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Electrokinetic Investigations of Oriented Cellulose Polymers

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Summary: Electrokinetic investigations of different cellulosic fibres were reviewed with special emphasis on polymer composite materials and textile applications of cellulose fibres. The possibilities in the interpretation of zeta-potential data regarding chemical and physical modification, specific adsorption, swelling and changes in hydrophobicity/hydrophilicity of cellulose polymers are discussed. Using recent data from literature, advantages and limitations of electrokinetic measurements of oriented polymers are described, finding that the zeta-potential is a valuable parameter in polymer surface characterisation.

Keywords: cellulose; composite; fibers; textile; zeta potential

Introduction

Oriented cellulose polymer fibres have been used for the production of textiles, ropes, weaved products and other articles of daily use since the early days of human civilisation. Besides their traditional use, natural cellulosic fibres, such as sisal, flax, jute and coir, have become of substantial interest in the manufacturing of fibre reinforced polymer composites.[1–6] These composites are attractive due to their low cost, availability, low density and biodegradability of the cellulosic components.[7]

Regarding more classical applications, natural cellulose fibres, like cotton, have become the most popular textile fibres, due to trends in the last years to wear ecologically friendly materials.[8] In addition, the market of man-made cellulosic fibres was established as an important factor in the textile industry since the development of the Viscose process in the late 19th century.

In all cases, like polymer composite development and textile applications, the raw cellulosic material has to be processed in many ways to yield a usable primary product. Natural fibres usually contain not only cellulose, but also hemicelluloses, lignin, waxes, fats and inorganic substances, which hinder the access to, or alter the properties of the cellulose polymer surface. This partially hydrophobic and hydrophilic surface yet constitutes the main starting point for modification and finishing processes. For this reason, the non-cellulosic residues have to be removed by washing, alkali treatment and bleaching, dewaxing, demineralisation or solvent extraction.

Once the cellulose surface is accessible, its hydrophilicity can be modified by graft polymerisation techniques, covalent bonding of fatty acids, silanes and other functional molecules.[9–13] These modifications lead to new properties of the cellulosic material, like better interaction with non-polar, hydrophobic polymer matrices or the introduction of new functional groups, which can then be used for further reactions. An alternative way to modify the cellulose fibre surface is non-covalent

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adsorption of molecules like polyelectrolytes, proteins and soluble polysaccharides.[14–16]

In textile applications, the cleaned and modified cellulosic fibres are then further processed in several dyeing and finishing steps, to comprise the look and functionality of modern clothing, as well as the requirements of highly specialised technical textiles. In technical applications, other finishing processes as the protection against wear using different coatings, creation of surface conductivity and compounding procedures have to meet the necessary requirements. Specific fields are hygienic and medical applications where antimicrobial properties, storage and release of drugs and pH regulating substances are required.

All these processing steps, starting from cleaning, modification and functionalisation to composite forming and dyeing procedures, need a tool to monitor and characterise the changes at the cellulose fibre surface. Several methods are used to characterise the polymer surface, from contact angle measurement to electron microscopy and spectroscopic applications. An important and very sensitive parameter characterising the solid/liquid interface of fibrous polymers is the zeta-potential (ζ), mainly facilitated via streaming potential measurements. This electrokinetic method can be used to characterise polymer surfaces, not only cellulosic fibres but also other natural and synthetic fibre forming polymers, as well as non-oriented polymer sheets and foils.[17]

The ζ-potential is the term describing the electrokinetic properties at that position of the solid/liquid interface which is accessible for interactions. This interface is described by chemical and electrochemical potential values different from those of the bulk phases since the molecules in the boundary are subject to interaction forces from both adjacent phases. The resulting net charge of the polymer-aqueous solution interfaces is generally attributed to the dissociation of functional surface groups on one hand, and on the other hand the preferential adsorption of potential determining ions from solution. These phenomena result in a surface charge of the polymer, which is balanced by counter-ions in the solution. The description of the charge distribution and the corresponding potential course in relation to the distance of the polymer surface is the objective of electrochemical double layer models. Figure 1 shows the double layer model

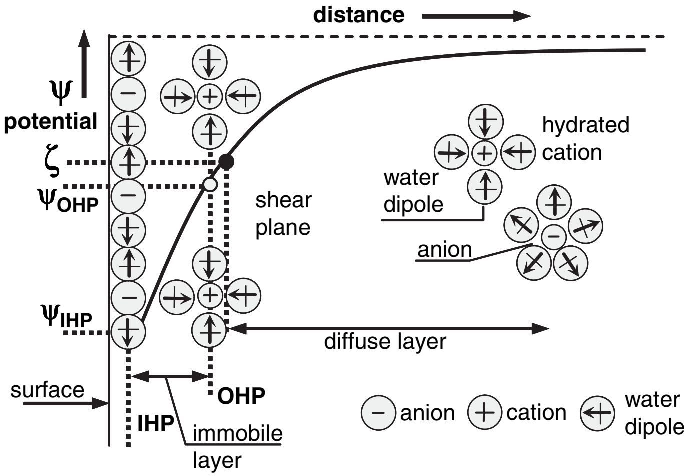

Figure 1.

Gouy-Chapman-Stern-Grahame (GCSG) model of the electrochemical double layer, adapted from[18]; IHP: inner Helmholtz plane; OHP: outer Helmholtz plane.

according to the Gouy-Chapman-Stern-Grahame model (GCSG) for negatively charged surfaces. In this model, two layers of fixed ions at the solid/liquid interface are discerned. The inner layer comprises partly dehydrated anions; the plane of the centres of these ions is called the inner Helmholtz plane (IHP). This layer is followed by a plane of hydrated cations, the so-called outer Helmholtz plane (OHP). The potential course between these two layers is assumed as linear. These two planes are considered as immobile. Adjacent to this plane, a diffuse layer of counter-ions and co-ions balances the net surface charge with decreasing concentration at increasing distance from the polymer surface. These ions are mobile and subjected to electrostatic forces from the solid surface as well as thermal motion. The potential course in this diffuse layer follows a Boltzmann distribution.

The potential at the immobile planes of the interface can not be assessed experimentally. Therefore, use is made of the experimental accessible ζ-potential. When the solid is moved in respect to the surrounding liquid phase, the ions in the mobile layer are sheared off and move along the polymer surface. This causes the establishment of a streaming current and an oppositely directed streaming potential. Both parameters can be measured experimentally and the ζ-potential (the potential at the distance of the shear plane from the polymer surface) can be calculated according to Smulochowski.[19] The position of the shear plane can be considered as identical with the outer Helmholtz plane, or at least very close to that layer, as long as the applied shear force is strong enough to remove the diffuse layer completely. The exact position of the shear plane is not known.

The characterisation of the solid surface regarding acidic and basic functional groups is done via ζ-potential measurements at different pH-values of the surrounding electrolyte solution. Figure 2 shows the theoretical shape of the ζ-potential course with varying pH for acidic and basic surface groups, as well as for non-polar, non-dissociating polymer surfaces.

Using extended theories on the double layer structure, pK values for dissociable surface groups and adsorption free energies of adsorbing ions from solution can be calculated.[20] Recording such pH-dependent ζ-potential curves, the amount and type of dissociable surface groups and adsorbing ions can be characterised.

The ζ-potential is not only sensitive to changes in the amount and type of dissociated or adsorbed charged species; it can also be used for characterising the hydrophilicity/hydrophobicity and structural changes of fibre surfaces. Hydrophilic polymers like cellulose show a high water uptake and therefore significant swelling. The swelling can be monitored via time dependent ζ-potential measurements. Cellulose-water interaction can best be understood as a competition of hydrogen bond formation between hydroxyl groups of the polymer and those of the polymer and a water molecule or water cluster.[21] The water penetrates into the fibre and breaks down hydrogen bonds between cellulose molecules and loosens up the structures of the polymer. In the case of a swelling cellulosic polymer, ζ-potential decreases with time, because of the shift of the shear plane towards the solution away from the fibre surface (Figure 3).

Besides the characterisation of adsorbed ions, another important application of ζ-potential measurements at cellulose fibres is the monitoring of adsorption processes of functional molecules, such as surfactants, dyes, polyelectrolytes, proteins and polysaccharides. Simultaneous measurement of adsorption isotherms and ζ-potential data can reveal structural features of the adsorbed layer.[23] In this context, the interpretation of ζ-potential data is often difficult. Exact information can only be provided when the results are supplemented by other physico-chemical investigations.[24]

Nevertheless, ζ-potential measurements of oriented cellulose provide valuable

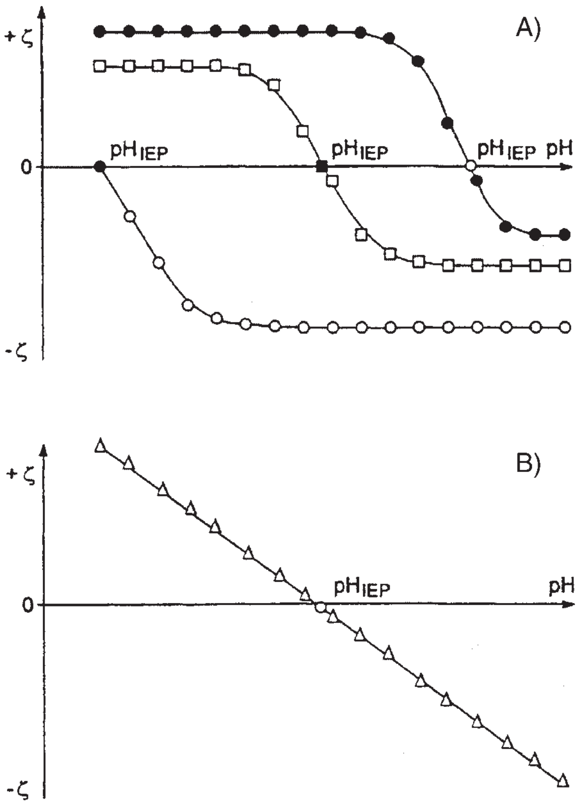

Figure 2.

Dependence of the ζ-potential of polymer surfaces on the pH-value: A) “dissociable acidic and basic surface groups, only basic groups, - only acidic groups; B) 8 non-polar surface without dissociable groups. IEP: isoelectric point.[18]

information on the surface properties of the fibres and the interaction behaviour of this polysaccharide with other polymers and functional molecules.

In the next sections, several of the above mentioned aspects of zeta potential measurements of fibrous cellulose polymers are discussed with emphasis on composite materials and textile finishing processes.

Fibres for Reinforced Composites

Extensive, recent research work is done on the development of natural fibre reinforced polymer composites using different fibres, matrices and techniques,[1–5,25,26] due to the low cost and good availability of the cellulose components. Also man-made cellulosic fibres, like Viscose and Lyocell, have been investigated as composite materials.[27,28] In spite of the sensitivity of the method, only view authors have made use of ζ-potential measurements to characterise the raw and modified fibre surfaces.

Bismarck and co-workers investigated modified jute fibres using the streaming potential technique.[9] They monitored the swelling behaviour of raw, dewaxed, methylmethacrylate (MMA) and acrylonitrile (AN) grafted fibres, calculating the water uptake at 100% relative humidity following the method of Kanamaru.[29] Dewaxed fibres adsorbed the highest amount of water as expected, followed by alkali treated and raw jute fibres. The MMA grafted fibres showed the lowest water uptake, decreasing with the amount

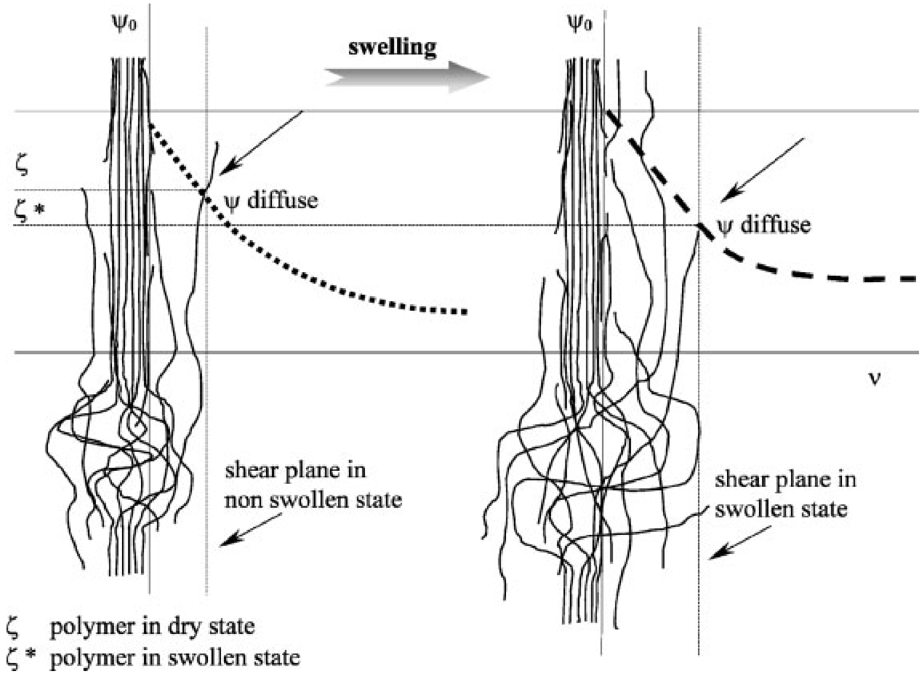

Figure 3.
Reduction in ζ-potential caused by swelling of the fibres.[22]

of grafted polymer. AN grafted cellulose showed almost no time dependence of the ζ-potential. Figure 4 shows the pH-dependent ζ-potential measurement of untreated, dewaxed and MMA grafted jute fibres.[9] The untreated and dewaxed, swollen fibres exhibit all a very small negative ζ-potential over a wide pH-range. Only the fibres with a high fraction of grafted polymer show a higher negative ζ-potential, due to the decreased hydrophilicity of the fibres. As to bee seen in Figure 4, a negative peak of the ζ-potential is found at a pH-value around 3. Even the ungrafted fibre shows potentials below 50mV. This is attributed to the protonation of ether linkages in the cellulose or lignin residues, followed by preferential chloride ion adsorption. This proposed mechanism is still questionable. There is no evidence that ether linkage protonation can occur at this pH-values. Preferential adsorption of chloride ions has not been observed for cationic surfaces in this pH-range. Furthermore the ζ-potential is decreasing again if the pH-value is further shifted in the acidic direction. In general, negative ζ-potentials of more than 200 mV for polymer surfaces are extremely unusual and might have to be doubted.

The same workgroup also characterised the surface properties of modified sisal and coir fibres for the use in reinforced polymer composites.[30] Time dependent ζ-potential measurements reveal that the water uptake of the differently treated fibres increase compared to the native fibre. This is attributed to the deterioration of the natural wax layer on the fibre surface, which is responsible for the low swelling tendency of the native fibre.[29] Figure 5 shows the pH-dependent ζ-potential measurements of native and treated sisal fibres.

The sisal fibres show, like jute fibres, very small negative ζ-potentials over a wide pH-range due to their hydrophilic nature and swelling. Again, a dramatic increase of the negative potential at pH 3 is observed. In addition, alkali treated samples show a charge reversal in the pH range from 6.5 to

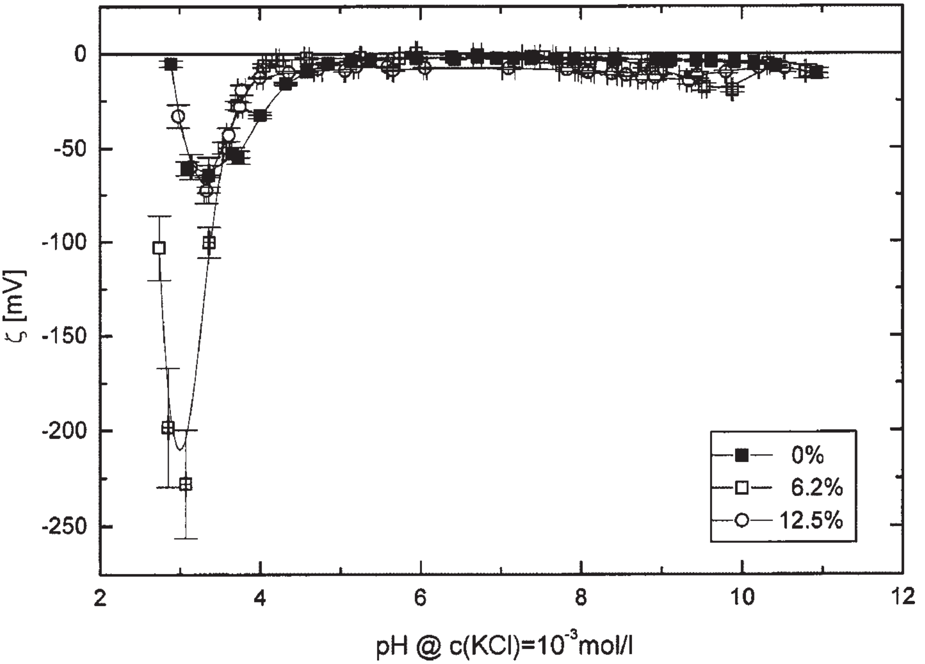

Figure 4.
pH dependence of the ζ-potential for untreated, dewaxed and MMA grafted jute fibres as a function of the percentage of the grafted polymer.[9]

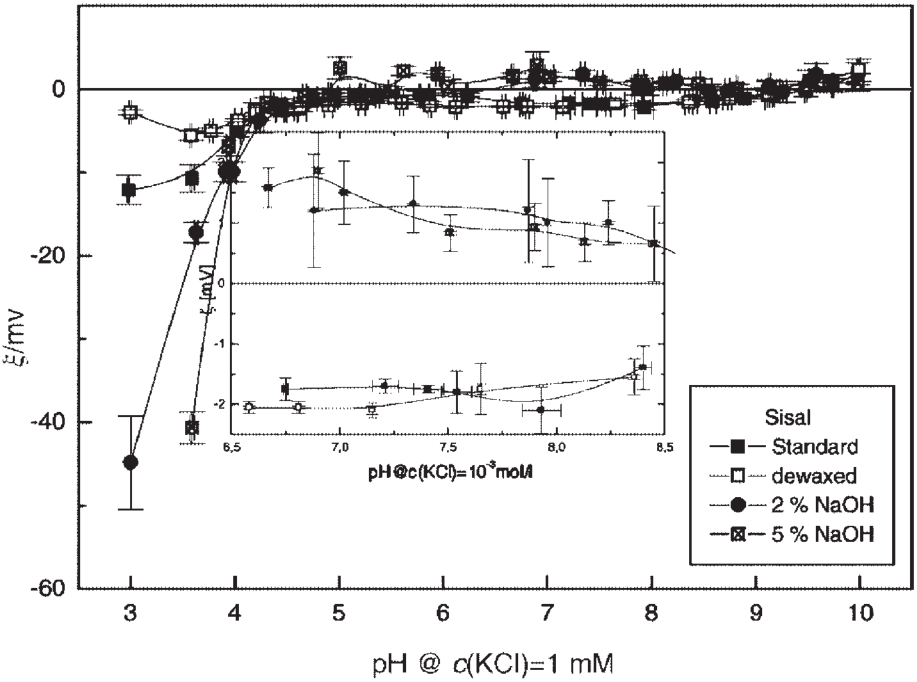

Figure 5.
ζ-potential pH-dependence of unmodified and modified sisal fibres.[30]

8.5. This is unusual, because the alkali treatment should give better access to the dissociable surface groups, in cellulose mainly carboxylic groups, which increase the negative surface potential. In this case, the charge reversal is attributed to strongly adsorbed alkali metal ions. In contrast, treated coir fibres do not show these effects and exhibit an isoelectric point near pH 3.[30]

Bismarck and co-workers also published an extensive report on the surface characterisation of flax, hemp and cellulose fibres with special emphasis on the water uptake behaviour.[31] Again, pH-dependent ζ-potential measurements show a significant increase of the negative potential around pH 3 for all fibres except the industrially modified Duralin flax. This type of fibre exhibits a stable plateau value over a wide pH-range and a decrease of the negative potential at low pH-values due to the protonation of carboxylic groups. An isoelectric point between pH 1.6 and pH 2.2 can be extrapolated.[31]

Stamboulis and co-workers reported similar results on flax fibres[32], showing that Green fibres absorb more water than Duralin flax fibres. The results are in good agreement to standard moisture absorption tests. pH-dependent ζ-potential measurements show that the Duralin fibres are less hydrophilic compared to the Green and dew-retted fibres.

Pothan and co-workers studied the influence of chemical treatments on the electrokinetic properties of banana leaf fibres.[33] The fibres were modified by alkali treatment, acetylation, coupling of long chain alkyl groups and functionalised silanes. Figure 6 shows the effect of the treatments on the pH-dependent ζ-potential values.

The untreated fibre shows the typical pH-dependent ζ-potential course for a single site dissociation of acidic surface

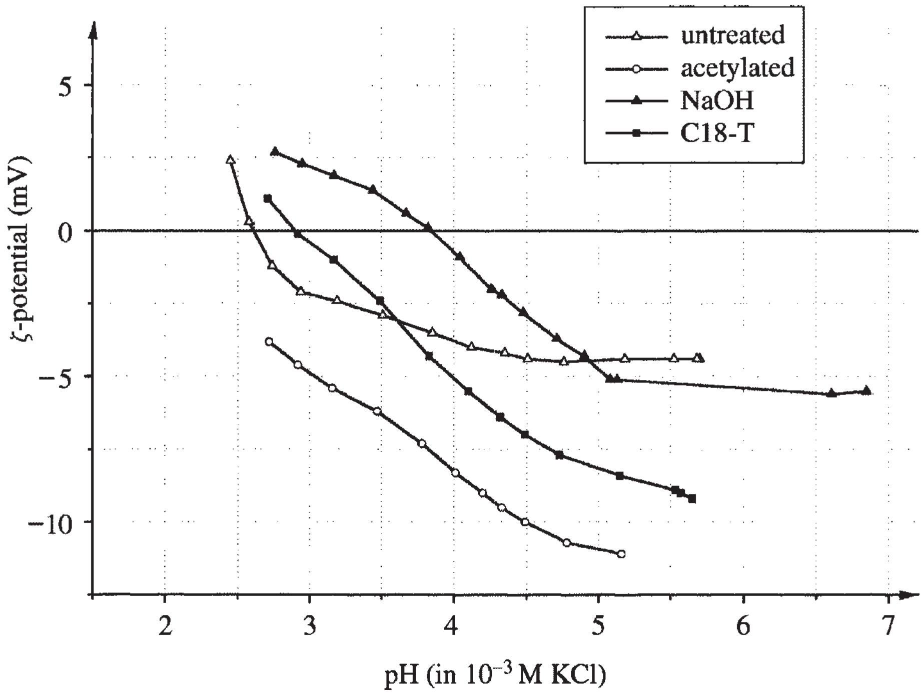

Figure 6.
pH dependence of the ζ-potential on untreated, alkali treated, acetylated and C18-T-treated banana leaf fibres.[33]

groups. Alkali treated fibres exhibit a substantial swelling tendency resulting in a small ζ-potential in the plateau region. Swelling and the dramatically shifted isoelectric point indicate strong adsorption of hydrated alkali cations, even charge reversal is possible due to a predominant proton adsorption at low pH-values.[33] The shift in the isoelectric point indicates a change in the ratio of accessible anionic and cationic surface groups towards a reduction of acidic functions. In this case, the acidic functions might not be reduced, but the adsorption of the alkali ions seems to be the reason for the shift in the isoelectric point (IEP). The results of the ζ-potential measurements are consistent with solvatochromic measurements on dyed fibres.[33] The fibres modified with long alkyl chains (C18) show an increased negative ζ-potential over a wide pH-range, reflecting the increased hydrophobicity and apolarity of the modified fibre surface. The IEP does not change significantly compared to the untreated fibre.

Acetylation gives rise to the formation of ester bonds at the cellulose hydroxyl groups, as confirmed by the occurrence of ester peaks in the IR spectrum of the modified fibre.[33] This modification leads to a significant increase of the negative ζ-potential and shift of the IEP, indicating a more acidic surface. Besides the C18 modification and acetylation, the fibres were treated with different silanes. Most silanes shift the IEP towards the neutral region, indicating less acidic surfaces due to the partial blocking of fibre carboxyl and hydroxyl groups. The effect is significantly increased with silanes containing free amino-functions, which can be protonated at acidic pH conditions. The results of the ζ-potential measurements were consistent with solvatochromic investigations of the silane modified fibres conducted earlier.[34]

Bellmann and co-workers investigated swelling and dewaxing processes of natural cellulose fibres.[35] All natural fibres containing significant amounts of hemicelluloses and exhibit low crystallinity, show a very high water uptake and therefore extended swelling behaviour. This results in very small negative ζ-potentials of the fibre surface (Figure 7). Cotton linters, with

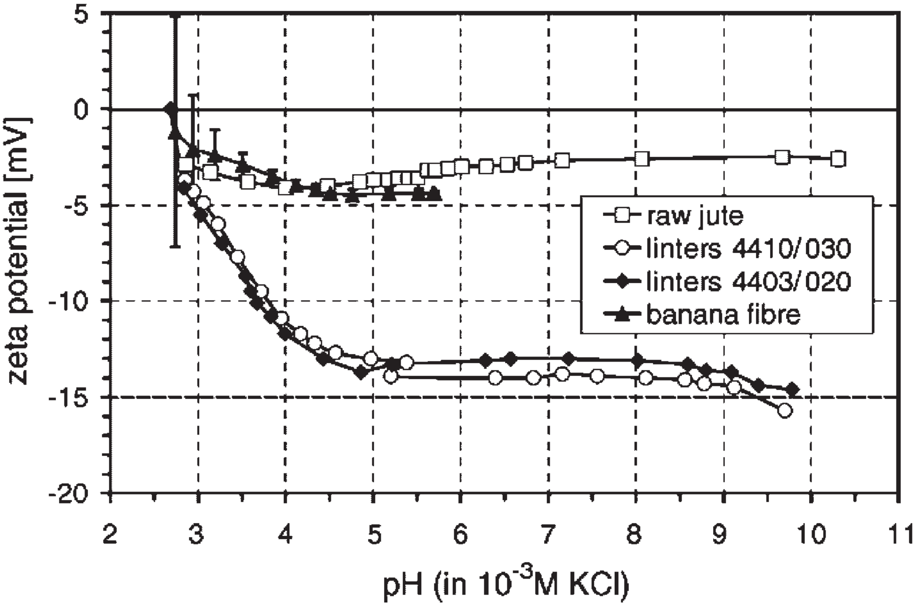

Figure 7.
pH-dependence of the ζ-potential for various natural cellulose-based fibres.[35]

higher cellulose content and higher degree of crystallinity, show reduced swelling and a higher negative ζ-potential. The IEP of all these fibres is very similar, due to the same chemical structure of cellulose based materials.[34] Time dependent ζ-potential measurements of cotton and viscose fibres show that the water uptake, and hence swelling, of the man-made fibres is very fast and could not be monitored with the method used. The cotton fibre needs at least 60 minutes to reach a stable ζ-potential plateau value due to swelling. This is consistent with water vapour adsorption measurements conducted with these two types of cellulosic fibres.[35]

The raw natural cellulose fibres were dewaxed and purified using solvent extraction. Monitoring of the cleaning and dewaxing procedures of the fibres via ζ-potential measurements is difficult, as a result of the high water uptake and swelling. The measured differences between the treated and untreated fibres become small, rendering only little space for interpretation. Nevertheless, trends can be deducted from the measurement results.

Cellulose Fibres in Textile Applications

The most frequently used natural cellulose polymer for textile and related applications, like cosmetic pads, is cotton fibre. Stana-Kleinschek and Ribitsch have published an extensive work on the electrokinetic properties of cotton, influenced by bleaching, alkali and enzymatic treatments, adsorption of fluorescent whitening agents and other substances.[8,36–40] ζ-potential measurements are used in combination with different other physico-chemical methods to elucidate the sorption behaviour and relate these results to structural properties of the fibres.

Cotton was dyed with different concentrations of a fluorescent whitening agent (FWA) and pH-dependent ζ-potential curves were recorded.[36] Up to a concentration of 0.8-1.0% FWA, the ζ-potential becomes more negative due to sulfonic acid functional groups of the FWA. Above this concentration, the potential is decreasing again, indicating a change in the adsorption mechanism. Calorimetric and fluorescence measurements strongly support the assumption that, beginning at this concentration, the adsorption of a second FWA layer on the fibre surface occurs.

pH-dependent ζ-potential measurement, water penetration and surfactant adsorption were used to characterise cotton fibres during textile processing steps.[8] The alkali treated fibres exhibit higher negative potentials than the untreated cotton. This is attributed to an increase of accessible surface due to the removal of non-cellulosic compounds. Swelling is shifting the shear plane towards the solution and therefore reduces the measured streaming potential. The IEP remains constant by treating the fibres with 2% NaOH, indicating no changes in the amount of dissociated surface groups.

Enzymatic treatments of cotton fibres result in similar changes in the pH-dependent ζ-potential course as the classical alkali treatments and solvent extraction. Lipase should remove most of the fats and waxes from the surface, leading to a higher negative ζ-potential of the fibre. Solvent extracted fibres show almost the same ζ-potentials, indicating that lipase treatment is able to remove nearly all of the fatty components from the fibre surface.[37]

Mercerisation of cotton fibres using 24% NaOH solution results in a less negative ζ-potential compared with raw cotton.[40] The amount of dissociable groups remains unchanged but the accessible surface is vastly increased due to the strong inter- and intra-fibrillar swelling of the fibre. Oxidative bleaching of the fibre leads to the formation of new functional groups at the surface, like carboxylic and aldehyde functions, indicated by the shift of the IEP towards lower pH-values. Calculated pK values show the same trend.[40]

Figure 8 shows the pH-dependent ζ-potential of differentially cleaned cotton fibres. In contrast to mercerisation, purifi-

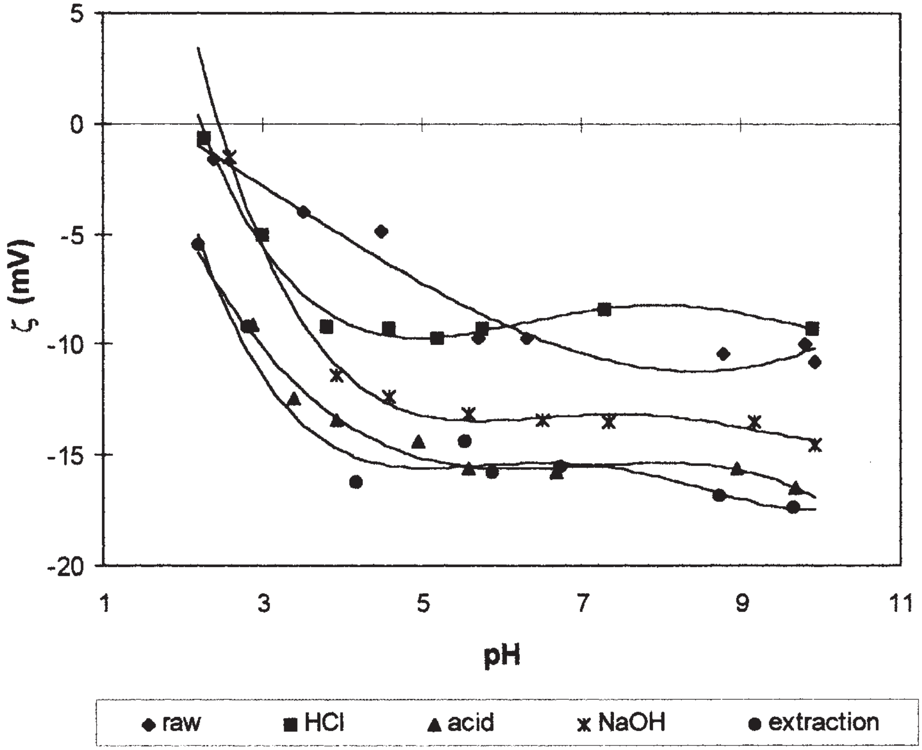

Figure 8.
ζ-potential of differently cleaned and purified cotton fibres as a function of pH; electrolyte solution 10^{-3} M KCl.[39]

cation with 2% NaOH solution leads to an increased negative potential of the cotton fibre. This treatment removes nearly all of the non-cellulosic compounds, but only about 50% of the waxes and fatty components. Alkali treatment causes swelling of the fibre surface, thus reducing the ζ-potential of the fibre. In this case, due to the removal of the waxes, the active size of the surface and the accessibility of functional surface groups are increased, resulting in a more negative net ζ-potential.[39] Extraction with petrol ether removes the waxes entirely, resulting in the most negative ζ-potential of the cotton fibre, due to the increased accessibility to the functional groups of the cellulose material. A very similar result can be obtained by acid-demineralisation using complex forming agents (i.e. poly phosphonic acid). The cations on the fibre surface are complexed and dissolved by this treatment.[39] Solvent extraction leads to a more negative ζ-potential. This can be explained by the total removal of waxes and fatty components by this treatment. The accessibility of the functional surface groups is very high, resulting in a more negative ζ-potential. Out of these measurements, it can be concluded that the waxes present at the fibre surface are the main influencing factor on the ζ-potential of the cotton fibre surface.

Conditioning the fibre with HCl leads to a completely different situation. The plateau value of the ζ-potential is reduced below the untreated cotton. This observation is attributed to the formation of hydrocellulose during the acid treatment at pH 2.5.[39]

Pusic and co-workers investigated the electrokinetic behaviour of processed cotton fibres and threads. They observed an increase of the negative ζ-potential after treatment in mildly alkaline scouring baths. Oxidative bleaching increases the electronegativity of the fibres.[41] This is in agreement with the findings of Stana and Ribitsch. However, for slack mercerised cotton, more negative ζ-potential values are reported compared with raw cotton. This is attributed to the better accessibility and increased specific surface of the fibre; effects of swelling seem to be less pronounced.

Stana and Ribitsch published several reports on the electrokinetic properties and sorption behaviour of man-made cellulose fibres.[22,42] These fibres are in general more hydrophilic compared with cotton. Figure 9 shows the pH-dependent ζ-potential courses for Viscose, Modal and Lyocell fibres.

The crystal structure of the Lyocell fibre differs from conventionally produced Modal and Viscose. The crystallinity index increases from Viscose (0.25) to Modal (0.37) and is highest for Lyocell (0.44), the crystallite diameter is large for Viscose and small for Lyocell.[42] The void volume of the pores in Lyocell is comparable with that of Viscose; the voids in Modal fibre are considerably smaller. The adsorbed water vapour is smallest on Modal (14.1%), Lyocell (14,6%) and highest on Viscose (15.1%).[21] The ζ-potential courses in Figure 9 show that Modal fibres differ significantly from Viscose and Lyocell fibres. Modal fibre exhibits the highest negative ζ-potential plateau value, whereas Viscose and Lyocell are very similar. This may be a reason of the reduced swelling due to small pore volumes. Figure 10 shows the time-dependent ζ-potential values for these three types of fibres. The highest relative change in ζ-potential is seen for Viscose, smaller changes for Lyocell and Modal. This correlates well with the swelling results determined microscopically[22], where Viscose shows the highest degree of swelling in water, Modal the lowest. These results indicate that for reactivity and accessibility, the parameters obtained in the swollen state of the fibre are the significant values. Sorption phenomena are sensitive to these parameters; whereas the crystallinity and orientation factor of the crystallites less influence the results on

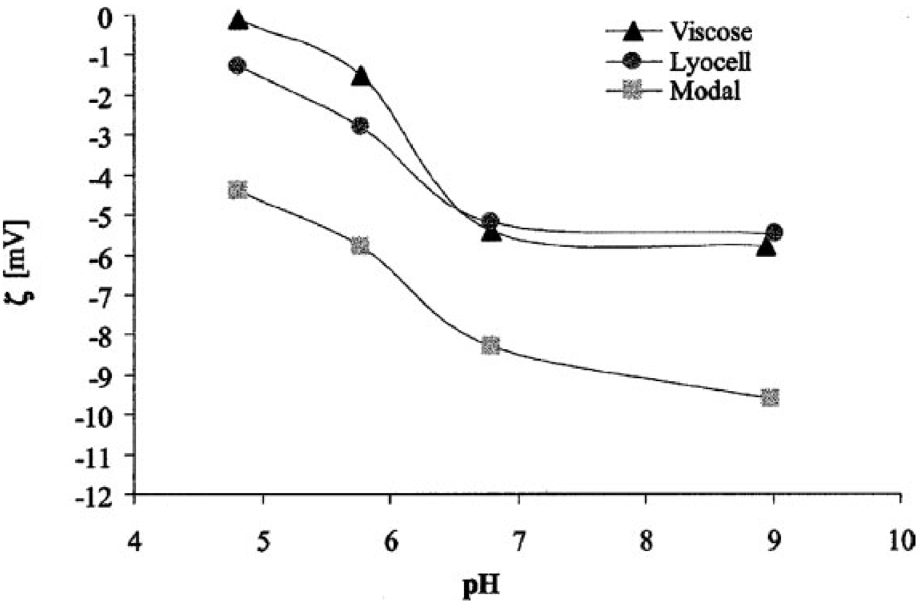

Figure 9.
ζ-potential as a function of pH for different man-made cellulose fibres; in 10^{-3} M KCl solution.[22]

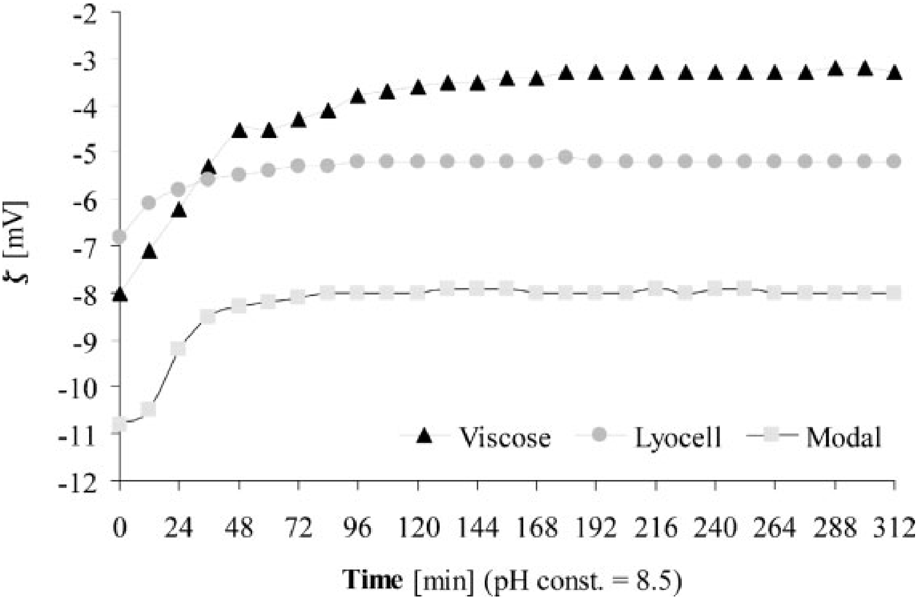

Figure 10.
Time-dependent ζ-potential course for different regenerated cellulose fibres.[22]

wet state processing, indirect effects of crystallinity may be seen in the swelling behaviour of the fibres.

Another parameter, where an excellent correlation between solution exhaustion and void fraction of the fibres can be observed, is the adsorption of a cationic surfactant (N-cetylpyridinium chloride, N-CPC) on the cellulose fibre.[22] Figure 11 shows the ζ-potential of the fibres as a function of surfactant concentration in solution. The highest amount of N-CPC is adsorbed on viscose fibre with the largest void fraction. In the case of water adsorption as well as in the experiment where surfactant is adsorbed, the crystallinity does not predict the sorption character of the fibre. Modal fibres, which have a mediate crystallinity, are unable to absorb the same amount of surfactant as Lyocell with the highest crystallinity and largest voids. In the saturation region, the modal fibre shows the highest positive ζ-potential, whereas viscose fibres, with the highest amount of absorbed surfactant, show the smallest positive ζ-potential. One possible explanation for this phenomenon is, that in the case of modal fibres, the surfactant adsorbs at the electrokinetically accessible outer surface of the fibre. In case of Viscose fibre, a certain number of surfactant molecules enter the pores of the fibre, contributing only weakly to the electrokinetic experiment.[22] When a smaller surfactant is used for adsorption, the effect becomes even more pronounced, due to higher amount of surfactant entering the voids, eluding the contribution to the outer surface charge.

Poppel and co-workers investigated the adsorption behaviour of cationic surfactants used for softening and antistatisation purposes on various fibres.[43] Measurements of the fibre electric resitivity during surfactant adsorption show an increase in resitivity up to concentrations near the critical micellar concentration of the surfactant. This is attributed to the conformation of the surfactant on the surface, with the polar charged groups towards the surface and the hydrophobic part pointing towards the solution. These results can be closely related to ζ-potential measurements of the fibre with surfactant adsorbed,

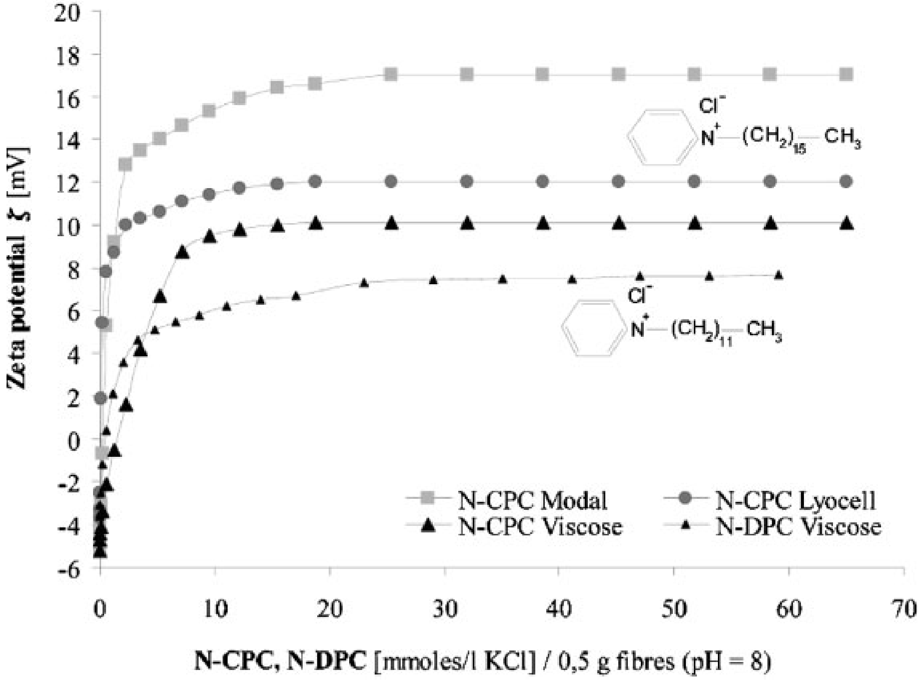

Figure 11.
ζ-potential of man-made cellulose fibres as a function of surfactant concentration in solution.[22]

assuming the point of charge reversal as indicator for monolayer formation.

A detailed investigation on the adsorption of cationic surfactants on cellulose pulp fibres was published by Alila and co-workers.[23] They combined adsorption isotherms and electrokinetic data to evaluate adsorption isotherm models available from literature, using differently charged substrates and different surfactants. Electrokinetic data gave additional information on the adsorbed layer structures, where the point of charge reversal is indicating surface saturation or the onset of hemimicelle formation, depending on the surface charge and the length of the surfactant hydrophobic tail.

Electrokinetic properties of cellulose fibres adsorbing non-ionic and an-ionic surfactants are described by Reischl and co-workers.[44] The ζ-potential of cellulosic fibres can be altered in a wide range also using anionic surfactants, which adsorb at the fibre surface due to interactions with easily polarisable groups, e.g. phenyl moieties, in the surfactant structure. Even uncharged surfactants influence the ζ-potential, by formation of a coating on the fibre surface, screening the negative charges. The shear plane is also shifted towards the solution, resulting in a less negative ζ-potential.

Electrokinetic data of dyed cellulosic fibres are rarely reported in literature. Gonzalez-Caballero and co-workers investigated the electrokinetic properties of bleached cotton in solutions of a reactive dye at different concentrations and temperatures.[45] A high negative ζ-potential of the fibre was observed at low dye concentrations, decreasing significantly at higher temperatures. An inversion of this trend was observed at higher dye concentrations. The same workgroup investigated the effect of sulphonate content of direct dyes on the non-linear electrokinetic behaviour of cotton fibres.[46]

Electrokinetic data allow not only interpretations on the changed charge conditions of the dyed surface; it can also be used to gain insights in the adsorption mechanism of the dye.[47] Figure 12 shows the pH-dependent ζ-potential courses of dyed and non-dyed Viscose fibres. One Viscose fibre is permanently cationised not only at the surface, but throughout the whole fibre. The ζ-potential course of this fibre shows the typical sigmoid form for "two site dissociation", containing both positive and negative charges. Introducing a direct dye containing four sulphonate groups per molecule on the cationised fibre surface renders the ζ-potential in the plateau region at pH 6 to 10 unchanged. The isoelectric point is shifted towards lower pH, due to the introduction of sulphonate groups at the fibre surface. The unchanged plateau value indicates an ion exchange mechanism as an important factor for the dye uptake. Sulphate ions from the spinning bath, which are strongly adsorbed by the cationic charges, are exchanged with dye anions. The total change of negative charge at the surface is therefore small. Thus, the ζ-potential plateau value remains nearly unchanged.

In case of standard Viscose fibres containing only negative surface charges, the introduction of the dye significantly shifts the ζ-potential plateau to more negative values. Here, the adsorption through dipole-dipole and van der Waals interactions is the predominant mechanism.

Not only the adsorption of dyes onto cellulosic fibres was studied, but also fibre treatments which should lead to a better dyeability of the fibre. Janhom and coworkers investigated the influence of previously adsorbed proteins and polyelectrolytes on the dyeability of cotton fibres.[15] Figure 13 shows the pH-dependent ζ-potential course of the treated cotton fibres. The adsorption of bovine serum albumin (BSA) has only small effects on the ζ-potential of the cotton fibre. Polyethyleneimine (PEI), a cationic polyelectrolyte, adsorbs strongly at the fibre surface, resulting in a charge reversal over a wide pH-range. The IEP is shifted from approx. pH 2-3 for pure cotton to pH 8.

Subsequently conducted dyeing of the fibres show that both pre-treatments

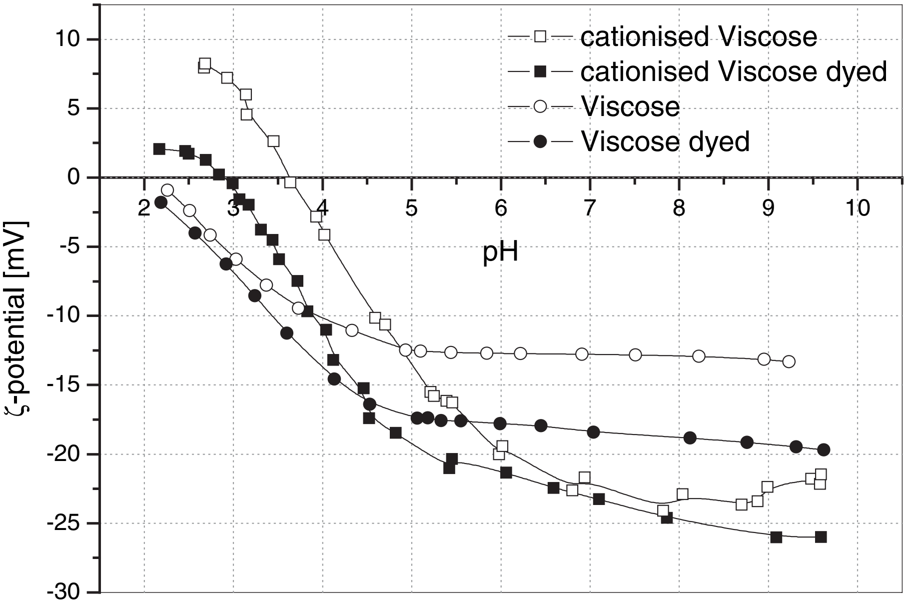

Figure 12.
pH-dependent ζ-potential curves for dyed and native Viscose fibres using a direct dye.[47]

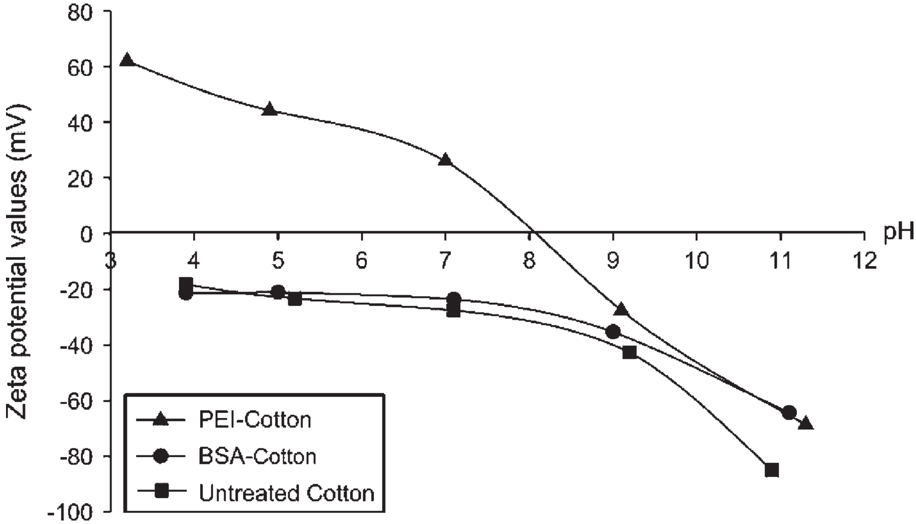

Figure 13.
pH-dependent ζ-potential courses of untreated, protein and polyelectrolyte treated cotton.[15]

increase the dye uptake of the cotton fibre. The effect is more pronounced with PEI. In addition, the dye uptake of the PEI treated fibres become independent from temperature and ionic strength in the ranges investigated.[15]

Conclusion

In a general sense, results of electrokinetic investigations on cellulose fibres can give an insight in the chemical potential of the polymer surface. Changes in surface charge are a main aspect influencing the ζ-potential. Therefore, all procedures changing the amount and type of charged surface groups can be monitored via ζ-potential measurements.

Not only the surface charge influences the potential, but also the hydrophilic/hydrophobic behaviour of the polymer. Introduction of uncharged hydrophobic groups on the cellulose surface have effects on the ζ-potential, therefore the monitoring of changes in the polarity of the surface can be monitored.

The third important polymer property that influences the ζ-potential is the morphology of and accessibility to the surface and the different functionalities thereupon. As a consequence, changes in structure, like swelling, will alter the ζ-potential. As can be seen from measurements carried out with man-made fibres, it is the non-crystalline, amorphous part of the fibre which controls the accessibility and reactivity of the fibre. This part is the one monitored with ζ-potential measurements.

The surface potential can be changed by dissociation of surface groups and introduction of covalently bound molecules. Another way to alter the surface properties is physical and chemical adsorption of molecules on the surface. Both kinds of adsorption are sensitive to ζ-potential measurements. Therefore, the electrokinetic properties of surfaces are a valuable tool to monitor sorption/desorption processes of any kind.

Consequently, the sensitivity and versatility of the ζ-potential measurement result in one major disadvantage. All these effects, from swelling to adsorption of potential determining ions, occur often simultaneously and their individual contributions to the net ζ-potential cannot be measured separately. This leads to inevitable uncertainties in the interpretation of ζ-potential measurement results. For this reason, some influential properties of the sample measured have to be known or characterised using additional physicochemical methods; e.g. charge titration, contact angle and moisture sorption measurements. As can be seen from the measurements of highly hydrophilic natural cellulose fibres, the water uptake and swelling is closely related to the content of non-cellulose components like hemicelluloses. This causes swelling, which changes the position of the shear plane in the ζ-potential measurements. If the sample is additionally treated with NaOH, adsorption of alkali ions can occur, changing the charge of the surface. All these effects reduce the negative ζ-potential of the fibre, resulting in very low potential surfaces. Modification of these surfaces then can hardly be monitored via ζ-potential measurement. In this case, for the monitoring of the surface modification, non-cellulosic compounds might have to be removed prior to modification. Nevertheless, for the application of the fibre in the native state, swelling behaviour, water uptake and degree of hydrophilicity derived from ζ-potential measurements are valuable information for the prediction of interaction properties with other polymers.

Another point, which has to be considered, is the accessibility of functional surface groups. This is closely related to surface morphology and fibre structure. ζ-potential measurements are only sensitive to changes in the amorphous, less ordered part of the cellulose fibre, where components from the liquid phase can interact. For the measurement interpretation, parameters like ratio of crystalline/amorphous regions of the fibre, void size and distribution influence the result and should be known beforehand.

In summary, ζ-potential measurements of cellulose fibres are a valuable tool for the characterisation of the polymers' surface and interaction properties. These measurements always have to be combined with other methods to guarantee proper interpretation of the results. Chemical composition and structural information of the sample investigated are the base of unambiguous conclusions out of ζ-potential measurements.

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