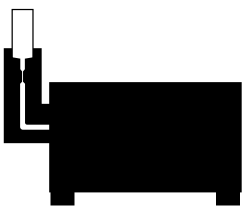
Application Note

Measuring the surface potential and isoelectric point of glass fibres with a zeta potential analyzer

– In cooperation with Anja Caspari and Dr. Astrid Drechsler, Leibniz-Institut für Polymerforschung Dresden e.V. –

It is well established that in an aqueous environment, the silanol groups on the surface of glass fibres interact not only with the water, but also with other ions and molecules. Sizings, surfactants and other additives carrying polar functional groups can adsorb by H-bonding, dipole-dipole interactions, and electrostatic interactions. Tailoring the surface properties of glass fibres, such as wettability, charge, or chemical composition, plays an important role in enhancing the adhesion of glass fibres in a polymeric matrix[1] by increasing the covalent bond density. Therefore, understanding the surface properties of glass fibres is important when developing surface treatments and thus optimise glass-fibre-reinforced polymer composites. Zeta potential analysis is a very powerful measurement technique and has been applied for more than 50 years to study the properties of glass fibre surfaces[2]. It is not only able to evaluate the charge situation and dissociable functional groups on solid surfaces, but also helps to evaluate the dispersion forces of solid surfaces regarding acidic or alkaline properties. The new ZPA 20 zeta potential analyzer from DataPhysics Instruments provides quick and reliable zeta potential measurements for fibres, powders, and plate-shaped solid surfaces by using an oscillating streaming potential technique. In this application note, we use the ZPA 20 to study the electrical properties and functional groups at the surface of glass fibres.

Measurement device
Zeta Potential Analyzer



Measurement method
Streaming potential

Measured quantities
Zeta potential
Isoelectric point

Environmental conditions
Room temperature

Samples
Non-woven glass fibre sheet

Industries
Insulation materials
Reinforced composite materials
Fibreglass plastics
Automobile parts
Telecommunication cables
Asphalt composites

dataphysics
Understanding Interfaces

Technique and Method

Solid surfaces in contact with an aqueous solution are in most cases charged – either by dissociation of functional groups or by adsorption of ions and molecules from the solution. Even primarily uncharged surfaces in simple salt solutions usually carry a negative charge due to the adsorption of OH^--ions. If the solution moves with respect to the solid (or vice versa), a shear plane is formed between ions and molecules strongly adsorbed to the surface and the mobile ions in the surrounding solution (Fig. 2). The electrical potential at this shear plane, the so-called zeta potential, is a very sensitive measure for the charge situation on the solid surface. From pH- and concentration-dependent zeta potential measurements, conclusions can be drawn regarding the nature of the functional surface groups and adsorption processes[3].

The ZPA 20 zeta potential analyzer from DataPhysics Instruments uses the streaming potential (Eq. 1) or streaming current (Eq. 2) method to determine the zeta potential. An oscillating flow of an electrolyte solution, through a thin slit between two flat surfaces or the capillary system formed by a dense fibre or powder package, shears off the mobile ion layer and creates an alternating potential and current in the measuring cell. From the ratio of the streaming potential U_{str} or current I_{str} and the pressure difference Δp (Fig. 3), the zeta potential ζ is calculated[4][5]:

$$\zeta = \frac{\eta\kappa}{\epsilon_0\epsilon_r} \cdot \frac{\partial U_{str}}{\partial \Delta p} \qquad \text{(Eq. 1)}$$

$$\zeta = \frac{\eta}{\epsilon_0\epsilon_r} \cdot \frac{L}{HW} \cdot \frac{\partial I_{str}}{\partial \Delta p} \qquad \text{(Eq. 2)}$$

Fig. 1: The ZPA 20 zeta potential analyzer from DataPhysics Instruments

η is the viscosity of the solution, ε_r is the relative permittivity of the solution, ε_0 is the absolute permittivity of vacuum, κ is the electrical conductivity of the solution, *L*, *H* and *W* are the dimensions of the streaming channel between plate-shaped samples.

Data analysis using the streaming current requires knowledge of the dimensions of the streaming channel and can be used for plate-shaped surfaces. The streaming potential allows calculating the zeta potential based on the viscosity and the conductivity of the solution and can be used for measurements of fibres, powders, and plate-shaped surfaces.

Experiment

In this application note, the zeta potential ζ and the isoelectric point of a commercial non-woven glass fibre sample was determined using the ZPA 20 from DataPhysics Instruments (Fig. 1) and the streaming potential method.

To ensure the cleanliness of the measuring device and fibre measuring cell, the equipment had been thoroughly cleaned with ultra-pure water (≤ 0.055 µS/cm) before the measuring cell was filled with the sample material, a non-woven glass fibre sheet.

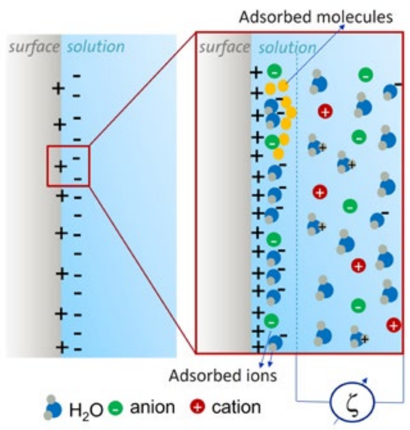


Fig. 2: Charge formation at solid surfaces in aqueous solution

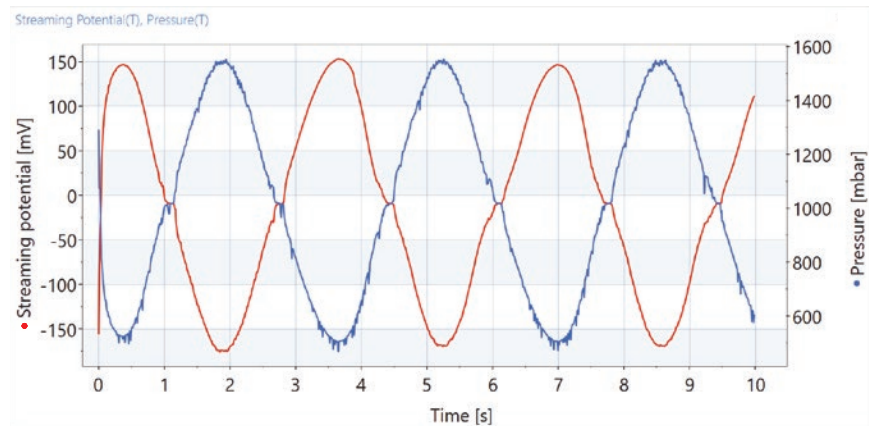


Fig. 3: Oscillating pressure (blue) and resulting streaming potential (red) vs. time

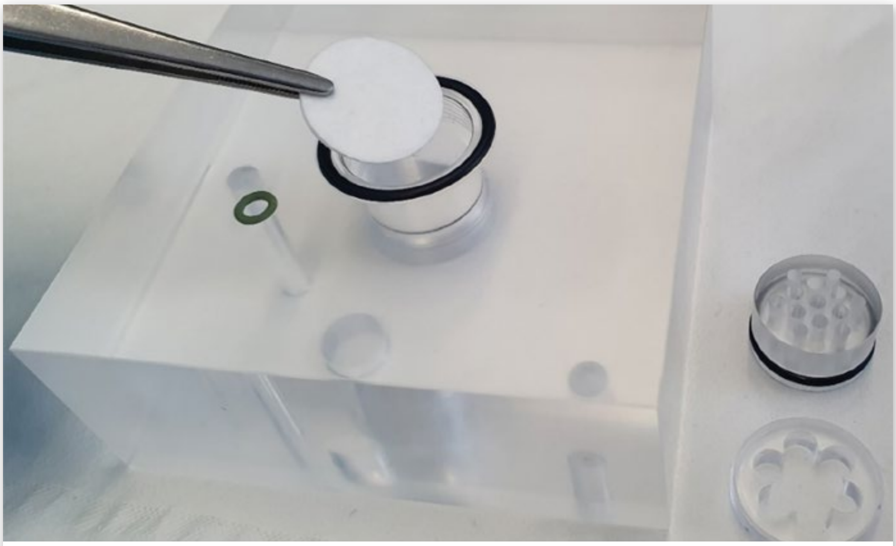


Fig. 4: Fibre measuring cell with compression transfer disc (top right) and compression disc (bottom right)

A compression transfer disc was inserted into the fibre measuring cell MC-ZPA/PF and tightened lightly. Two circles with a diameter of 19 mm were cut from the non-woven glass fibre sheet. The circles were then inserted into the measuring cell (Fig. 4). After this, the second set of compression transfer disc and compression disc were inserted and tightened lightly.

After fixing the cell to the ZPA 20, the storage vessel was filled with a KCl solution (1 mmol/L, pH ≅ 6). By using the 'bubble purging'-function of the ZPA 20, possible air bubbles in the measuring cell and in the device's streaming channel were be removed before starting the measurement. From the streaming potential vs. pressure ramps obtained in several oscillations (Fig. 3), the zeta potential was calculated for the given pH values. For each of a solution's pH value, a measurement time of only few seconds is sufficient to generate results with excellent statistical quality underlining the benefits of the new method, based on a bidirectional and oscillating solution flow. Thanks to the automatic titration function of the LDU 25 liquid dosing unit from DataPhysics Instruments (Fig. 5), the zeta potential can be determined automatically in the pH range from 2.8 to 9.6. Titrations were done once from the neutral to the acidic range and once from the neutral to the alkaline range. As titrants, HCl (0.1 mol/L) and KOH (0.1 mol/L) solutions were used.

After the measurement, the device and the measuring cell were thoroughly cleaned using ultra-pure water, which was especially easy since no pipes are used in the ZPA 20, reducing the surface area and complexity of the parts.

Results and Discussion

Fig. 6 shows the zeta potential of the glass fibre sample as function of the pH value. The curve shows the typical decrease of the zeta potential from positive values at low pH values to negative values at increasing pH values. This is partly an effect of the dissociation of functional groups, but also of the pH-dependent adsorption of H_3O^+- and OH^--ions.

An important parameter for the verification of dissociable functional groups is the so-called isoelectric point, i. e. the pH value at which the zeta potential is zero. An isoelectric point below pH 4 and a plateau in the alkaline range indicate acidic surface groups, an isoelectric point above pH 5 and a plateau at low pH values are characteristic for alkaline groups. Isoelectric points around pH 3 and 4 are obtained for primarily uncharged or amphoteric surfaces. In Fig. 6 an isoelectric point at a pH value of 3.3 can be seen, indicating the presence of acidic hydroxyl groups on the glass fibre surface.

Additionally, the pH value at the isoelectric point is consistent with the reported value for standard glass fibres[1], confirming the high reliability of the zeta potential measurement with the ZPA 20. In addition, there is a well-established zeta potential plateau in the alkaline pH range of 6 to 10.

Fig. 5: The LDU 25 liquid dosing unit allows operators to change the concentration of the solution automatically.

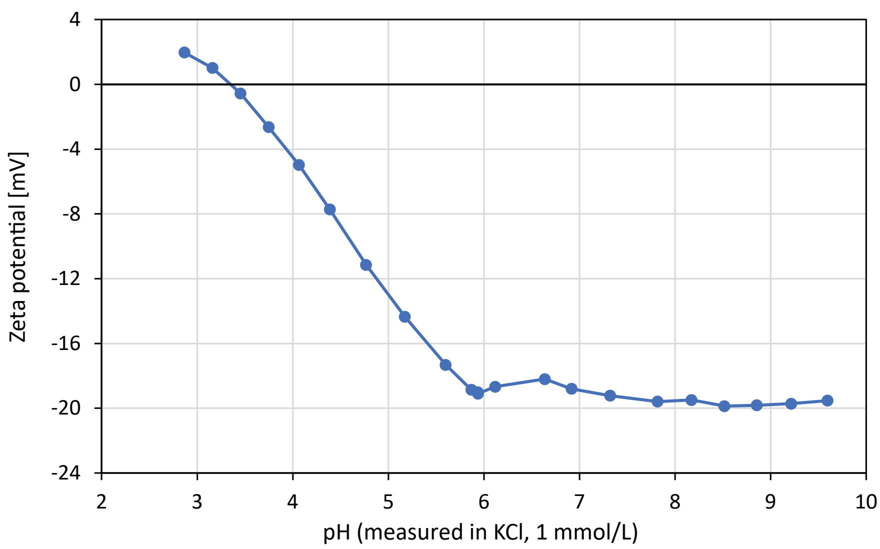


Fig. 6: Zeta potential of a glass fibre surface as function of the solution's pH value

This suggests that all acidic hydroxyl groups are fully dissociated creating a negative surface charge in the neutral to alkaline pH range.

A look at the measurement diagram in Fig. 3 shows that the bidirectional pressure ramps formed an even, sinusoidal curve, giving the operator a clear indication that the sample was packed well and homogeneously. In view of the often-challenging preparation of a homogeneous sample layer for zeta potential measurements, the bidirectional approach easily reveals any issues that stay unnoticed when using unidirectional measurement techniques.

Summary

Using the ZPA 20 zeta potential analyzer from DataPhysics Instruments and the patented oscillating streaming potential technique, the pH-dependent zeta potential and isoelectric point of a glass fibre surface were determined easily and reliably. This technique helps to identify functional groups on the glass fibre surface as well as those created by sizings or other modifying agents. This is very important in various application areas, such as the surface modification of glass fibres for fibre-reinforced polymers, studying the adhesive behaviour between glass fibres and coatings, or to prevent defects in manufacturing. The article furthermore showcases the beneficial effects of the bidirectional measurement principle regarding sample preparation verification and measurement speed compared to other methods.

References

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DataPhysics Instruments GmbH • Raiffeisenstraße 34 • 70794 Filderstadt, Germany
phone +49 (0)711 770556-0 • fax +49 (0)711 770556-99
sales@dataphysics-instruments.com • www.dataphysics-instruments.com

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