INVESTIGATION OF COMPETITIVE ADSORPTION OF FIBRE SIZING COMPONENTS: POSSIBILITIES OF ELEKTROKINETICS

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Abstract
Electrokinetics are a convenient tool for characterizing surface properties of solids, but also for studying adsorption processes on such surfaces. One topic of our interest was the sizing mechanism of glass fibres. With the help of electrokinetic measurements we found an interesting change of surface properties of glass fibres depending on the size composition. In the case of adsorption of AMEO (γ-aminopropyltriethoxisilane) the surface has strong basic properties with an isoelectric point (IEP) of $pH_{IEP} > 9$. In the case of modification with a mixture of AMEO and surfactant (in our case alcyltrimethylammoniumchloride) the IEP changes to $pH_{IEP} = 6.3$. The shape of the function zeta potential versus pH corresponds to a curve of surfaces without any functional groups. This result was astonishing. Due to the cationic functional groups of the AMEO and the surfactant a high polar cationic surface was expected.

1 Introduction

The mechanical behaviour of composite materials is determined by the properties of the reinforcing fibre, the polymer matrix and the interface between fibre and matrix. The matrix will be reinforced only in case of a high level of stress transfer between fibre and polymer matrix.

For increasing the adhesion forces in the interface of glass fibre reinforced materials, coupling agents are used. But the coupling agent is only one part of a sizing system which is responsible for good processing properties in the entire process chain. Furthermore, for reaching a good performance in the finale composite the sizing has to be optimised [1]

Normally, the glass fibre sizing is a multi-component system consisted of silane coupling agent (~10%), film former (~79%), lubricant (~4%), emulsifying surfactant (~4%), and anti-stats (~3%) in water and were applied to glass fibre prepared directly from molten glass [2]. In case of E-glass fibre, ~5 wt% of the sizing mixture in water is applied. This composition is the result of a long time of experience in glass fibre industry. Much research has focused on the effects of silanol coupling agent on polymer/glass interactions [3-6]. But, it is known nothing about action mechanisms of this multi component mixture. Until now, nobody was looking to the influence of surfactants on the adsorption process and the effectiveness of the coupling agents.

Investigations of the adsorption of various components of the preparation show interesting effects through competitive adsorption of various parts of the finish mixture [7]. Own research results in the field of ageing effects of sizing indicate similar effects for sizing

mixtures [8]. To study such adsorption process, only two components of a glass sizing will be regarded: the coupling agent and the lubricant.

2 Materials and testing methods

2.1 Material

E-glass fibres were manufactured using the continuous spinning equipment at the Leibniz Institute of Polymer Research (IPF) and sized immediately after cooling in the continuous spinning process. For sizing γ-aminopropyltriethoxysilane (AMEO) as coupling agent and oleyltrimethylammoniumchloride (Arquad S 50) as cationic lubricant were applied. For comparison, a second cationic lubricant with a shorter alkyl chain was utilized: dodecyltrimethylammoniumbromide (DDTMABr).

2.2 Methods

Electrokinetic measurements are known as a comfortable method for investigations of surface properties of solids [9]. But it is also possible to study adsorption processes at solid surfaces with this method [7]. Systematic studies of surfactant adsorption showed the possibilities of streaming potential measurement [10]. It was possible to confirm the four-region model of surface adsorption according to Fuerstenau [11]. The streaming potential measurements we carried out with the Electrokinetic Analyser (EKA) by A. Paar GmbH, Graz, A using the Cylindrical Cell, which was developed for the measurement of fibrous, but also of granular and powder samples [12]. The fibre plug was build between a pair of perforated Ag/AgCl disc electrodes. The measuring fluid was streaming through this fibre plug and the streaming potential U was determined. The electrokinetic- or zeta-potential ζ was calculated according to Smoluchowski [13]

$$\zeta = -\frac{dU}{dp}\frac{\eta\kappa}{\varepsilon_r\varepsilon_0} \tag{1}$$

with p as the pressure loss in the cell, ε_r and ε_0 as dielectric constant and vacuum permittivity, η as the viscosity and κ as the conductivity of the measuring fluid.
In case of adsorption measurements the adsorptive will be titrated to the electrolyte solution.
The atomic force microscope (AFM) Dimension 3100 with Nanoscope IV controller by Veeco Instruments GmbH, Mannheim was used as surface imaging tool. The topography of the samples was studied in tapping mode.

3 Results and Discussion

Electrokinetic measurements of different treated glass fibres show different functionalities at the surface (Fig.1).
Fibres coated with the coupling agent have alkaline functional groups at the outermost surface whereas the coating with a mixture of coupling agent and surfactant creates a mixture of anionic and cationic dissociable functional groups at the outermost surface. It is to assume that the adsorption process of the coupling agents will be influenced by the surfactant. So we studied the adsorption process of these two agents by streaming potential measurements (Fig.2 and 3).

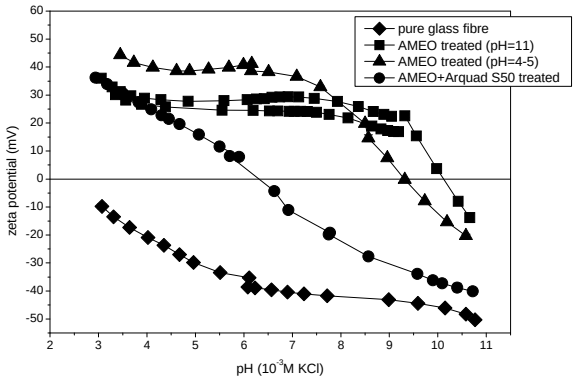

Fig. 1: Streaming potential measurements of different treated fibres

In both case can be shown the competition of the two adsorption partners. In addition it is to consider, that amino-silane has two possibilities for docking on the glass surface: the silanol groups and the amino-groups. Thomason could show that the molecule rotates during the adsorption [1].

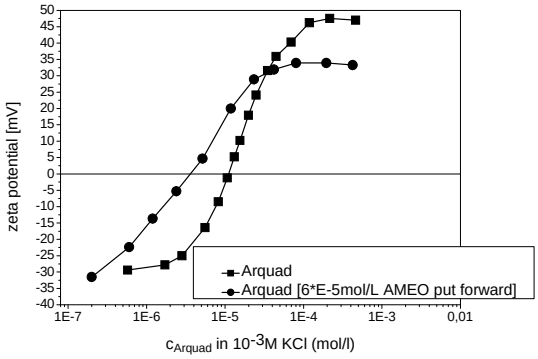

Fig. 2: Adsorption of the surfactant

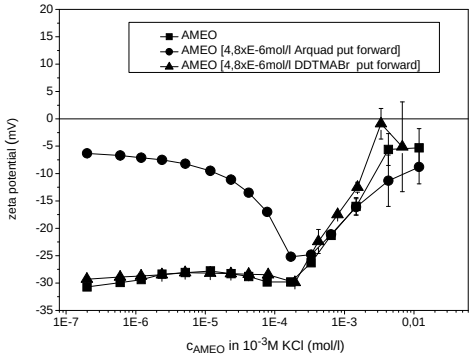

Fig. 3: Adsorption of the coupling agent

On the other side the adsorption of the mixture of surfactant and coupling agent creates structured surfaces as shown by AFM investigation (Fig. 4 and 5).

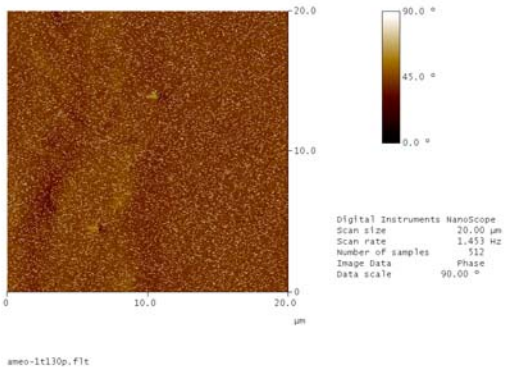

Fig. 4: Phase picture of AMEO adsorption layer

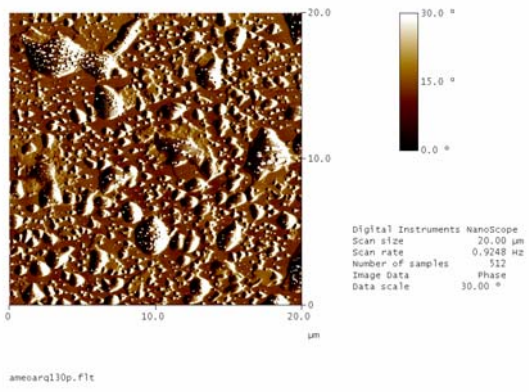

Fig. 5: Phase picture of AMEO/Arquad adsorption layer

In the end of our investigation we could show, that the adsorption process of amino-silane and cationic lubricant is a competitive process. Electrokinetic and topographic tools were qualified for studying of adsorption processes. Structural and chemical changes were observed. Influence parameters as concentration, chain length, and carrier liquid were quantified.

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