

## Beyond surface charge to wettability: The extra gear of the zeta potential

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Zeta potential analysis and contact angle measurement are complementary techniques that address the solid-water interface. The zeta potential represents the surface and interfacial charge and helps to characterize surface functional groups, which trigger the wettability of material surfaces. Contact angle provides information about the wettability of surfaces and is used to calculate surface energy. This application report shows correlations between these interfacial parameters and highlights where surface zeta potential analysis provides an additional benefit in material surface characterization.

### 1 Introduction

The measurements of contact angle and zeta potential address properties of the solid-liquid interface. When focusing on water and aqueous solutions these interfacial parameters deliver complementary information on surface hydrophilicity or hydrophobicity, and surface and interfacial charge. The physico-chemical properties of surface functional groups determine the interaction with water and are responsible for the formation of surface charge as well as for the degree of surface hydrophobicity and hydrophilicity. Although water contact angle and surface zeta potential results originate from different analytical methods, it is not surprising to find an empirical correlation among these parameters for a certain family of materials such as polymers.

In this report we will revisit the different techniques for the direct or indirect measurement of the water contact angle and for the surface zeta potential, and emphasize the complementarity of these interfacial parameters by selected application examples. We will review the correlation between the water contact angle and the surface zeta potential and highlight the applicability of the corresponding measuring techniques and the extra benefit of the surface zeta potential analysis.

### 2 Contact angle

#### 2.1 Measurement by goniometry

When considering wetting of a material surface by a liquid, the measurement of the contact angle at the solid-liquid-vapor interface is usually selected as the method of choice. Furthermore the picture of a

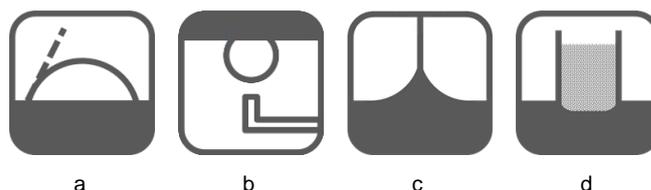


Figure 1. Icons for contact angle measurement techniques. (a) Sessile drop. (b) Captive bubble. (c) Wilhelmy single fiber. (d) Washburn capillary rise.

**sessile drop** of the liquid resting on a flat, non-porous, and smooth solid surface is imagined at first (Figure 1a). However, for solid samples that deviate from the ideal geometry (fibers, granular media, powder) and structure (porous, swelling) other techniques such as the captive bubble method (Figure 1b), the Wilhelmy plate or single fiber approach (Figure 1c), and the Washburn capillary rise method (Figure 1d) are available.

The definition of the contact angle  $\theta$  is given by the equilibrium of the interfacial tension between solid and vapor  $\gamma_{sv}$  (also referred to as the surface energy), solid and liquid  $\gamma_{sl}$ , and liquid and vapor  $\gamma_{lv}$  according to Young's equation [1]:

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad \text{Eq. 1}$$

When considering water with  $\gamma_{lv} = 72 \text{ mN/m}$  (at  $25^\circ\text{C}$ ) we obtain good wetting for surfaces with a high surface energy (Figure 2a) and poor wetting of surfaces with a low surface energy represented by a large contact angle (Figure 2b). Materials are classified as hydrophilic if wetting by water is favorable ( $\theta < 90^\circ$ ) and as hydrophobic if wetting by water is rather poor ( $\theta > 90^\circ$ ). We note that the

classification of materials' surfaces by their hydrophilicity is only relative.

Surface roughness at the nanoscale affects the water contact angle ("Lotus effect") and helps to generate superhydrophobic surfaces (Figure 2c). The interaction of such material surfaces with water is no longer driven solely by the surface chemistry. Complete wetting of a solid surface by water gives diminishingly small contact angles (Figure 2d).

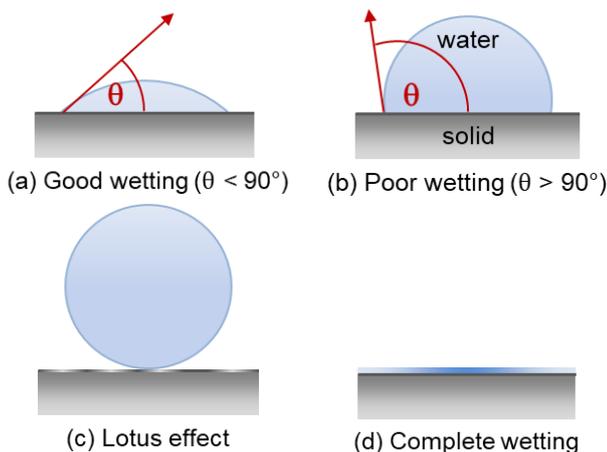


Figure 2. Contact angle of water droplet on flat solid surface indicating (a) good wetting (hydrophilic surface), (b) poor wetting (hydrophobic surface), (c) superhydrophobicity on a surface with nanoscale roughness ("Lotus effect"), and (d) complete wetting.

We note that a fast penetration of water into a porous material surface may indicate the behavior of a highly hydrophilic surface. For porous materials such as polymer membranes and filters the **captive bubble** method is therefore recommended. Here the sample remains immersed in water or an aqueous solution and air bubbles are injected to attach to the wet surface. The measured angle corresponds to the supplementary of the contact angle, i.e.,  $180^\circ - \theta$ .

## 2.2 Measurement by tensiometry

The **Wilhelmy plate** technique offers an alternative method for the determination of the contact angle for solid materials with a flat surface. The specimen with a known perimeter must exhibit the same surface properties on opposite sides, which is why the sessile drop method is preferred. However, the Wilhelmy technique offers a possibility to determine the contact angle on single fibers, which are immersed in a test liquid. Gravitational, interfacial, buoyancy and shear forces act on the fiber [2]. For low molecular liquids such as water, the shear force can be neglected. For fibers with a diameter  $< 100 \mu\text{m}$ , the contribution of the buoyancy force is negligible. Under these boundary conditions, the contact angle may be determined by

$$\gamma_{lv} \cos \theta = \frac{mg}{p} \quad \text{Eq. 2}$$

which still requires an accurate determination of the fiber perimeter  $p$  that must not change during the experiment (e.g., due to fiber swelling).  $m$  is the mass of the fiber sample and  $g$  is the gravitational acceleration.

For porous materials such as fabrics but especially for powder samples, the **Washburn capillary rise** method is employed. A tubular sample holder is filled with the powder sample thereby focusing on a reproducible and tight packing. Upon contact of the test liquid by the sample, capillary forces pull the liquid upwards. When measuring the temporal change of the liquid front the contact angle may be calculated by the Washburn equation [3]. For a powder sample the observation of the rising liquid is difficult or even impossible but may be replaced by measuring the mass  $\Delta m$  gained by the liquid penetration into the porous material.

$$\gamma_{lv} \cos \theta = \frac{2}{A^2 r} \frac{\eta (\Delta m)^2}{\rho^2 t} \quad \text{Eq. 3}$$

However, the effective geometry of the capillary network within the powder sample represented by the effective cross-section  $A$  and radius  $r$  still remains unknown and may be determined experimentally by using a liquid that completely wets the powder sample (i.e.,  $\cos \theta = 1$ ). By using this approach the challenges are (1) the selection of an appropriate reference liquid that completely wets the sample and (2) the needs for at least two specimen of the same powder sample with a highly reproducible packing. For these reasons a modified Washburn equation has been proposed to determine the surface energy  $\gamma_{sv}$  empirically by using a series of test liquids with similar surface tensions  $\gamma_{lv}$  [4].

## 3 Surface zeta potential

Upon contact of a material surface with an aqueous solution, surface and interfacial charge is generated. This charge is compensated by ions of opposite charge that accumulate in the vicinity of the material surface. According to the model of the electric double layer these compensating ions arrange in a thin immobile layer (Stern layer) next to the surface and a more extended mobile layer (diffuse layer). The zeta potential is defined at the virtual interface between the Stern and diffuse layers of charge-compensating ions [5].

When applying an electric or mechanical force either to the solid material or to the liquid phase, a relative motion between liquid and solid is activated thereby generating an "electrokinetic" response. For small particles in dispersion the electrophoretic mobility gives access to the particles' zeta potential. For large

solid samples the surface zeta potential is determined from the measurement of the streaming potential  $U_{str}$  according to

$$\zeta = \frac{dU_{str}}{\Delta p} \times \frac{\eta}{\varepsilon_{rel} \times \varepsilon_0} \times \kappa_B \quad \text{Eq. 4}$$

$\Delta p$  is the pressure gradient applied across a flow channel filled with an aqueous solution of electric conductivity  $\kappa_B$ .  $\varepsilon_{rel}$  is the relative permittivity of water and  $\varepsilon_0$  the permittivity of free space. For the discussion of complementarity and correlation between water contact angle and zeta potential we refer to large solid samples and the streaming potential method.

Surface and interfacial charge are triggered by different mechanisms that depend on the material surface chemistry:

1. Acid-base interaction between surface functional groups and water drives the formation of negative and positive surface charge by the deprotonation of acidic and the protonation of basic functional groups.
2. Hydrophobic surfaces attract water ions (hydronium,  $H_3O^+$ , and hydroxide,  $OH^-$ ) to suppress the repulsive force between such surfaces and water molecules.
3. Partial dissolution of lattice ions create charged defects in crystalline lattices, which is the main contribution to surface charge for minerals and ceramics.

Mechanisms 1 and 2 are strongly depending on the pH of the aqueous test solution whereas other potential-determining ions are responsible for changes in the zeta potential of materials belonging to category 3.

The streaming potential method is applicable to any kind of solid sample that may be arranged to create a capillary flow channel. For materials with a flat surface, either porous or non-porous, two samples are aligned in parallel and separated by a (capillary) distance of approximately 100  $\mu m$  to enable the tangential mode of measurement. Fibers and powder samples are measured as a randomly arranged plug with voids serving as a capillary network for the permeation mode of the streaming potential measurement. Since the geometry of the capillary is not decisive for a reliable and reproducible determination of the surface zeta potential, the streaming potential method is indeed universally applicable to a variety of samples with different shapes and sizes.

#### 4 Why are water contact angle and zeta potential complementary?

The behavior of a solid material in an aqueous environment is determined by the nature of the

material surface and furthermore by the properties of the solid-water interface. Two major types of forces, electrostatic and hydrophobic, trigger the solid-solute interaction. Knowledge about the crucial parameters that help to estimate and to describe these forces is fundamental for the development of new materials. The water contact angle and the calculated surface energy as well as the zeta potential and the calculated (electrokinetic) charge density are indispensable contributions to a comprehensive description of material surface properties.

Particularly the sessile drop method for the contact angle measurement on flat surfaces has received a high acceptance due to its apparent simplicity and direct correlation with surface hydrophilicity and hydrophobicity. These features make goniometry attractive to test the effect of surface modification processes. However, what often remains unknown is the surface chemistry that drives a material surface hydrophilic or hydrophobic.

As an example, Figure 3a shows the decrease in the water contact angle with increasing exposure time of a

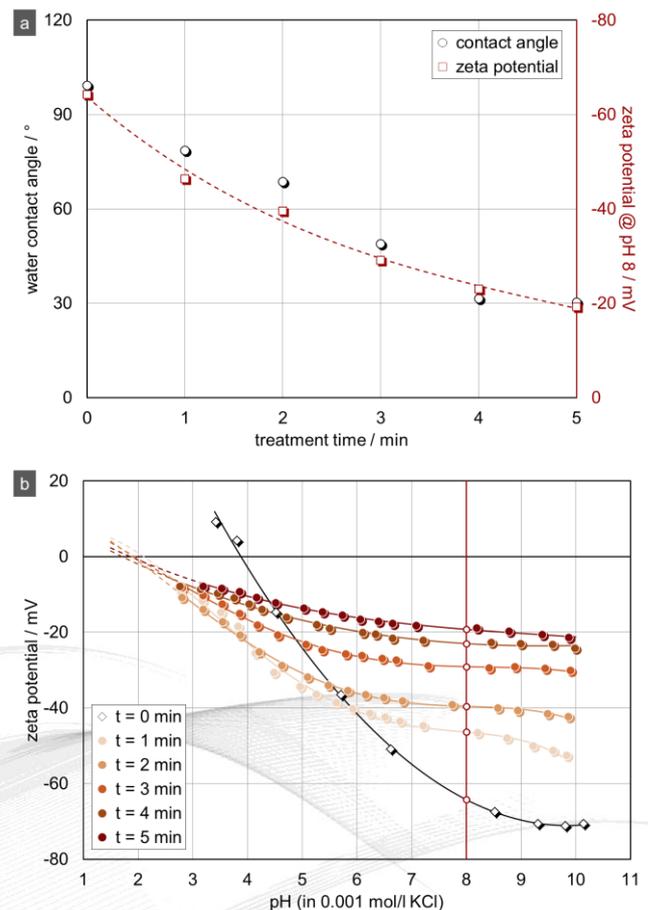


Figure 3. (a) Water contact angle and surface zeta potential (determined in 0.001 mol/l KCl, pH 8) of pristine and UV/SO<sub>2</sub>-treated low density polyethylene films. (b) pH dependence of zeta potential for LDPE films [6]. The zeta potential at pH 8 used for the correlation with water contact angle is indicated by the vertical line.

low density polyethylene (LDPE) film to UV irradiation in the presence of gaseous  $\text{SO}_2$  [6, 7]. Obviously the surface energy of the LDPE film turns from initially low  $\gamma_{sv}$  ( $\theta_{\text{water}} = 99^\circ$ ) to high  $\gamma_{sv}$  after 4 min of treatment ( $\theta_{\text{water}} = 32^\circ$ ) with no further obvious change after 5 min treatment. The evolution of the surface zeta potential for the same series of pristine and irradiated LDPE films shows the same trend, i.e., an increase in the zeta potential from  $\zeta = -64$  mV for pristine LDPE to  $\zeta = -19$  mV after 5 min of treatment.

The additional analysis of the dependence of the zeta potential on the pH of an aqueous test solution reveals the chemical reason for the drop in the water contact angle (Figure 3b). While the untreated LDPE film shows an isoelectric point (IEP, i.e. the pH of the aqueous solution where  $\zeta = 0$  mV) at pH 4, which is indicative for a pristine polymer surface [8], UV irradiation in the presence of the reactive  $\text{SO}_2$  atmosphere shifts the IEP to lower pH. Obviously some strongly acidic surface functional groups get introduced to the LDPE film and are recognized as sulfonic acid groups,  $-\text{SO}_2(\text{OH})$ . With the progressive surface treatment the IEP remains unaffected thereby confirming a homogeneous surface chemistry.

Like the water contact angle, the surface zeta potential illustrates the effect of the progressive treatment of the LDPE film and complements this information by the confirmation of the modified surface chemistry.

Figure 4 shows another example where the water contact angle measurement complements the surface zeta potential results. Adamczyk et al. [9] employed these solid-water interfacial parameters to accompany the formation of polyelectrolyte (PE) multilayers composed of the cationic PE poly(allylamine hydrochloride), PAH, and the anionic PE poly(sodium 4-styrene sulfonate), PSS. Polyelectrolyte multilayer coatings are commonly applied to tune the surface properties of polymer membranes (to enhance membrane selectivity and antifouling capability), biomaterials (to improve biocompatibility or enable controlled drug delivery), or advanced textiles.

By using different buffer solutions, 0.001 mol/l Tris and 0.15 mol/l NaCl, Adamczyk et al. obtained a different quality of the PE multilayer coatings. As indicated by the surface zeta potential the coatings are highly reproducible if the polyanion PSS represents the outermost layer. Obviously the structure of the polycation PAH is more sensitive to the ionic strength of the buffer solution. A high uniformity of the PAH layer is achieved in 0.15 mol/l NaCl while the positive character of this polycation is already decreased in the second bilayer when PE multilayer formation takes place in 0.001 mol/l Tris. The water contact angle results confirm the better quality of the PE multilayer deposited in 0.15 mol/l NaCl. However, the water contact angle fails to reveal the alternating hydrophilicity of layers 1-5 for the preparation of the PE multilayer in the dilute Tris buffer solution.

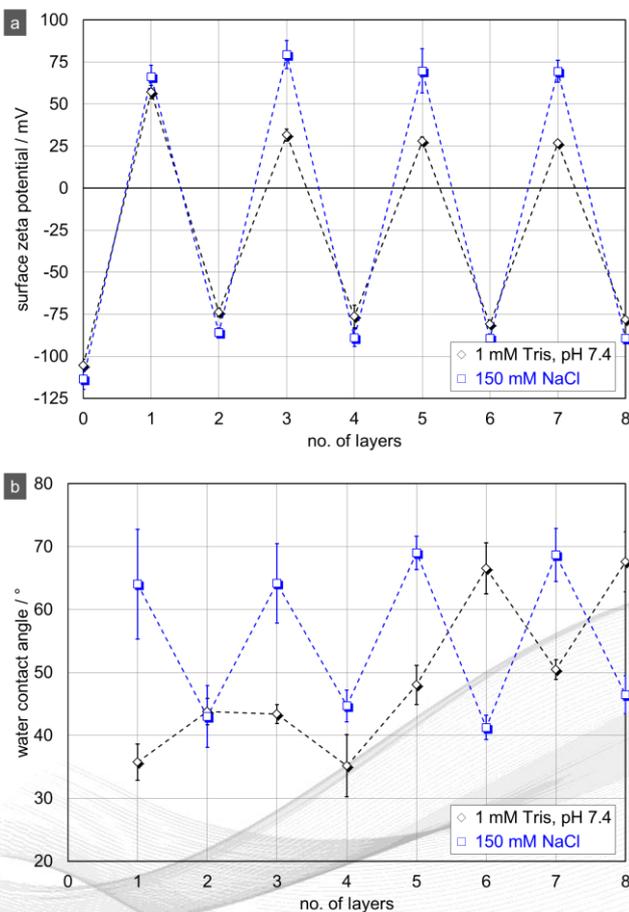


Figure 4. Formation of PAH/PSS polyelectrolyte multilayers in different buffer solutions monitored by (a) the surface zeta potential and (b) the water contact angle [9].

## 5 Correlation between water contact angle and surface zeta potential

The example above of the UV/ $\text{SO}_2$  treatment of LDPE films has shown a similar trend for the water contact angle and the surface zeta potential and revealed a potential correlation between these solid-water interfacial parameters. Already in the past a correlation between the surface zeta potential and the water contact angle was reported for various polymer surfaces [10]. Werner et al. [11] investigated the correlation between surface hydrophobicity and charge for a series of polystyrene derivatives spin-coated on a silicon oxide wafer. The summary of these results in Figure 5 indicates an acceptable linear correlation for a certain set of data obtained on a specific series of polymers.

These empirical correlations are expected when considering the behavior of water at the polymer-water interface. The polymer-water interfacial charge represented by the surface zeta potential is generated

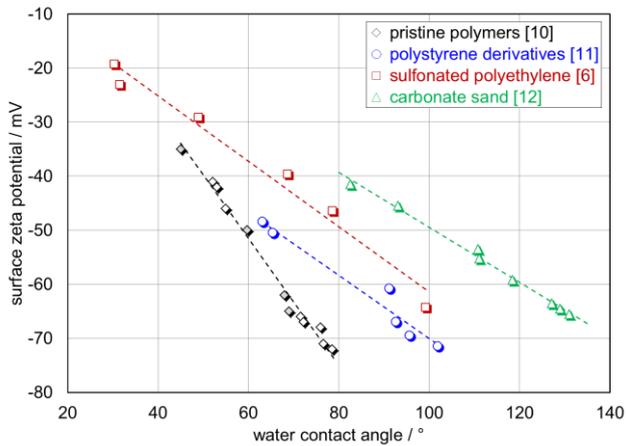


Figure 5. Correlation between surface zeta potential and water contact angle for a series of pristine polymers [10], derivatives of polystyrene [11], polyethylene with different degree of sulfonation [6] and carbonate sand exposed to stearic acid [12].

by the competitive adsorption of water molecules and water ions. Highly hydrophobic surfaces attract a large number of OH<sup>-</sup> ions whereas uncharged water molecules dominate the interfacial region at hydrophilic surfaces.

A correlation between the surface zeta potential and the water contact angle is not restricted to polymers. Rezaei Gomari et al. [12] reported a correlation between the surface zeta potential and the water contact angle for carbonate sand that was treated with different concentrations of stearic acid, which is also shown in Figure 5. Interestingly the slope of the linear correlation is very comparable when investigating a single base material that is subject to surface modification (polystyrene, polyethylene) and carbonate sand.

## 6 Added value of the surface zeta potential analysis

The observed correlation between the water contact angle, commonly determined by the sessile drop method on flat surfaces, and the surface zeta potential may be transferred to other materials that occur in a different shape such as fibers, fabrics (or other highly porous materials), and powder samples. While for non-planar materials the determination of the contact angle requires a technique different from the sessile drop method (and tensiometry instead of goniometry), the zeta potential analysis follows the same principle of the streaming potential measurement.

Let us consider the example of the surface characterization of glass fibers. The unknown capillary dimensions in Eq. 3 restricts the applicability of the Washburn method to calculate the contact angle for a bundle of glass fibers. Instead the estimation of the surface energy  $\gamma_{sv}$  is possible by re-arranging Eq. 3,

$$C \gamma_{lv} \cos \theta = \frac{\eta (\Delta m)^2}{\rho^2 t} \quad \text{Eq. 5}$$

and plotting the term on the left side of Eq. 5,  $C \gamma_{lv} \cos \theta$ , versus the measured temporal mass gain  $(\Delta m)^2/t$  and the known liquid density  $\rho$  and viscosity  $\eta$  for a series of liquids with surface tensions  $\gamma_{lv}$  in the proximity of the expected surface energy of the glass fiber sample. Figure 6a shows the results for untreated and sized glass fibers. According to the proposed modified Washburn method, the surface energy of the glass fiber sample corresponds to the surface tension of that test liquid, which yields the maximum in  $C \gamma_{lv} \cos \theta$ . For the untreated glass fiber the selected solvents reveal a surface energy of  $\gamma_{sv} = 49.6 \text{ mJ/m}^2$  whereas the sized glass fiber exhibits a slightly lower surface energy of  $\gamma_{sv} = 47.8 \text{ mJ/m}^2$ .

The surface zeta potential of untreated and sized glass fibers shown in Figure 6b makes the effect of sizing more visible [13]. It becomes evident that the sizing mixture contains cationic components (here an

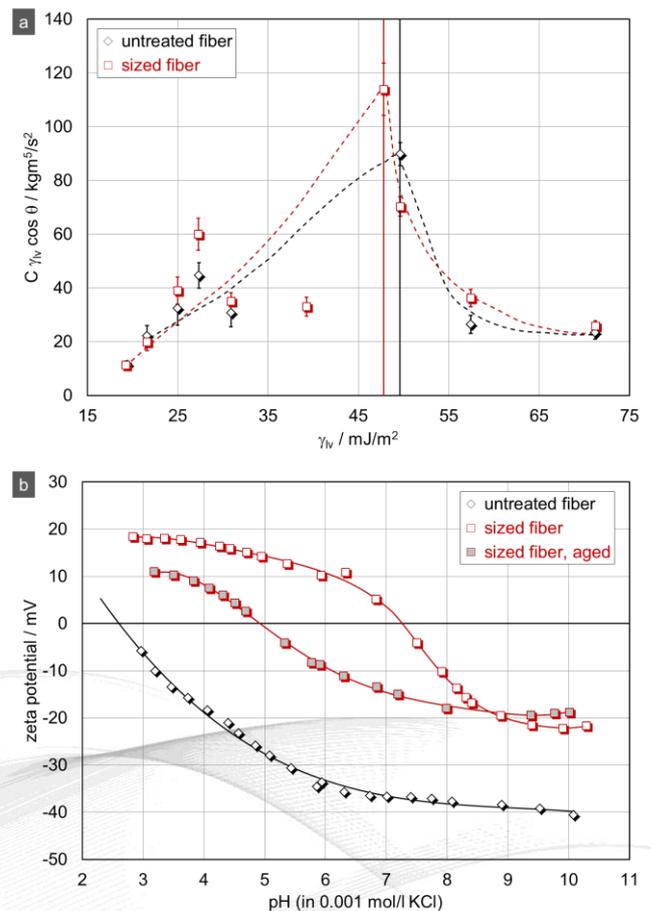


Figure 6. (a) Estimation of the surface energy for untreated and sized glass fibers by the modified Washburn method. (b) pH dependence of the zeta potential for untreated and sized glass fibers enables the observation of ageing of glass fibers upon storage.

aminosilane) that gets successfully adsorbed on the glass fiber surface. The large difference in the zeta potential for untreated and sized glass fibers further enables the observation of small changes in the surface properties that may occur upon ageing of the sized glass fiber. The Washburn capillary rise method disables the observation of such marginal changes.

## 7 Conclusions

The combination of water contact angle measurement and surface zeta potential analysis is frequently used to complement material surface characterization. Both parameters focus on the material-water interface and are determined primarily by the interaction of water with surface functional groups. While both zeta potential and contact angle confirm the effect of material surface modification, the zeta potential also reveals the chemistry behind a change in surface hydrophilicity.

For a certain series of alike material surfaces a linear correlation between the zeta potential and the water contact angle may be established. Such correlation is applicable to estimate changes in the surface hydrophilicity from zeta potential analyses for sample geometries that challenge the measurement of the contact angle.

## 8 References

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