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Electrokinetic Properties of Natural Fibres

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The study of *Electrokinetic Properties of Natural Fibres* was done at the Institute of Polymer Research in Dresden, Germany, in collaboration with Anton Paar company in Graz, Austria.

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20-minute talk presented in the session on *Environmental Electrokinetics* at the International Electrokinetics Conference, Pittsburgh, PA, June 15, 2004

Aim of our Investigation

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Technological background

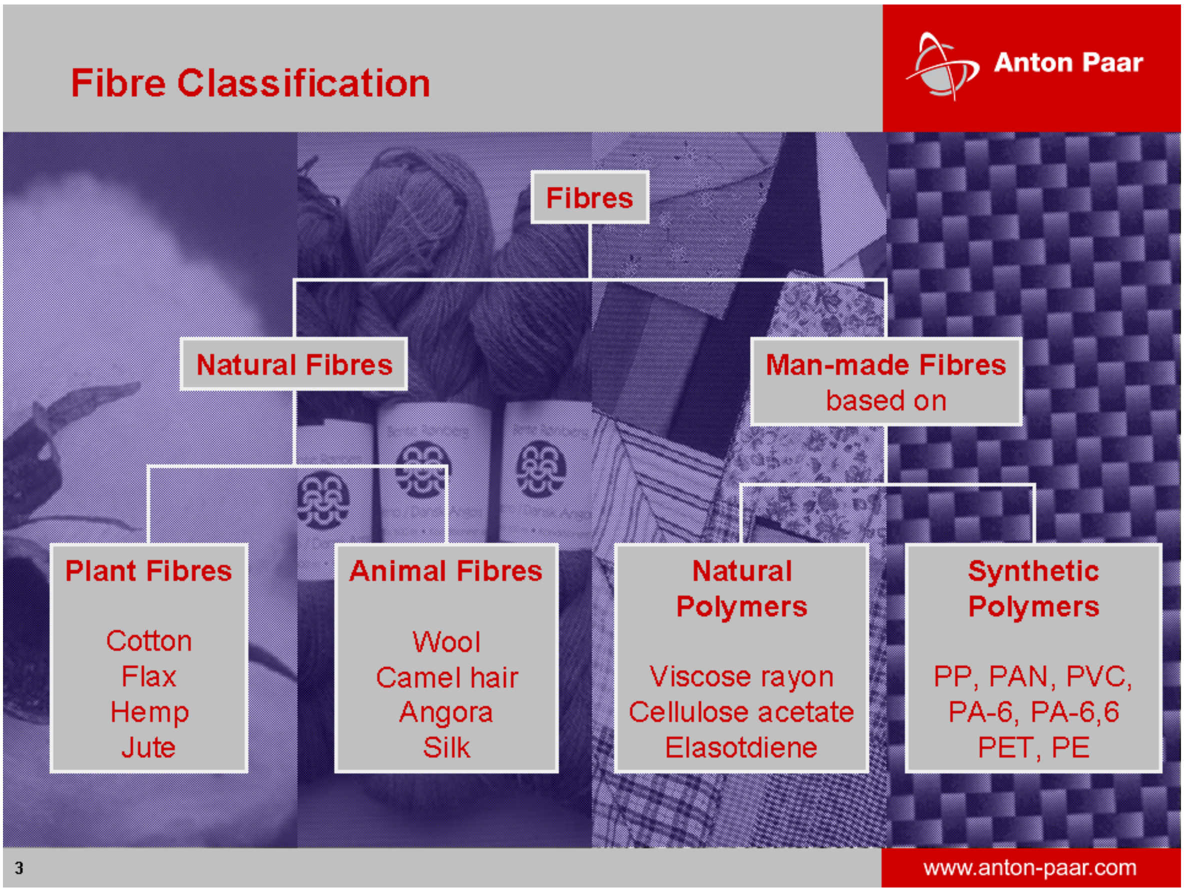
- Natural cellulose-based fibre application in composite material engineering
- Requirement for fibre surface treatment
- Control by electrokinetic investigation

Contents of the presentation

- Streaming potential measurement for characterization of fibre swelling behaviour
- Interaction with coupling agents
- Comparison with solvatochromism experiments

Natural cellulose-based fibres are gaining increasing attention in the engineering of composite material where light weight is required.
Beside their light weight, plant fibres have the advantages of low cost and little tool wear during processing.
Cellulose fibres exhibit a highly polar surface due to the presence of hydroxyl groups. These hydroxyl groups enable the formation of hydrogen bonds in the interface of reinforced composite materials. But in order to get access to these hydroxyl groups, a cover of pectin and other waxy substances must be removed.
On the other hand the high polarity of the cellulose fibre surface is the reason for their hydrophilic behaviour which induces fibre swelling.
Intense surface treatment is therefore required for fibre cleaning and preparation for interfacial bonding. Such surface treatment may be monitored and controlled by the electrokinetic method of streaming potential.

The streaming potential measurement for the characterization of fibre swelling and for the understanding of the interaction between fibres and coupling chemicals is presented.



Fibres are classified as natural fibres and man-made fibres. Among the natural fibres we find plant fibres like cotton, flax, hemp or jute, and animal fibres like wool or silk. Man-made fibres are either based on natural polymers, like viscose rayon or cellulose acetate, or based on synthetic polymers, like polyolefines, polyacrylonitrile, polyamide or polyester fibres.

Experimental

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Experimental set-up

- EKA Electro Kinetic Analyzer for streaming potential measurement
- Cylindrical cell with perforated Ag/AgCl electrodes

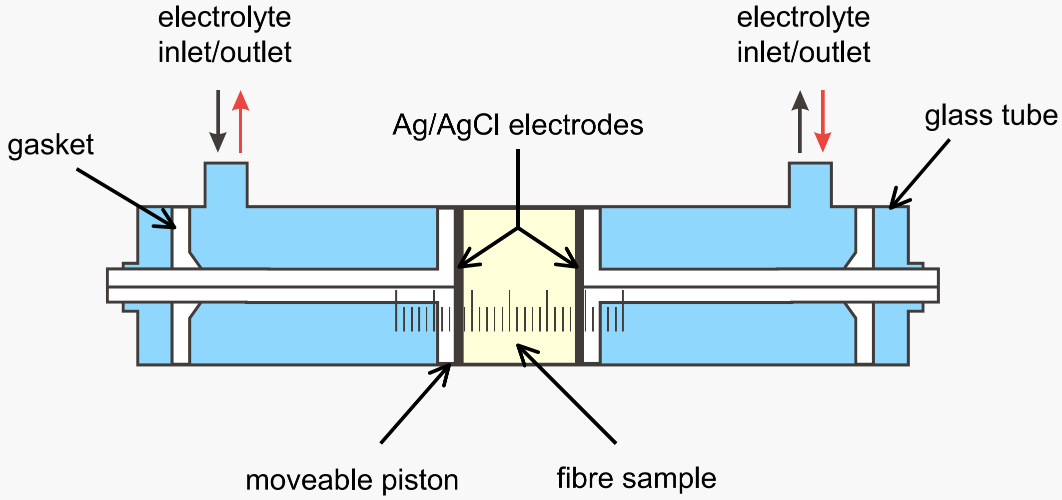
Measurement conditions

- Appropriate fibre plug placed between Ag/AgCl electrodes
- pH dependence measured in the presence of 10^{-3} M KCl

$$\zeta = \frac{dU}{dp} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \kappa$$

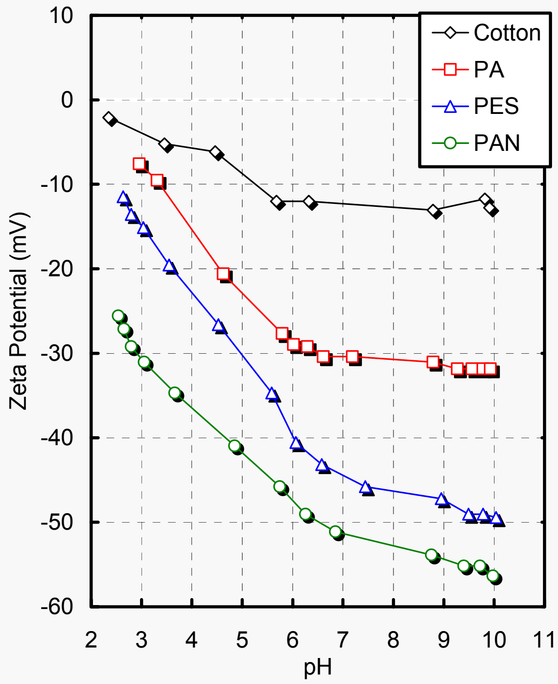
The streaming potential experiments were carried out with the Electro Kinetic Analyzer using the Cylindrical Cell, which was developed for the measurement of fibrous samples, but also for the measurement of granular and powder samples. For each measurement, an appropriate fibre plug was placed between the Ag/AgCl disc electrodes of the Cylindrical Cell. The pH dependence of the zeta potential was investigated with the background electrolyte of 1 mM KCl solution.
The evaluation of zeta potential is based on the Smoluchowski equation. Surface conductivity of the fibrous samples was not taken into account.

Cylindrical Cell



The measuring cell consists of a glass cylinder with inlet and outlet tubes for the electrolyte solution. The fibre sample is mounted between a pair of perforated Ag/AgCl disc electrodes. The electrodes are mounted onto moveable pistons which allow a variation of the distance between these electrodes and therefore an adjustment of the packing density of the fibre sample.

Characterization of Textile Fibres



- IEP acts as an indicator for association and dissociation processes on the fibre surface
- $\zeta_{plateau}$ reveals hydrophobicity or hydrophilicity of the fibre surface
- Hydrophilic character of cotton fibres induces swelling

Fibre	IEP	$\zeta_{plateau}$ (mV)
Cotton	2.8 – 3	-12
Polyamide	2.8	-28
Polyester	2.3	-48
Polyacrylnitrile	1.0	-55

The surface of various fibres for textile and technical application may be characterized by their zeta potential. The maximal zeta potential of the fibre surface, which generally occurs in the alkaline range, indicates their hydrophilic or hydrophobic behaviour. Man-made fibres based on synthetic polymers show a rather hydrophobic surface where the adsorption of electrolyte ions causes the surface charge and the negative zeta potential. Natural fibres contain acidic surface groups which are completely dissociated in the alkaline range. A pronounced plateau in zeta potential is observed for such fibres.
The hydrophobic character decreases in the series from polyacrylonitrile to polyamide. The acidic functional groups of cotton fibers make them very hydrophilic which induces swelling and therefore a significant decrease in the zeta potential.

Swelling Behaviour

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$$-\frac{d\zeta}{dt} = k\left(\zeta - \zeta_\infty\right)$$

$$-\ln\frac{\zeta - \zeta_\infty}{\zeta_0 - \zeta_\infty} = kt$$

ζ_0	initial zeta potential at first contact with water
ζ_∞	final zeta potential (asymptotic approach)
k	depending on fibre structure

Electrokinetic properties of fibres influenced by

- chemical composition
- surface polarity
- microstructure
- fibre porosity
- swelling behaviour

Decrease of zeta potential with increasing water adsorption caused by

- expansion of inner fibre surface
- competitive adsorption of water molecules and potential determining electrolyte ions

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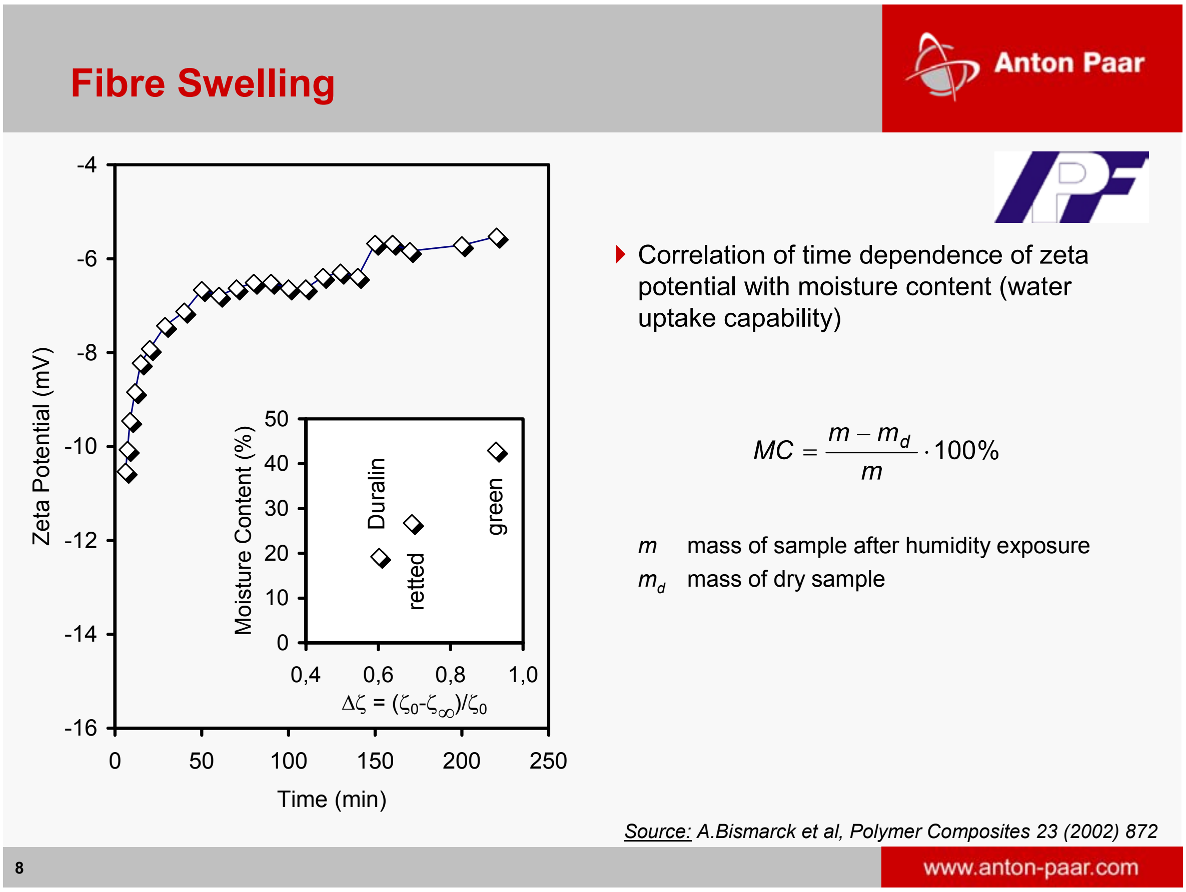
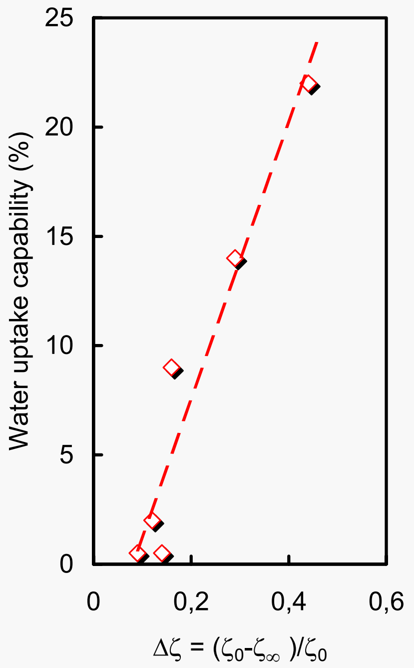
The electrokinetic properties of fibres are determined by the chemical composition of the fibre surface, the presence or absence of surface functional groups, the fibre porosity and the swelling behaviour.
The adsorption of water on the fibre surface causes a shift of the shear plane of the electrochemical double layer into the electrolyte solution. During fibre swelling, potential-determining electrolyte ions are further replaced due to the competitive adsorption of water molecules.
The kinetics of fibre swelling may be expressed by the given equations where ζ_0 is the initial zeta potential measured for the dry fibre at first contact with the aqueous solution. ζ_∞ is the zeta potential of the fibre surface which is approached asymptotically at infinite time, and k is some kinetic constant depending on the fibre structure.



The variation of zeta potential with time is shown here for a certain flax fibre as an example for the determination of the swelling characteristics of natural fibres.
The relative change in zeta potential is found proportional to the water uptake capability of the fibre respectively the moisture content after swelling.
In this example the initial zeta potential, ζ_0, is determined as –13.8 mV, the zeta potential at infinite time approaches –5.5 mV. This gives a relative change of 0.6. The moisture content measured independently for different flax fibres shows a linear correlation with this relative change in zeta potential.

Swelling of Technical Fibres



Fiber	Water uptake capability (%)	Zeta potential (mV)		
		ζ_0	ζ_∞	$(\zeta_0 - \zeta_\infty)/\zeta_0$
Cotton	22.0	-54.0	-30.2	0.44
Cellulose diacetate	14.0	-71.0	-50.1	0.29
Cellulose triacetate	9.0	-47.8	-40.2	0.16
PAN	2.0	-43.0	-37.7	0.12
PET	0.5	-81.6	-74.2	0.09
Glass fibre	0.5	-41.1	-35.2	0.14

Source: K. Kanamaru, Kolloid Z. 168 (1960) 115

The linear relation between the change in zeta potential and the water uptake capability is not restricted to natural fibres. It is possible to show such relation also for synthetic polymer fibres although the extent of water uptake respectively swelling is suppressed.

The swelling behaviour decreases from cotton to cellulose acetate and further to synthetic polymer fibres like polyacrylonitrile and polyester. Inorganic fibres like glass fibres also show some measurable water uptake.

However at low extent of swelling both the determination of the moisture content and the evaluation of the time dependence of zeta potential are affected by some significant measuring errors.

Swelling of Different Cellulose Fibres

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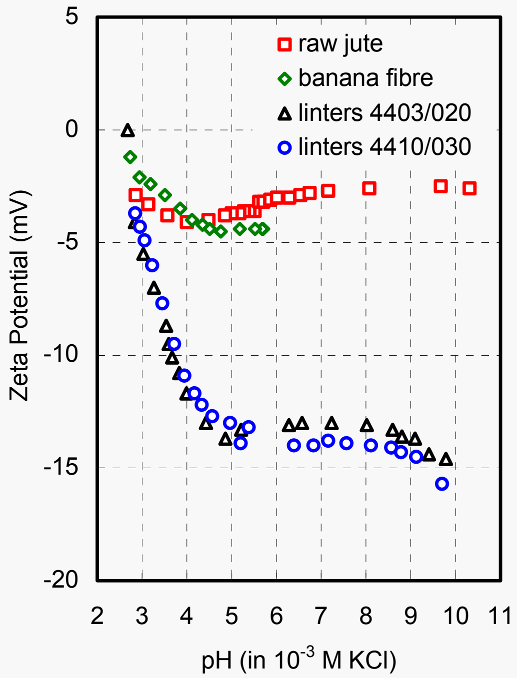

Jute and banana fibres

- Water adsorption up to 34%
- Low content of crystalline parts
- High content of non-cellulose compounds

Cotton fibres (linters)

- Water adsorption only up to 8%
- Higher degree of crystallinity
- Higher content of cellulose

The pH dependence of zeta potential for various natural cellulose-based fibres is shown in this graph.
The evolution of zeta potential with pH shows a plateau region in the alkaline range where the maximal zeta potential for cotton linters on the one hand and jute and banana fibres on the other hand differs significantly.
The isoelectric point below pH 3 is at a similar position for both types of fibres, which indicates the same chemical constitution of surface functional groups.
The behaviour of zeta potential with varying pH may be related to the chemical properties of the fibres. Jute and banana fibres exhibit a low content of crystalline parts and a high content of non-cellulose compounds. Cotton linters show a higher degree of crystallinity and a high content of cellulose.
The water adsorption capability is reflected by the level of the plateau value in zeta potential. Jute and banana fibres may adsorb 34 weight-% of water whereas for the cotton linters used for these investigations, the water uptake capacity is only 8 weight-%.

Silane Treatment of Fibres

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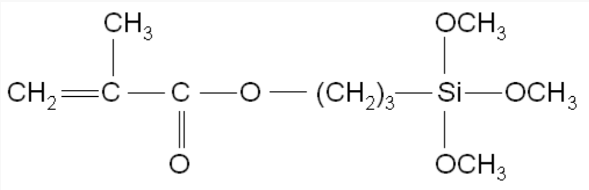
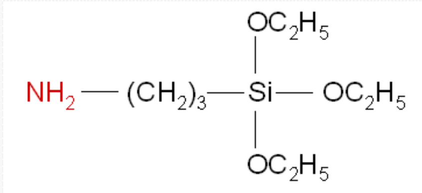
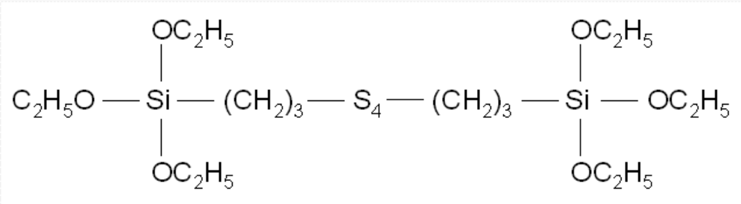
A 174
γ-methacryloxypropyltrimethoxysilane



A 1100
γ -aminopropyltriethoxysilane



Si 69
bis(3-triethoxysilylpropyl)-tetrasulphone



For high adhesion strength in fibre composite material polar functional groups are required. On the other hand such polar groups increase the hydrophilic behaviour of the fibre surface and induce swelling which may damage the interfacial bonds. Surface treatment after cleaning is therefore necessary to prepare the fibres for further processing steps.
Appropriate coupling agents based on silanes are composed of a silane group and an organic group. The silane group may hydrolyse in aqueous environment and condense with the hydroxyl groups of the cellulose fibre. The organic group does interact with the polymer matrix of fibre-polymer composite materials.
Among the selected silanes, A 1100 exhibits another basic functional group and the zeta potential of A 1100 treated fibres is to be expected to show the most significant change.

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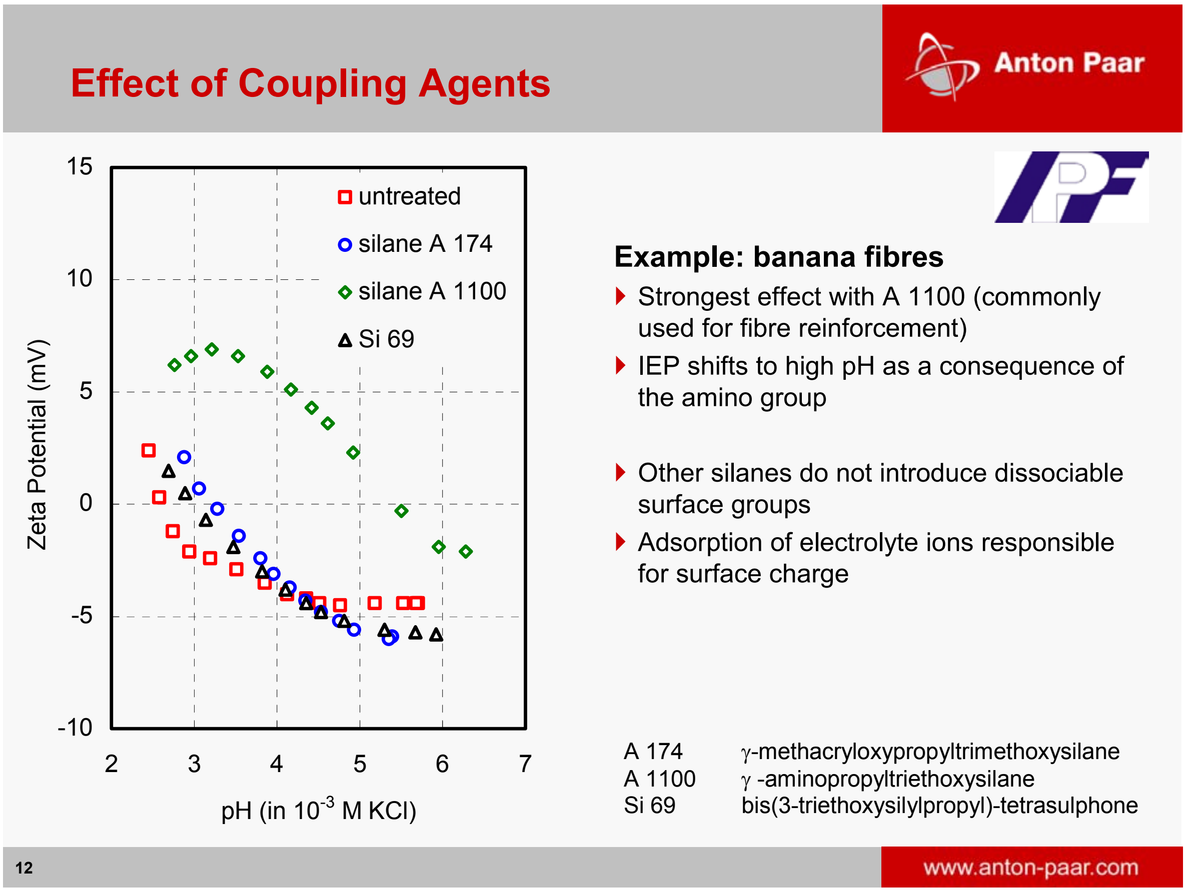
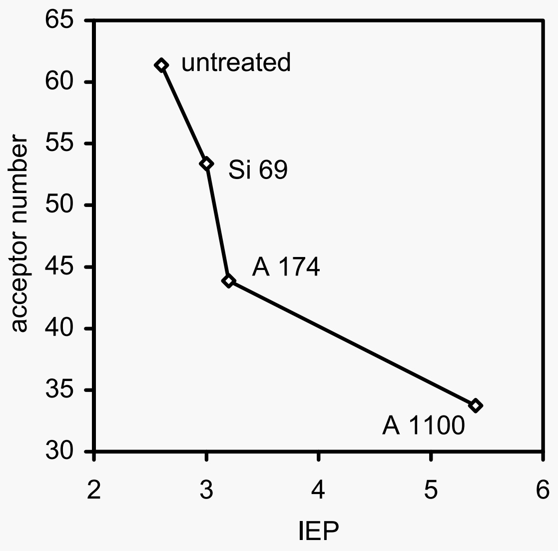


The pH dependence of the zeta potential of banana fibres treated with different silane coupling agents is shown in this graph.
For fibres treated with the silanes A 174 and Si 69 the effect is small. The plateau in zeta potential is less pronounced due to the coverage of the hydroxyl surface groups by the condensed silane molecules. The mechanism for charging turns from dissociation of acidic groups to adsorption of electrolyte anions.
As expected the strongest effect is observed for A 1100 which is commonly used in fibre reinforcement processes. The A 1100 silane introduces an amino group which shifts the IEP towards the alkaline range. At low pH the zeta potential is positive due to the protonation of these amino groups.

Comparison with Solvatochromism



Example: banana fibres

- Acceptor number of fibre surface as indicator for Lewis acid property
- The lower the IEP, the higher the acceptor number, the stronger the acidic property of the fibre surface

A 174	γ-methacryloxypropyltrimethoxysilane
A 1100	γ -aminopropyltriethoxysilane
Si 69	bis(3-triethoxysilylpropyl)-tetrasulphone

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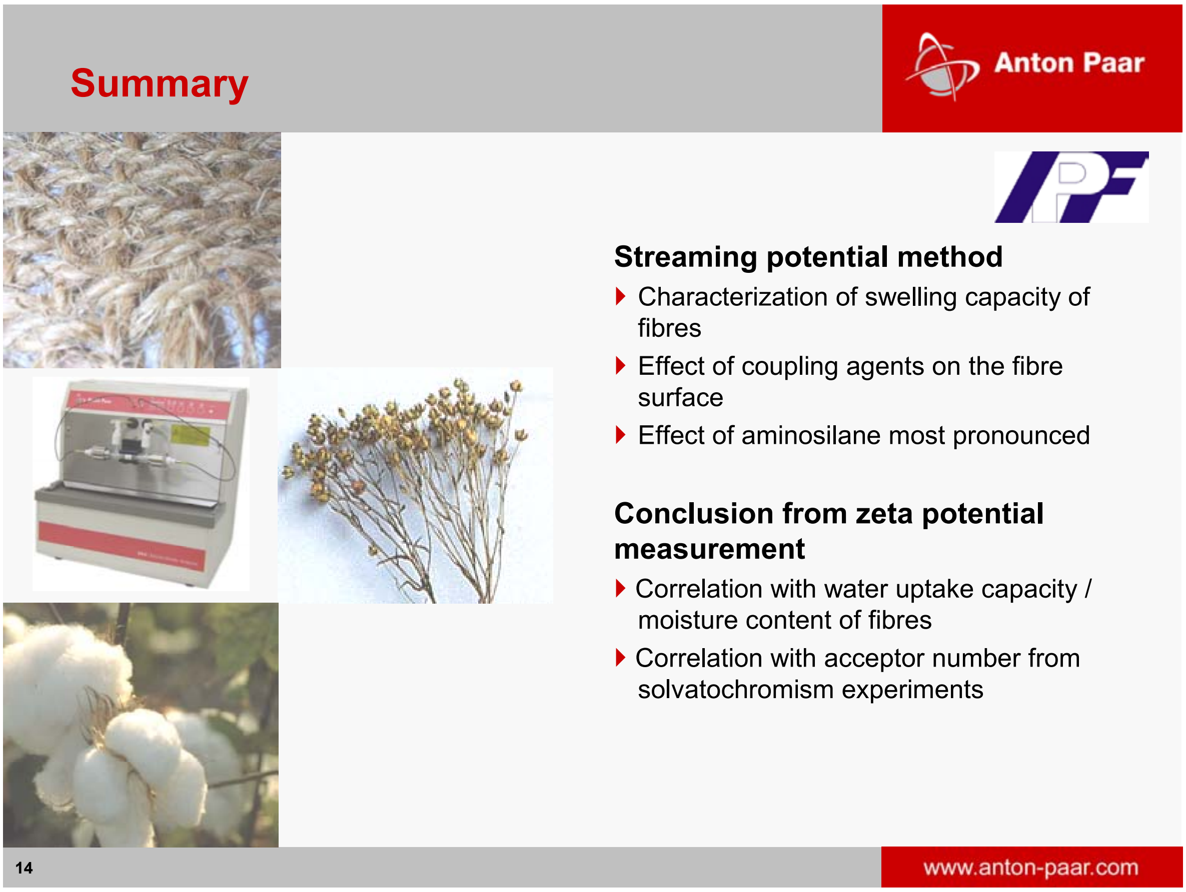
The results of the zeta potential measurement on silane treated banana fibres has been compared with solvatochromism experiments. From solvatochromism experiments, acceptor numbers may be extracted which are an indicator for the Lewis acid property of the fibre surface. The acceptor number correlates well with the position of the isoelectric point. The higher the acceptor number the higher the acidity of the fibre surface. On the other hand the higher the isoelectric point the lower the acidity of the fibre surface.



The electrokinetic effect of streaming potential is suitable to analyse the swelling characteristics of any kind of fibres.
The time-resolved zeta potential measurement shows good correlation with the water uptake capacity of fibres.
The effect of coupling agents, which are applied for processing of fibre-reinforced polymers, was presented for banana fibres.
The isoelectric point of fibres treated with various silanes correlates well with the acceptor number respectively acidity of the fibre surface which may be derived from solvatochromism experiments.