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The zeta potential of textile fabrics: a review

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The electrostatic interaction of a material surface with solutes in an aqueous solution plays an important role in many textile processes such as dyeing or finishing. The surface charge of textile fibers is driving this electrostatic interaction. Knowledge of the surface charge is accessible through the analysis of the surface zeta potential, which again is assessed by the measurement of the streaming potential. We explain the principle of the surface zeta potential analysis and highlight challenges in the streaming potential measurement of textile fabrics. A review of applications of the zeta potential in state-of-the-art textile research reported in the scientific literature is complemented by our recent results obtained for flame-retardant cotton-modacryl fabrics and the analysis of the adsorption and desorption kinetics of fabric softeners.
Key words*: surface charge, zeta potential, streaming potential, knitted fabrics*

1. Introduction

Whenever a solid surface is brought into contact with an aqueous solution, surface and solid-water interfacial charge are generated spontaneously. The charge distribution at the solid-water interface drives the electrostatic interaction between the solid surface and solutes contained in the aqueous solution. For small particles or tiny fibres in dispersions, surface charge may be directly determined either by a potentiometric titration [1] or by using a particle charge detector [2]. For any other solid material, the analysis of surface charge is restricted to an indirect assessment of the zeta potential. Besides monitoring surface and solid-liquid interfacial charge, the zeta potential may be used as a sensitive indicator for the interaction between solutes contained in an aqueous solution and the solid surface. Such processes are important in textile application and comprise of the detection of the adsorption of surfactants (e.g., of fabric softeners, laundry detergents), dyestuff molecules, polyelectrolytes, and even nanoparticles.

We report on case studies for textile treatment and surface modification, which employ the surface zeta potential as an indicator for changes in the surface charge of textile fabrics during and after applying these processes.

2. Surface zeta potential

In colloidal dispersions and emulsions the zeta potential is determined from the measurement of the electrophoretic mobility or of an electro-

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acoustic effect [3] and primarily employed to estimate the long-term stability of such colloidal systems. For macroscopic solid surfaces, the zeta potential is calculated from the measurement of the streaming potential and of the streaming current [4] and a useful indicator for surface charge and surface functional groups. The theoretical background of the zeta potential is common for colloids and solids and based on the model of the electrochemical double layer (EDL) at the solid-liquid interface. Fig.1 shows a schematic drawing of the interfacial charge distribution at a solid-water interface. The surface charge, generated, e.g., by the interaction of water with surface functional groups, gets partially compensated in a stagnant layer of water and counter-ions. Full compensation of the surface charge requires additional counter-ions that are accumulated in the diffuse layer. The distribution of counter-ions (cations in Fig.1) and co-ions (anions in Fig.1) in this diffuse layer differs from the ion distribution in the bulk aqueous phase. Upon a relative motion between the solid and the liquid phase, an electrokinetic effect is established. The measuring parameters of electrophoretic mobility or streaming potential mentioned above belong to the series of such electrokinetic effects.

Streaming potential occurs when liquid flows through a capillary that is formed by the solid material. A pressure difference applied between both ends of such capillary drives the liquid flow through this capillary. The interfacial charge distribution gets disturbed in such a way that surface-charge compensating ions of the diffuse layer move in the direction of the liquid flow. An excess of charges with a sign determined by the surface charge remains, which leads to a charge separation and furthermore to the formation of an electric potential. This streaming potential U_{str} is related to the pressure difference Δp according to Eq. (1). In the correlation factor we find the zeta potential ζ as the representative contribution from the solid surface.

$$\mathrm{d}U_{str} = \zeta \times \frac{\varepsilon \times \varepsilon_0}{\eta \times \kappa_B} \times \mathrm{d}\Delta p \quad (1)$$

In Eq. (1), ε_0 is the permittivity in free space, ε and h are the dielectric coefficient and the viscosity of water, respectively, and κ_B is the conductivity of the aqueous solution. The model of the EDL introduces several boundary conditions for the streaming potential analysis, which are hardly fulfilled by technical material samples. Among these we find the requirement of a flat surface with an infinite extension. This is certainly not the case for textile fabrics. Secondly, the solid surface must be non-porous and non-conductive. Natural fibres with an open structure and a certain swelling propensity or fabrics definitely con-

tradict this requirement. Nevertheless we succeed in using the zeta potential as an indicator for surface charge and for processes at the solid-water interface such as liquid-on-solid surface adsorption or desorption.

The restrictions of the model of the EDL are mainly applicable to the calculation of the zeta potential. There are certain extensions of the theory of Helmholtz and Smoluchowski, which relates either the streaming potential or the streaming current measurement to the surface zeta potential. As early as in the 1920s, Fairbrother and Mastin [5] introduced a simple approach to correct for the effect of surface or interfacial conductance in the evaluation of the zeta potential from streaming potential measurement of fibrous samples. They suggested to suppress the effect of surface conductance by determining the cell constant of a fibre plug at high ionic strength. However, what they did not consider is the additional ionic conductance introduced by the porosity of natural fibres [6] that changes with the ionic strength of the aqueous solution. Even for a porous material such as textile fabrics with a macroscopically flat surface, where streaming current measurement can be applied, the effect of streaming current inside the porous structure of such samples was considered only recently [7]. For the analysis of the surface charge and of surface functional groups for complex material surfaces, it is therefore recommended to apply the measured parameters of streaming potential or streaming current [8] instead of the zeta potential.

3. Experimental

The aim of this paper is to review past and recent results for the zeta potential analysis of textile fabrics. Streaming potential measurements of plugs of fabrics were performed with either the EKA Electro Kinetic Analyzer (available in 1990-2005) or the SurPASS instrument (available in 2006-2015) of Anton Paar, Austria. Prior to
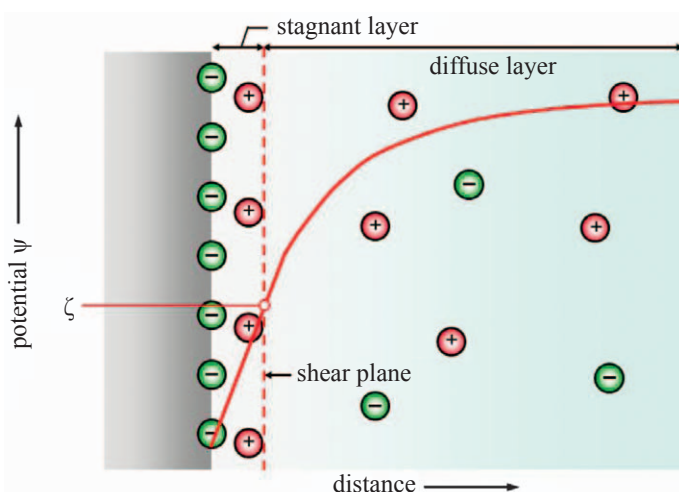

Fig.1 Model of the electrochemical double layer at the solid-water interface.

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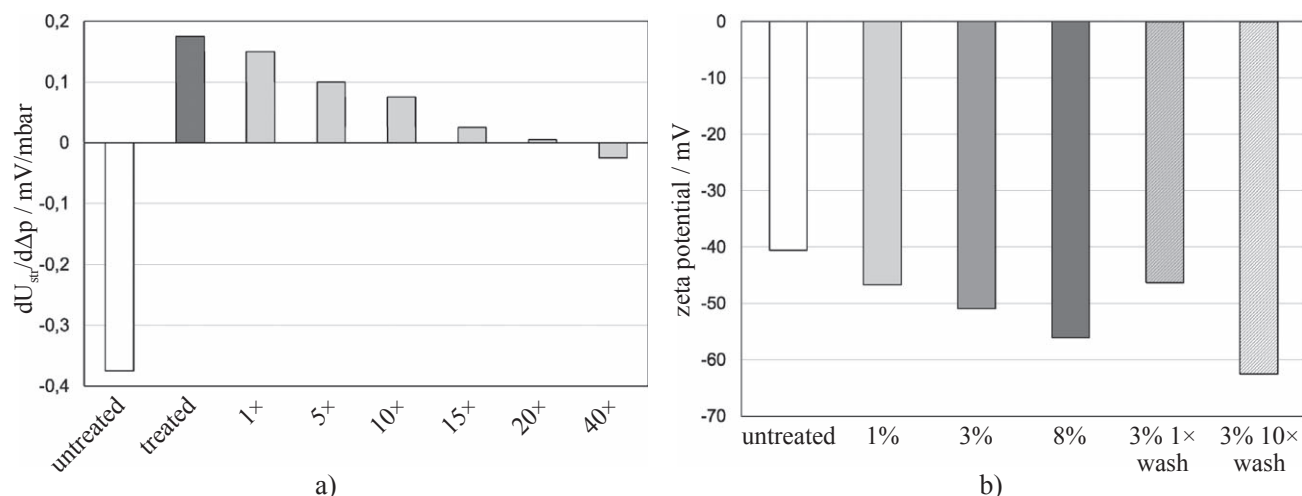*Tekstil* **65** (9-10) 346-351 (2016.)

Fig.2 Effect of washing cycles on the durability of: a) cotton fabric treated with positively charged nanoparticles (pH 6) [13] and b) pantyhose treated with microcapsules (pH 9) [14]

the availability of a commercial instrument for surface zeta potential analysis, various research groups have used a self-made streaming potential apparatus for the surface characterization of textile fibres. A cylindrical cell was used for the sample mounting, whose design is also different for EKA and SurPASS.

The experimental conditions may deviate from the standard protocol of using a dilute aqueous solution of a 1:1 electrolyte such as NaCl or KCl at an ionic strength of 0.001 mol/l. Deviations from these conditions are indicated. A common approach is the evaluation of the pH dependence of surface charge, which is accomplished by adding dilute acid or base with a concentration of 0.05-0.1 mol/l to the measuring solution. The pH dependence of the zeta potential reveals the isoelectric point of the material-water interface, i.e., the pH of the aqueous solution where $\zeta = 0$ mV and thus the interfacial charge diminishes.

4. Discussion of results

The focus of first applications of the streaming potential for textile fibre and fabric characterization was primarily an assessment of processes such as the adsorption of surfactants [9] or pretreatment of cotton, e.g. scouring and mercerization [2, 10, 11]. The corresponding zeta potential

data has been reviewed [12]. More recently the focus was drawn on the introduction of functional groups to the fabric surface.

4.1. Adsorption of nanoparticles

A possible route for the functionalization of textile fabrics is the attachment of nanoparticles or microcapsules to the fabric surface. Ripoll et al. have used the streaming potential as an indicator to assess the kinetics of adsorption of positively charged nanoparticles on cotton and polyamide fabrics [13]. After modification of these fabrics with nanoparticles, they looked at the durability during a series of wash cycles. A similar study was reported by Luxbacher et al. on the removal of microcapsules from pantyhose after 1, 3, and 10 wash cycles [14]. Fig.2 compares the results of these studies. The use of nanoparticles with strongly cationic functional groups by Ripoll et al. [13] gives evidence for the release of nanoparticles by the zeta potential analysis in a wide pH range. However, the negative charges of both microcapsules and pantyhose require a pH scan of the zeta potential to determine the measuring conditions that reveal the most significant difference between samples. The zeta potential was thus recorded at pH 9. Note that after 10 wash cycles, the detergent obviously changes the properties of

the polyamide fabric of the pantyhose.

4.2. Textile care

Durability of surface treatment is a requirement, which thus can be addressed by the surface zeta potential. On the other hand, the ability to observe the removal of a deposit from a textile fabric is important for an evaluation of the washing efficiency of detergents. Luxbacher et al. [15] have shown the changes in the surface zeta potential of cotton knitted fabrics stained with blood to illustrate the effect of a standard detergent and the cleaning enhancement at 60 °C. The zeta potential of a standard test strip of raw cotton (empa testmaterials, Switzerland) was employed as reference data for the zeta potential obtained after laundering raw cotton test strips stained with blood.

Fig.3 compares the pH dependences of the zeta potential for virgin and blood-stained raw cotton fabrics after washing with a standard detergent at a bath temperature of 60 °C. Despite of the small range of ± 10 mV obtained for the zeta potential of these fabrics, we can clearly distinguish the surface properties of the different samples. We conclude on a partial removal of blood stain after a conventional wash cycle because a standard detergent does not contain enzyme protease that is a key ingredient

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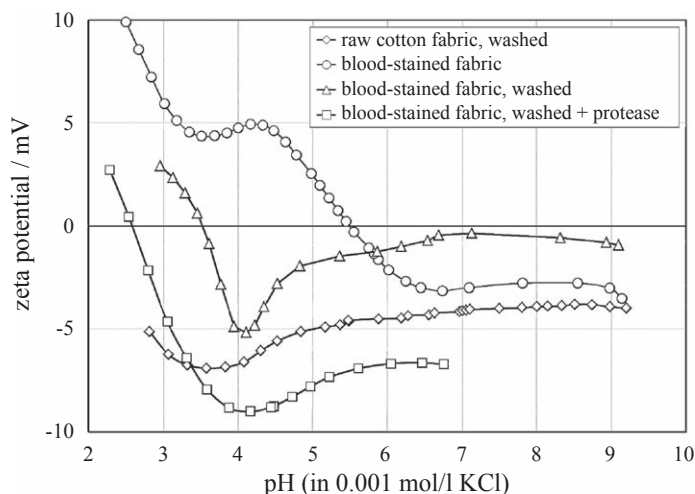*Tekstil* **65** (9-10) 346-351 (2016.)

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Fig.3 pH dependence of zeta potential for raw cotton knitted fabrics. Comparison of pristine and blood-stained fabrics after laundering with a conventional detergent and with a detergent containing protease [15]
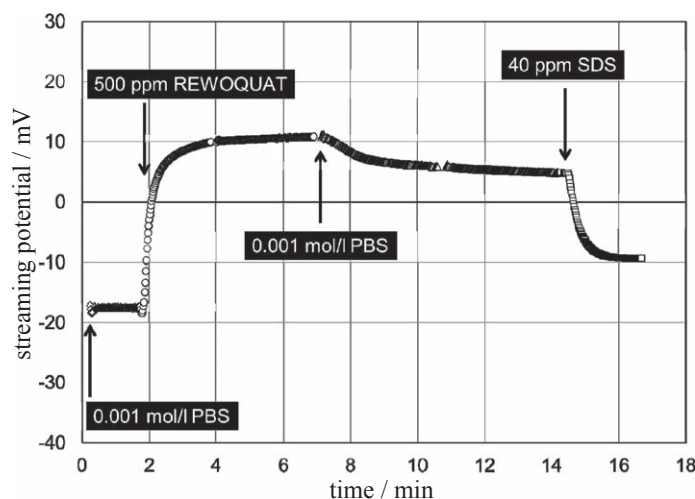

Fig.4 Adsorption and desorption kinetics of fabric softener containing esterquat in a cotton-modacryl knitted fabric monitored by the streaming potential [16]

a concentration of 500 ppm esterquat was added to the solution and exposed to the fabric. The initially fast adsorption process slows down and approaches equilibrium after 2 min. Subsequent rinse with fresh buffer solution indicates partial removal of the cationic surfactant. The added concentration obviously introduced an excess for the fabric surface provided by the sample. However, the softener-treated fabric remained positively charged until a harsh treatment with the anionic surfactant sodium dodecyl sulphate (SDS) triggered a more efficient removal. Even after rinse with PBS solution containing 40 ppm SDS, the streaming potential did not return to the initial value of the untreated cotton-modacryl fabric.

4.3. Heterogeneous material surfaces

The scope of the analyses of softener adsorption on knitted fabrics included the investigation of the effect of blend composition by using the surface zeta potential. The significantly different surface properties of cotton, i.e., a natural cellulose-based fibre, and modacryl, i.e., a man-made polymer fibre, enables the clear differentiation of the fibre-water interfacial charge. Cotton fibres exhibit acidic functional groups such as hydroxylic and carboxylic, are porous, hydrophilic, and show swelling in water. Modacryl fibres show opposite properties. They are non-porous, hydrophobic, and do not exhibit a significant number of surface functional groups. These differences are reflected by the surface zeta potential. The properties of cotton lead to a negative zeta potential, which gets estimated too low when calculated by Eq. (1). Man-made polymer fibres commonly exhibit a strongly negative zeta potential due to the accumulation of water ions (hydroxide and hydronium) at the polymer-water interface [17].

Fig.5 shows the pH dependence of the zeta potential for a series of cotton-modacryl knitted fabrics with dif-

for a removal of proteinaceous stain. A comparison with the zeta potential for the raw cotton fabric and for bleached cotton [11] let us assume that protease not only removes blood stain but also non-cellulosic compounds of the raw cotton fabric.

Related to the laundry process is the application of a fabric softener on textiles. Luxbacher et al. [16] have monitored the charge reversal for fabrics knitted from blended yarn of cotton and modacryl. The changes in the surface charge were recorded with time during the adsorption process. The streaming potential, generated at a constant pressure difference applied between both ends of a plug of the fabric sample, was used to indicate the adsorption kinetics of an esterquat softener. Since this cationic surfactant affects the pH of the dilute aqueous solution of 0.001 mol/l KCl even at low concentration, a phosphate buffer (PBS) was utilized to stabilize pH. Changes in the streaming potential are thus solely related to the deposition of esterquat on the surface of the cotton-modacryl fabric. Figure 4 shows a typical scan of the adsorption and desorption process for esterquat on a knitted fabric with 60 % cotton and 40 % modacryl. After stabilizing the fabric sample in phosphate buffer,

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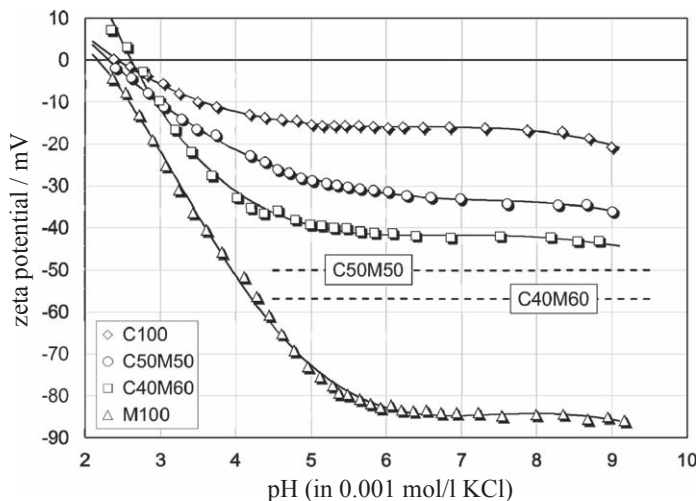*Tekstil* **65** (9-10) 346-351 (2016.)

Fig.5 pH dependence of zeta potential for cotton-modacryl knitted fabrics with different composition (dotted lines indicate the estimated zeta potential for cotton-modacryl blends by assuming equal contributions of cotton and modacryl fibres)

ferent composition. In this case we refer to the negative zeta potential at medium and high pH rather than to the IEP in order to distinguish between the different fabrics. In addition to the experimental data, the dotted lines in Figure 5 indicate the predicted results for cotton-modacryl blends C50M50 (50% cotton, 50% modacryl) and C40M60 (40% cotton, 60% modacryl) assuming equal contribution of cotton and modacryl to the surface zeta potential. Obviously the cotton fibres dominate the zeta potential of the cotton-modacryl blends. We interpret this result by the increased surface area of the porous cotton fibres as compared with modacryl fibres. Although surface area does not affect the zeta potential analysis when looking at an individual material surface (since z is related to the interfacial charge density), the ratio of corresponding surface areas has to be considered for the investigation of heterogeneous sample configurations consisting of two or even more materials.

5. Summary and outlook

The analyses of the zeta potential reported in this paper demonstrate the evolution of its use in textile characterization from classical textile pro-

cesses, such as pretreatment, towards tuning fibre and fabric surface properties for high-end applications. Nowadays the scope of textile research expands towards the use of textiles for membrane filtration or biomaterials. Besides the verification of surface modification and surface treatment, the zeta potential is a powerful indicator for solute-on-surface adsorption processes. Monitoring the interaction of solutes, ranging from molecules to nanoparticles, with fabric surfaces introduces an exciting application for the surface zeta potential analysis. Protein interactions with textile scaffolds for tissue engineering or with fabrics for wound dressings, or the deposition of foulants on the surfaces of fabrics for water treatment are representative examples for current and future studies.

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