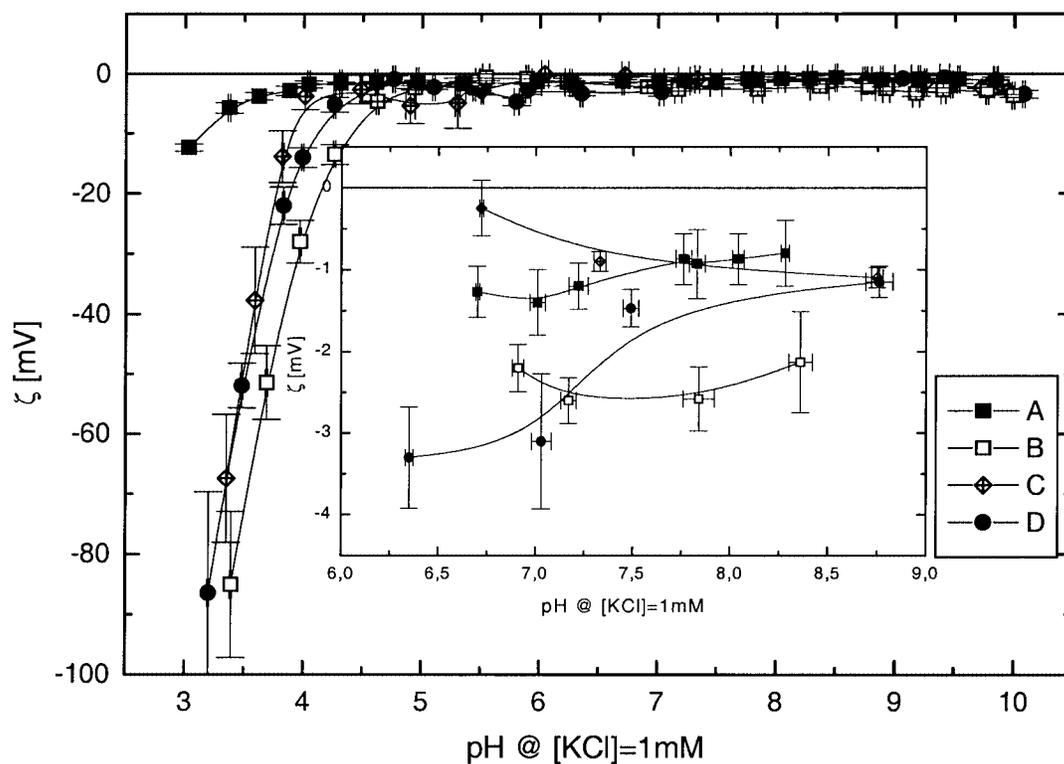


Fig. 15. ζ -Potential pH-dependence of untreated (A: pure retted flax (RFA)) and different modified flax fibers (B: washed in hot toluene; C: grafted with 3% MAH-graft-PP; D: grafted with 5% MAH-graft-PP).

The influence of grafting MAH-graft PP at the surface of retted flax on the surface chemistry of these fibers was also studied (Fig. 15). Hot toluene was used to extract the non-bonded amount of PP from the fibers. Therefore a 'blind-test' was necessary to be carried out by extracting retted flax in hot toluene. This process possibly leads to a total removal of the wax components from the fiber, which leads to very hydrophilic fibers and, therefore because of the competing water/ion adsorption results in the small negative ζ_{plateau} -value. Grafting of MAH-graft PP at the fiber surfaces, however, does not result in a significant difference in the ζ_{plateau} -values. And therefore, it can also be concluded that such grafting procedures does not lead to the desired increase in hydrophobicity of flax fiber surfaces, since such a modification will result in a patch-like PP-grafted fiber surface (which on the other hand can still improve the mechanical properties of a composite). Even if the ζ_{plateau} -values are unaffected by the grafting, the pH-value where the ζ -potential curve changes rapidly ($\text{pH}_{\zeta, \text{changes}}$) is clearly influenced due to the grafted PP. After washing the RFA-fibers ($\text{pH}_{\zeta, \text{changes}} \leq 4$) in hot toluene the $\text{pH}_{\zeta, \text{changes}}$ is shifted to a higher value ($\text{pH}_{\zeta, \text{changes}} \approx 4.8$), which is lowered after PP grafting to the value of the 'original' fiber. Again, if the protonation of surface functions is possible, such described behavior might then be due to the changes in the accessibility of these surface groups.

In correspondence with the ζ -potential time dependence, the functions $\zeta = f(\text{pH})$ reflect also the hydrophilic/hydrophobic character of these natural materials. The ζ_{plateau} -value should be correlated with the

hydrophilicity of the fiber surfaces, as it has been proved for several textile fibers including pure cotton (43). It can *roughly* be stated that the higher the water uptake of the natural fibers, the smaller is the plateau-value (at $\text{pH} \geq 7$) in the ζ -potential-pH dependence.

NMR Measurements

In order to prove whether such an assumed 'protonation process' of functional groups present in natural fiber surface could be possible and therefore a tentative explanation of the obtained increase of the negative ζ -potential at decreasing pH-values or if there is not at all such a possibility it was decided to perform some ^{15}N -CP/MAS NMR experiments under similar conditions. Figure 16 shows the ^{15}N -NMR spectra of the two purified RFA-flax samples, the 'simply' dried sample and the sample, which was first stored in HCl-solution. For the sample **a** the only signal at 267 ppm arises from bulk frozen collidine. No traces of hydrogen bonded collidine molecules with the flax surface or residual water could be detected. In contrast, for the sample **b** in addition to the same signal at 267 ppm there is another well pronounced signal at 161 ppm corresponding to protonated collidine molecules. And again, no collidine molecules involved in hydrogen bonding with water could be detected.

However, there are still two possible explanations for such a behavior: i) storing the flax fibers in aqueous HCl solution creates some stable acidic centers on the flax fiber surfaces. Although concentration of these centers must be rather small they are stronger bonded to the surface than water is or ii) there are

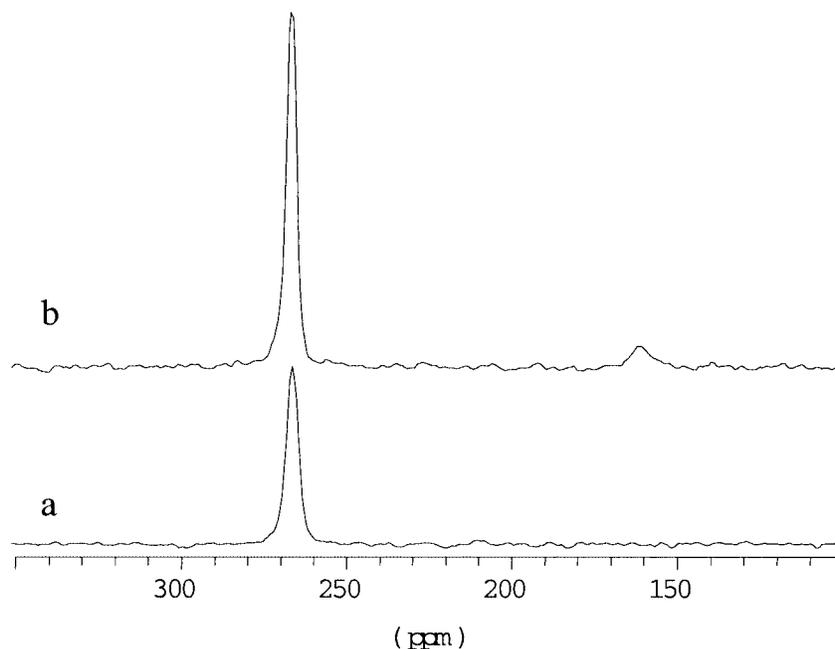


Fig. 16. ^{15}N -CP/MAS NMR-spectra for industrial purified RFA-flax fibers; **a** for 'simply' vacuum dried flax and **b** for flax fibers, which were first stored in 10% aqueous HCl and then dried.

some traces of residual HCl/water mixture 'trapped' within the flax fibers, which somehow could *not* be removed after drying the fibers in vacuum. The interaction of either protonated surface groups or 'trapped' HCl-molecules with the organic base collidine causes the appearance of collidinium cation. The counter ion is always the Cl⁻ anion. However, since no traces of trapped water could be detected after the 'excessive' drying in vacuum it seems quite improbable to have simple somehow 'trapped' HCl molecules within or at the fibers, if they are not chemisorbed (for instance bonded in stable protonated groups) at suitable 'active' surface sites.

CONCLUSIONS

From the above results it can be concluded that the different flax-fiber separation processes lead to fibers, which display different surface characteristics as proved by SEM, BET-adsorption and ζ -potential measurements. As shown by the SEM investigations, the applied fiber separation processes affect the fiber surface morphology, which also influences the specific fiber surface area.

ζ -Potential measurements reflect clearly differences in the degree of hydrophilicity of the natural fibers. The green natural fibers (flax as well as hemp) are the most hydrophilic ones, whereas a retting process leads to fibers, which are less hydrophilic, because they contain a relatively high amount of waxes on their surfaces. Compared to the other original fibers, the DDA-flax fibers together with upgraded Duralin-fibers (both obtained from STEX-processes) display obviously the most 'hydrophobic' surfaces. However, one has to bear in mind, that water uptake and therefore swelling reduce the ζ -potential, whereas a greater accessibility of dissociated surface functional groups increases the surface charge and thus the ζ -potential. On the other hand, the ions dissolved in the measuring electrolyte (K⁺, Cl⁻ and H⁺ and OH⁻) will also affect the ζ -potential by adsorbing on the fiber surfaces, however this process takes places in competition to water adsorption at the 'hydrophilic' sites, namely the surface functional groups. Within the alkaline pH-region all of the acidic surface groups are dissociated or the maximum amount of OH⁻ or other anions are adsorbed on the fiber surface. The absorption of water becomes less favorable the more hydrophobic a solid surface becomes (46). Since all natural fibers are very hydrophilic materials, the ζ -potential therefore should be influenced strongly by the different water absorption behavior and the accessibility of dissociable surface functional groups. Comparing the DDA-flax fibers with flax fibers alkalinized in 10% NaOH (they display nearly the same ζ_{plateau} -values) one should expect that the degree of hydrophobicity/hydrophilicity is similar. On the other hand, in the case of alkalinized fibers it was not possible to measure a time depending decrease of the negative ζ -potential. This indicates a very fast swelling process, which cannot be followed using streaming potential measurements.

For some flax samples (fibers from CERES B.V.) the data obtained using time-dependent ζ -potential measurements ($(\zeta_0 - \zeta_{\infty})/\zeta_0$) were compared with conventional water absorption measurements (average maximum moisture content (\overline{MC})) and indeed, the results obtained from the two different methods are in good agreement (Fig. 8). This confirms the high potential of ζ -potential measurements to estimate fast the swelling behavior of investigated solids in water.

Performed CP-MAS NMR measurements on one exemplarily chosen flax fiber sample (just dried and dried after storage in aqueous HCl) showed that the speculative explanation for the observed increase of the negative ζ -potentials in the low pH-region *might* be due to a protonation of suitable surface functional groups. For the fibers, which were stored in HCl and then dried, an additional NMR-signal (absent for just dried fibers) corresponding to a protonated collidine species could be observed.

OUTLOOK

Finally, considering the above results it can be stated that the future prospects to manufacture "high quality" natural fiber composites for lower mechanical loads, are very promising when using a suitable procedure, consisting of a well chosen fiber separation process, subsequent fiber treatment and coupling agents such as MAH-grafted PP.

(Natural) fiber bundle pull-out tests allow to characterize the interfacial adhesion between fibers and matrix, it is possible to determine the interfacial shear strength τ_{IFSS} as measure of the fiber/matrix adhesion. Basically, two types of interface exist in natural fiber reinforced composites and should be considered: one between the fiber bundle and the matrix and the other between the cells of the natural fibers. A higher binding strength at the former interface than the latter is desirable, because of loss of coherency among the cells, probably leading to interfibrillar failure and uncoiling of the helical fibrils. The composites would be remarkably strengthened and toughened in this way (39). A lot of fiber bundle pull-out tests were performed between several flax fibers and (2%-MAH-grafted (Novolen TPAR 504) and pure (Novolen PPN 1060 F) PP-matrices (47). The results clearly indicated that the interfacial adhesion between flax fibers and PP (RFA/PP: $\tau_{\text{IFSS}} \approx 10$ MPa) can be improved by using an appropriate coupling agent (RFA/2% MAH-graft PP/PP: $\tau_{\text{IFSS}} \approx 13.5$ MPa) and a further increase in adhesion can be achieved when treated flax fibers are used as reinforcement (industrial purified and alkalinized RFA/2% MAH-graft PP/PP: $\tau_{\text{IFSS}} \approx 15$ MPa). The increased adhesion can be explained by the following facts; i) using the coupling agent (2% MAH-graft PP) might lead to covalent bond formation between the 'polar' fiber surface functions and the 'reactive' components in the matrix (9, 48) and ii) the applied fiber treatments (purification and alkalization) will result in a better fiber separation and therefore a higher specific surface but also to an improved accessibility of the

surface groups by removal of waxes. The enlarged surface area accompanied by an enhanced surface polarity (compare ζ -potentials) results in improved adhesion by a higher probability of bond formation between the coupling agent and the fiber itself. The improved adhesion between the 'original' and treated RFA-fibers correlates with the increase in the negative ζ -potentials (in the plateau values of $\zeta = f(t)$ and $\zeta = f(\text{pH})$).

ACKNOWLEDGMENTS

We would like to thank Enrico Dietzsch (TU-Chemnitz, Institut für Technische Chemie (ITC)) for the BET-adsorption measurements and many helpful discussions. We are also grateful to David Richter (ITC of the TUB) for fruitful discussions. Financial support of the Deutsche Forschungsgemeinschaft (DFG), the Berliner Verband für Polymerforschung e.V. (BVP) and the Fonds der Chemischen Industrie is acknowledged. A.S. would also like to thank for a Marie Curie Fellowship (TMR) and Dr. Caroline Baillie (Imperial College of Science, London) for many helpful discussions.

We would also like to acknowledge Dr. G. Pott (CERES B.V., Wageningen, The Netherlands) for supplying us with some of the flax fibers used in this project.

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