Formation Mechanism of Silane-PVA/PVAc Complex Film on Glass Fiber Surface

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Mechanical properties of glass fiber reinforced composite materials are affected by fiber sizing. A complex film formation, based on silane film and PVA/PVAc (polyvinyl alcohol/polyvinyl acetate) microspheres on glass fiber surface is determined by means of (i) nano-scale by using atomic force microscopy (AFM), and (ii) macro-scale by using zeta potential. Silane strongly bonds through the Si-O-Si bond to the glass surface providing the attachment mechanism as a coupling agent. The silane forms islands, homogeneous film, as well as empty sites. The value of average roughness for silanized surface changes to 6.5 nm from unsized glass surface with only 0.6 nm. The silane film then vertically penetrates in a honeycomb fashion from the glass surface through the deposited PVA/PVAc microspheres forming a hexagonal close pack structure. The silane film not only penetrates, but also deforms the spheres from a dispersion (600 nm) to a ellipsoidal shape on the surface. The surface area value $S_{\text{glass}}$ represents an area of PVA/PVAc microspheres which are not affected by the silane penetration, changes as 0.2, 0.08, and 0.03 $\mu$m$^2$ and the ellipsoids size are 320/570, 300/610, and 270/620 nm for silane concentrations of 0, 3.8, and 7.2 $\mu$g/ml, respectively. The silane film also moves PVA/PVAc microspheres in the process of the complex film formation from the low silane concentration areas into the complex film area providing enough silane to stabilize the structure. The values of residual silane honeycomb structure height $H_s$ are 6.5 nm, 7 nm, and 12 nm for the silane concentrations of 3.8, 7.2, and 14.3 $\mu$g/ml, respectively. The pH dependent zeta potential results suggest a specific role of the silane with effects on the glass fiber surface and also on the PVA/PVAc microspheres. The unsized glass fiber surface and the silane film have similar zeta potentials ranging from -64 mV to -12 mV at the pH range of 10.5 and 3, respectively. The zeta potentials for the PVA/PVAc microspheres on the glass fiber surface and within the silane film significantly decrease and range from -25 mV to -5 mV. The shapes of the pH dependent zeta potentials are typically different in the case of silane in the pH range from 7 to 4. A triple layer model is used to fit the unsized glass surface and the silane film. The value of surface site density for $\Gamma_{\text{glass}}$ and $\Gamma_{\text{silane}}$, where X states for Al-O-Si, differs by factor of $10^4$ suggesting an effective coupling of the silane film. A soft layer model is used to fit silane-PVA/PVAc complex film which is approximated with four layers. Such a simplification and a compensation of the microsphere shape approximate the relevant lengths as the layer of silane with 10% of the total length (27 nm), the layer of first PVA shell with 30% (81 nm), the layer of PVAc core with 30% (81 nm), and again the layer of second PVA shell with 30% (81 nm). The coverage simulation resulted in the value of 0.4, in accord with the assumption of the low order coverage, and indeed it is supported by the AFM scans. Correlating the results of AFM, and zeta potential shed some light on the formation mechanism of the silane-PVA/PVAc complex film.

Introduction

Mechanical properties of fiber reinforced composite materials are greatly affected by bond strength at fiber-matrix interface. The bond strength at the interface depends on distribution of functional groups and the specific topography. Both of these properties are strongly dependent on controlled chemical modification of the fiber surface.

The glass surface modification is usually based on a multi-component system consisting mainly of a coupling agent which improves the bond quality[1] and a film former. The combination of components improves the fiber strength and other properties of the final composite.[2] In addition, lubricants reduce fiber to fiber friction and prevents possible damage of the fiber during the manufacturing processes. In general, the fiber sizing consists of the coupling agent with 5-10 wt %, usually silane compounds, the film former with 80-90 wt %, and additional components with 5-10 wt %.[3] Dependence of the silane coupling agent on interaction with parallel fibers and polymer matrix has been reported.[4] The reactive adhesion at the interface between the fiber and the matrix is based on chemical, mostly covalent bonds, physical, mostly polar interactions, and mechanical roughness of the surface.[5] Silane functional groups react with the surface of the glass fibers primarily through hydrogen bonds forming covalent bonds.[5] Hydrolysis of alkoxy functional groups allow silane coupling agents to react with the glass fiber surface and with each other to form multi-layered polymer film on the surface.[5-8]

The first layer of silane coupling agent is chemically bound to the glass fiber surface through Si-O-Si covalent bonds.[7]

Approximately 10 next layers are chemisorbed as polysiloxane film and further layers are physisorbed silanes, mainly as monomers, and oligomers.[9]

Polyvinyl alcohol/Polyvinyl acetate (PVA/PVAc) microspheres were used as the film former. The PVA/PVAc structure forms a core-shell microsphere. The PVA is partially soluble in the aqueous phase, forming the outer shell. The PVAc is water not compatible polymer phase, forming the spherical core. The PVA/PVAc microspheres synthesis is typically performed by the suspension polymerization of vinyl acetate to produce PVAc, followed by the saponification of the PVAc particles. PVA/PVAc microspheres are synthesized in a sequential two-stage process. In the first stage, the suspension polymerization of vinyl acetate is carried out in a batch reactor. In the second stage, PVA/PVAc microspheres are prepared by the partial saponification of PVAc beads.[10]

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Atomic Force Microscopy (AFM) has proven to be an excellent tool for high-resolution surface characterization. AFM is non-invasive technique providing quantitative measurements of morphology, studying the sample in real time with high spatial resolution, as well as measuring the physical properties on the nano-metric level. AFM is a scanning technique providing very high resolution 3-D scans of sample surface. The measurements can be performed in contact, non-contact and also in semi-contact modes. In the semi-contact mode, which is also known as intermittent or tapping mode is probe forced to oscillation near its resonant frequency. Adhesive Van der Waals forces and repulsive forces between the oscillating probe tip and sample surface are measured by amplitude variations of frequency in topography mode and phase shift of frequency in phase imaging mode. The benefit of phase imaging mode is phase signal sensitivity to variations in composition, adhesion, friction, and viscoelasticity. AFM is very suitable technique for studying also the morphology of polymers. AFM has been successfully used to characterize the glass surface coated with different silane coupling agents and other components of the fiber sizing.

The pH-dependent zeta potential measurements can be applied to characterize the surface of sized fiber. A contact between the fiber surface and solution generates a distribution of surface charges, which differs from the surface to the liquid phase. The accumulated surface charges form an electrochemical double layer. The layer oriented towards the liquid phase is divided into the immobile Stern layer, where the charge carriers are fixed on the solid/liquid interface, and the mobile or diffuse layer, where the charge carriers are subject of thermal movement. The zeta potential is then the voltage difference between a plane of the surface and the solvent beyond the double layer. The zeta potential depends on the surface charge density and the double layer thickness. The surface charge density depends on the concentration of “potential determining ions” in the solvent which have a particular affinity for the surface, as H+ ions in many systems. Therefore the zeta potential depends on pH and reflects the chemical character of surface groups due to acidic/basic groups. The zeta potential characterizes the fiber sizing as the interactions on surface and also provides a degree of surface coverage by the deposited polymers. To simulate the electro-kinetic effect for clay minerals, glass, or silica, a triple layer model can be used. The electrical phenomena of soft particles was also widely studied, based on Poisson-Boltzmann equation for the potential in the polymer layer and Navier-Stokes equations for the liquid flow. The polymer segments are regarded in this model as resistant centers distributed in the polymer. However there are more options to model polymer as polymer dissociation, soft step for dissociated ions of PVA in polymer, and multilayer polymer.

In our contribution, the characterizations of the complex film based on silane and PVA/PVAc microspheres on glass fiber surface are presented: (i) at the nano-scale by using AFM, and (ii) at the macro-scale by using zeta potential. Silane strongly binds to the glass surface providing the attachment mechanism of PVA/PVAc microspheres at the surface. Since the details of interaction between the silane film and the PVA/PVAc microspheres are not well known, our study is focused to determine steps of the attachment mechanism. The aim is to obtain correlation between the surface topography, using AFM measurements due to its performance of high-resolution surface characterization and the surface charge, using streaming potential measurements as a measure of chemical composition.

Results and Discussion

AFM Surface Topography

Silane strongly binds through the Si-O-Si bond to the glass surface providing the attachment mechanism for PVA/PVAc microspheres at the surface.

In Fig. 1, the topography of the glass fiber surface is shown for different measurement conditions of the silanization process. The histograms inset of Fig. 1 represents an average roughness \( R_a \). The average roughness is the arithmetic average of the absolute values of the surface height deviations. The first scan of Fig. 1, assigned as A, corresponds to the unsized glass fiber surface. As expected, we observed relatively neat and smooth surface of the unsized glass fiber, where the value of \( R_a \) is 0.6 nm. The activation process with acetic acid, used also as hydrolysis agent for silane, resulted in a slightly rougher surface as shown in Fig. 1 and assigned as B. This result might be explained by a simple hydrolysis of the Si-O bonds on the surface which might result in an enhancement of natural defects on the glass fiber surface, yielding slightly more heterogeneous and rougher topography. Although the value of \( R_a \) is only 0.7 nm for the B sample, the local defects are clear in comparison with the A sample in Fig. 1. Finally, the scan, assigned as C in Fig. 1, shows the silanized glass fiber surface after deposition of silane. The silane generates a structured topography forming islands on the glass fiber surface. In general, these silane films usually resulted in the island topography, dependent on the silane deposition conditions as concentration, temperature, and deposition time. Concluding, the silane on the glass fiber surface seems to have distributions where besides the islands, the homogeneous film areas are also observed, as well as the empty sites might be considered.

Figure 1. AFM topography images of glass fiber surface, before acetic acid activation (A), after acetic acid activation (B), and after silane deposition (C). Histogram insets show comparison of average roughness \( R_a \) in nm.

Figure 2. AFM phase images and illustration insets of glass fiber surface after deposition of PVA/PVAc microspheres (D), and after deposition of PVA/PVAc microspheres and silane solution (different concentrations E1, E2, and E3).
The interaction of the silane film with the PVA/PVAc microspheres is the base of a complex film formation. Silane acts as a coupling agent between the glass surface and PVA/PVAc microspheres. The silane film is formed from polymerized silane molecules, strongly bound through Si-O-Si bond to the glass surface. A role as the coupling agent is based on interaction with PVA/PVAc microspheres, which represent the film former. The details of the silane-PVA/PVAc interaction are shown in Fig. 2 and Fig. 3. The silane film penetrates in a honeycomb fashion from the glass surface through the PVA/PVAc microspheres forming a hexagonal close pack structure. The result of the interaction is a formation of the complex film consisting of two separate domains corresponding to the silane film and the PVA/PVAc microspheres. Fig. 2 shows AFM scans at 4x8 µm in phase imaging mode of semi-contact mode and the insets represent an illustration of the interaction between silane honeycomb structure and seven PVA/PVAc microspheres forming the hexagonal close pack structure, and their cross section. The vertical penetration is shown in detail in Fig. 3, providing the 3-D scanning by using AFM in topography mode of semi-contact mode. The insets of Fig. 3 represent a result of the changing PVA/PVAc shapes from spherical to ellipsoidal. The illustrations in the insets of Fig. 3 provide also PVA/PVAc ellipsoids. Note that the vertical axis on the AFM scans in Fig. 3 is also 10 times increased in comparison with the horizontal axis, in order to emphasize the vertical penetration of silane through the PVA/PVAc microspheres. The first scans in Fig. 2 and Fig. 3, assigned as D, show only PVA/PVAc microspheres on the glass fiber surface. The scans in Fig. 2 and Fig. 3, assigned as E1 and E2, show an evolution of the complex film formation, as the silane concentration increased from 3.8 to 7.2 µg/ml, respectively. The complex film consists of two domains corresponding to the silane film which is vertically penetrating and the PVA/PVAc microspheres placed in the silane honeycomb network. The further evolution of the silane-PVA/PVAc complex film formation is shown in Fig. 2 and Fig. 3, assigned as E3 where the concentration of silane was increased to 14.3 µg/ml. The penetration reached a saturation providing even an overlayer of silane on the PVA/PVAc microspheres. The insets of Fig. 3, assigned as S0, define a surface area value. The surface area value represents the area of PVA/PVAc microspheres which is not affected by the silane penetration. The PVA/PVAc microspheres layer on the glass fiber surface without silane film, assigned as D in Fig. 2 and Fig. 3, form hexagonal close pack structure with the S0 value of 0.2 µm². The increasing silane concentration from 3.8 to 7.2 µg/ml resulted in the penetration through the PVA/PVAc microspheres structure. The penetration of initially prepared silane film, providing the S0 value of 0.08 µm², increased and therefore the S0 value decreased to 0.03 µm², as shown in insets of Fig. 3 assigned as E1 and E2, respectively. Note that the silane film not only penetrates through the PVA/PVAc microspheres structure, but also deforms the PVA/PVAc microspheres, as discussed below. Concluding, that the S0 value of PVA/PVAc microspheres decreases with increasing silane concentration, due to the increasing vertical penetration of silane.

PVA/PVAc microspheres are embedded in the silane film within the honeycomb structure which also causes a change in the shape of PVA/PVAc microspheres. The PVA/PVAc microspheres are being deformed from the spherical shape to an ellipsoidal shape. The insets of Fig. 2, and Fig. 3 represent an illustration of the interaction between silane and PVA/PVAc microspheres in a form of seven PVA/PVAc microspheres forming hexagonal close pack and the silane honeycomb structure. These insets of Fig. 2, and Fig. 3 provide also the vertical cross section of these seven microspheres and the honeycomb. The PVA/PVAc microspheres have spherical shape in a suspension and when they are adsorbed on the glass fiber, they change into the ellipsoidal shape. Due to surface interaction, the PVA/PVAc microspheres of approximately 600 nm size transform into the ellipsoids on the surface with approximate dimensions of 300/600 nm. The shorter dimension belongs to the microsphere size towards the vertical surface direction. Initially the size of PVA/PVAc ellipsoids on the unsized glass fiber surface was approximately 320/570 nm, as shown in insets of Fig. 2 and Fig. 3, assigned as D. The silane-PVA/PVAc complex film is formed from the silane-PVA/PVAc suspension. The formation of complex film is described in insets of Fig. 2, and Fig. 3, assigned as E1, E2, and E3. The increasing silane concentration resulted in the deformation of PVA/PVAc microspheres. The silane concentration of 3.8 µg/ml, resulted in the change of PVA/PVAc ellipsoids size to approximately 300/610 nm, as shown in insets and scans, assigned as E1. The increase of silane concentration to 7.2 µg/ml, resulted in only slight increase of PVA/PVAc ellipsoids deformation to the approximate size of 270/620 nm. Although the deformation of PVA/PVAc microspheres is slight, the vertical penetration is more significant, as observed in detail in Fig. 3, assigned as E2. The silane concentration of 14.3 µg/ml resulted in the further deformation of PVA/PVAc microspheres and the penetration even reached a saturation providing the overlayers of silane on the PVA/PVAc microspheres, as shown in insets and scans of Fig. 2 and Fig. 3, assigned as E3.

Interestingly, silane not only penetrates through the PVA/PVAc microspheres, deforms them, and eventually covers them with the overlayers, but silane might also move some of PVA/PVAc microspheres in the process of the complex film formation. The PVA/PVAc microspheres moving process leaves behind the honeycomb structure, suggesting that the silane film was in the contact with PVA/PVAc microspheres, as shown in Fig. 4. The
presence of residual silane honeycomb structure confirms also the proposed mechanism of the complex film formation on the glass fiber surface. The histogram inset of Fig. 4 shows the illustration of a residual silane honeycomb structure and also the values of residual silane honeycomb structure height (H6). The H6 values are 6.5, 7, and 12 nm for the silane increasing concentrations from 3.8, to 7.2, and up to 14.3 µg/ml, respectively. Note that the H6 values are relatively low in comparison with the penetration values up to 270 nm, as shown in Fig. 3 in the case of E2. These low values are the reason why the PVA/PVAc microspheres are moved on the surface due to a lower binding energy between silane film and PVA/PVAc microspheres, caused by the thin silane film on the glass fiber surface. The lower binding energy is in a competition with the higher binding energy, represented by the high penetration as shown in Fig. 3 as E2. The AFM scan and also the illustration in Fig. 3 as E2 clearly showed the result of such a competition, where the PVA/PVAc microspheres are moved from the low silane concentration areas into the complex film area providing enough silane to stabilize the complex film structure.

Zeta Potential Measurement and Simulation

The pH dependent zeta potential results of the unsized glass fiber surface (A), the silane film on the glass fiber (C), the PVA/PVAc microspheres on the glass fiber (D), and the PVA/PVAc microspheres within the silane film on the glass fiber (E2) are shown in Fig. 5. Note that sample E2 has silane concentration of 7.2 µg/ml, which is an average concentration used also for theoretical modeling of zeta potential. The pH dependence for all samples was measured from alkaline pH=10.5 to acidic pH=3 solutions, where the zeta potential increased from -65 mV to approximately -2 mV, respectively. An isoelectric point was not reached in this interval. Note that the pH might have a chemical effect on the surface during the zeta potential measurements. To eliminate such an effect, we have chosen to start measurements from alkaline solution since the glass fiber surface consists mainly of SiO and SiOH groups, where the alkaline OH ions might stabilize such a surface.

The unsized glass fiber surface (A) in the pH range from pH=10.5 to pH=3 had pH dependent zeta potentials which increased from approximately -64 mV to -10 mV, while the values in literature are -40 mV and 0 mV,[18] and -50 mV and -10 mV,[23] respectively. The values for silica in literature in the pH range from pH=10.5 to pH=3 are -70 mV and 0 mV.[24] The trend is clearly the same and the values are in good agreement taking in account an effect of the slightly different chemical composition of these glass surfaces. The unsized glass fiber surface (A) and the silane film on the glass fiber surface (C) had similar pH dependent zeta potentials which increased from approximately -64 mV to -12 mV. The highly negative zeta potentials at pH=10.5 for both samples suggest an effective separation between negative charge of SiO groups on the glass fiber surface and positive charge of H+/K+ cations present in the solution of zeta potential measurement. Interestingly, although the limit values are very similar, the shapes of zeta potentials are different in the same pH range from 7 to 4 resulting in opposite trends and forming kind of hysteresis. The trend in this pH range suggests that H+/K+ cations have higher affinity to unsized glass fiber surface than to silane film on the glass fiber surface. The zeta potentials for the PVA/PVAc microspheres on the glass fiber surface (D) and the PVA/PVAc microspheres within the silane film on the glass fiber surface (E2) significantly decreased in comparison with A and C, respectively. The significant change of zeta potentials is from -25 mV to approximately -5 mV at the pH range of 10.5 and 3, respectively. The shapes of the pH dependent zeta potentials for D and E2 are different also in the same pH range from 7 to 4. We suggest that in this pH range, H+/K+ cations have higher affinity to PVA/PVAc microspheres (D), than to PVA/PVAc microspheres within the silane film (E2). The shapes of the pH dependent zeta potentials for D and E2 are different also in the same pH range from 7 to 4. We suggest that in this pH range, H+/K+ cations have higher affinity to PVA/PVAc microspheres (D), than to PVA/PVAc microspheres within the silane film (E2). The trend in this pH range suggests that H+/K+ cations have higher affinity to unsized glass fiber surface than to silane film on the glass fiber surface. The zeta potentials for the PVA/PVAc microspheres within the silane film (E2) had also similar pH dependent values of the zeta potential. The zeta potential for the PVA/PVAc microspheres within the silane film on the glass fiber surface (E2) has values from -25 mV to -2 mV at the pH range from 10.5 to 3, respectively. The significant change of zeta potentials is from -25 mV to approximately -5 mV at pH=10.5 is a result of the PVA/PVAc microspheres on the surface. The PVA/PVAc microspheres not only block the SiO groups on the glass fiber surface, but also provide less effective separation between negative charge and positive charge of H+/K+ cations present in the solution of zeta potential measurement. This less negative zeta potential is due to a chemical nature of PVA/PVAc microspheres providing less negative charge in comparison with SiO groups, as discussed in a simulation section. Although the absolute values of the zeta potentials are lower in the cases of D and E2 than in the cases of A and C, the similar opposite trends for pH dependent zeta potentials were observed for A and D and for C and E2, respectively. The shapes of the pH dependent zeta potentials for D and E2 are different also in the same pH range from 7 to 4. We suggest that in this pH range, H+/K+ cations have higher affinity to PVA/PVAc microspheres (D), than to PVA/PVAc microspheres within the silane film (E2). These observations suggest a specific role of the silane with effects on the glass fiber surface and also on the PVA/PVAc microspheres. The silane presence clearly lowers the affinity of H+/K+ cations, providing more neutral surface. The opposite trends for pH dependent zeta potentials in the pH range from 7 to 4 are associated with the silane film. The zeta potential measurements correlate with the presence of silane films on the surface and are supported by AFM scans describing either the silane film, as shown in Fig. 1 assigned C, or the silane penetration, as shown in Fig. 2, Fig. 3, and Fig. 4 assigned E2. The unsized surface of the glass fibers has a roughness of approximately 0.6 nm. Such a surface is relatively smooth taking in account that they are the real industrial glass fibers without a special preparation. Moreover the size of silane molecule can be approximated to 1 nm. The silane film has a roughness of approximately 6.5 nm and the PVA/PVAc microspheres with dimensions of 320/570 nm have a roughness of approximately 46 nm. The roughness is increasing from 0.6 nm, through 6.5 nm, to 46 nm for unsized glass, silane film, and PVA/PVAc microspheres, however the zeta potentials at pH 10.5 are -64 mV, -64 mV, and -25 mV, respectively. There is no clear correlation between the roughness and the zeta potential, where the ratios are 6.5/0.6 (approximately 10), -64/-64 (1) for glass/silane and 46/6.5 (approximately 8), -25/-64 (approximately 0.5) for PVA/PVAc/silane. Moreover the PVA/PVAc microspheres within silane film has a minimal roughness of 8 nm and the silane film has a roughness of 6.5 nm, these values are almost the same, while the zeta potentials at pH 10.5 with values of -25 mV and -64 mV are very different, respectively.

The unsized glass fiber surface and the silane film on the glass fiber surface. Note that electron-dispersive X-ray spectroscopy (results not shown)
provided a composition of the glass fiber surface consisting of Si, O, and Al, as major elements, B, C, and Ca as minor elements, and K, Na, and Se as trace elements. The dominant concentrations of Si and Al were used as a base for the model utilizing the following equilibrium equations:[16]

\[
\text{SiOH}^2+ \rightarrow \text{SiOH}^3+ + H^+, K_1
\]

\[
\text{SiO}^2+ \rightarrow \text{SiO}^3+ + H^+, K_2
\]

\[
\text{XH}^+ \rightarrow \text{X}^- + H^+, K_3
\]

\[
\text{XNa} \rightarrow \text{X}^- + Na^+, K_4
\]

where \(K_1, K_2, K_3, K_4\) are the equilibrium constants, \(>\) refers to glass crystalline network and \(>X\) stands for the surface sites \(>\text{Al-O-Si}<\) which carry a negative charge. The negative charge can be counterbalanced by \(H^+\) and can form electro-neutral \(>\text{Al-OH-Si}<\) species. Using the equilibrium constants, the density sites can be determined.[16] The mineral surface charge density \(Q_0\) and the charge density in the Stern layer \(Q_\beta\) are determined as a sum of the surface site densities.

\[
Q_0 = \frac{1}{2}(\Gamma_{\text{SiOH}} + \Gamma_{\text{SiO}} - \Gamma_{\text{alkaloids}} - \Gamma_{\text{X}})
\]

(5)

\[
Q_\beta = \epsilon(\Gamma_{\text{X}} + \Gamma_{\text{alkaloids}})
\]

(6)

\[
Q_z = -Q_\beta - Q_0
\]

(7)

where \(\Gamma\) are the site densities, \(\epsilon\) is the electron charge, and \(Q_0\) is the charge density in the diffuse layer. In the triple layer model, the surface site densities are concentrated in two planes. The potentials \(\varphi_0, \varphi_\beta, \varphi_\theta\) are calculated for the inner surface charge plane, the outer surface charge plane, and Stern, respectively as

\[
\varphi_0 - \varphi_\beta = Q_0 / C_1
\]

(8)

\[
\varphi_\beta - \varphi_\theta = Q_\beta / C_2
\]

(9)

\[
Q_\theta = -40\sqrt{2} \sinh\left(\frac{\varphi_\theta}{2k_BT}\right)\sqrt{k_BT\epsilon\kappa_{\text{eff}}Nc(M) + c(M)}
\]

(10)

where \(C_1\) and \(C_2\) are the integral capacities of planes corresponding to potentials \(\varphi_0\) and \(\varphi_\beta\), respectively. \(T\) is the temperature, \(k_B\) is Boltzmann constant, \(c(H)\) is \(H^+\) the concentration, and \(c(M)\) is the salinity of supporting electrolyte KCl. All equilibrium constants, integral capacities, and total surface site densities were optimized in the nonlinear least square fit. The experimental data for both, glass fiber surface and silane film on the glass fiber surface, were optimized. The \(\Gamma_{\text{glass}}, \Gamma_{\text{silane}}, \text{and } \Gamma_{\text{silane}}\) are the glass surface site densities of Al, Si, and X, respectively. The \(\Gamma_{\text{alkaloids}}, \Gamma_{\text{silane}}, \text{and } \Gamma_{\text{silane}}\) are the silane film on the glass fiber surface site densities of Al, Si, and X, respectively. Note that \(\Gamma_{\text{alkaloids}}\) is sum of surface site densities AlOH and AlOH2, for \(\Gamma_{\text{silane}}\) is sum of surface site densities SiOH, SiO, \(\Gamma_{\text{silane}}\) is sum of XH, XNa, X. Note that \(\Gamma_{\text{alkaloids}}\) is sum of surface site densities AlOH and AlOH2, for \(\Gamma_{\text{silane}}\) is sum of surface site densities SiOH, SiO, \(\Gamma_{\text{silane}}\) is sum of XH, XNa, X. Results are shown in Table 1.

Table 1. Equilibrium constants, integral capacities, and glass fiber surface site densities in the triple layer model simulation.

<table>
<thead>
<tr>
<th>(pK_1)</th>
<th>(pK_2)</th>
<th>(pK_3)</th>
<th>(pK_4)</th>
<th>(\Gamma_{\text{alkaloids}})</th>
<th>(\Gamma_{\text{silane}})</th>
<th>(\Gamma_{\text{silane}})</th>
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<tr>
<td>3.9</td>
<td>-7.1</td>
<td>4.3</td>
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<td>1E16.1</td>
<td>1E18.0</td>
</tr>
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<td>1.9</td>
<td>0.5</td>
<td>1.4</td>
<td>0.5</td>
<td>1E16.3</td>
<td>1E16.5</td>
<td>1E13.7</td>
</tr>
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</table>

Figure 6. Zeta potential pH dependence calculated from the triple layer model for the glass (a), and silane film (b) on the glass fiber surfaces. The insets show the dependence of calculated zeta potential on KCl concentration.

The Fig 6 a, b show the dependence of zeta potential on pH for the glass and silane film on the glass fiber surfaces. The circles represent the measured experimental data. The solid line represents diffuse potential from simulation. The agreements between the data points and the fitting lines in Fig. 6 a, and b, are very good describing in an excellent way the different shapes. As shown for the values of \(\Gamma_{\text{alkaloids}}, \Gamma_{\text{silane}}, \text{and } \Gamma_{\text{silane}}\), and \(\Gamma_{\text{alkaloids}}, \Gamma_{\text{silane}}\) in Table 1, the simulation resulted in relevant ratios of approximately 1, 1, and 10^4, respectively. Interestingly the values of \(\Gamma_{\text{alkaloids}}, \Gamma_{\text{silane}}\) differ significantly suggesting an effective alternation of the glass surface with the silane film as it was expected for the coupling agent. This result is in agreement with the AFM results, shown in Fig. 1 c, where it is clear that the parts of the silane film block the sites on the glass surface. The insets of Fig. 6 a, b show the dependence of zeta potential on the different concentration of KCl, however at the higher KCl concentration, the fit describes effectively only a trend.
where \( d \) is the polymer (soft-layer) width with boundary conditions

\[
\frac{dy(X)}{dX} = 0 \quad \text{at} \quad X = 0
\]

\[
\frac{dy(X)}{dX} = 0 \quad \text{at} \quad X = 1/2
\]

On the interfaces of silane-PVA, PVA-PVAc the boundaries for \( i \) layer are

\[
y_i(X) = y_{i+1}(X) \]

\[
\frac{dy_i(X)}{dX} = \frac{dy_{i+1}(X)}{dX}
\]

where \( X = x/H \) and it is the dimensionless space variable, where \( H \) is the height of electro-kinetic channel. The channel value is an estimated average distance between surfaces of two glass fibers and was set to \( H = 10 \) µm. The parameter \( z_i \) is the \( i \)-th ion valency, \( c_i = n_i/N \) with \( n_i \) is the concentration of this ion in the bulk, \( N \) is Avogadro constant, and \( F \) is Faraday constant. We assumed presence of only 2 ions in solution, \( K^+ \) and \( Cl^- \). The parameter \( \kappa \) represents the reciprocal Debye thickness

\[
\kappa = \left[ \sum_{i=1}^{N} F^2 z_i^2 c_i \right]^{-1/2}
\]

where \( \epsilon_0 \) is the vacuum permittivity, \( \epsilon_r \) is the relative permittivity, and \( e \) is the elementary charge. The surface charge density \( \rho_{en}(x) \) depends on the corresponding local concentration of the ionizable sites. The dimensionless factors \( y_{i/N} \) are given by \( \nu_i \rho_{en} \). To ensure that the total amount of ionizable sites remains constant, the constant \( \gamma \) is defined as

\[
\gamma = \sum_{i=1}^{N} \gamma_i = \sum_{i=1}^{N} \int_{0}^{1} \left[ \sum_{j=1}^{N} (n_j - n_{j,i}) f_j(x) + n_j f_j(x) \right] dX
\]

\[
f_{j+1,i}(x) = \frac{1}{2} \left[ 1 - \tanh \left( \frac{x - x_0 - \sum_{j=1}^{N} \delta(pH_j \alpha(pH_j))}{\alpha(pH_j)} \right) \right]
\]

where

\[
\delta(pH) = d_1 \left[ 1 + \frac{d_0 - d_1}{d_1} \left( 1 - \tanh \left( \frac{pH_{en} - pH}{\Delta pH} \right) \right) \right]
\]

\[
\alpha(pH) = d_0 \left[ 1 - \tanh \left( \frac{pH_{en} - pH}{\Delta pH} \right) \right]
\]

The list of equations is given below:

\[
\frac{d^2 y(X)}{dX^2} = \nu_i \rho_{en}(x) \frac{d}{dX} \left[ \sum_{j=1}^{N} \gamma_j \exp(-z_j y(X)) \right] \frac{d}{dX} \left[ \sum_{j=1}^{N} \gamma_j \right]
\]

\[
\frac{d^2 y(X)}{dX^2} = \nu_i \rho_{en}(x) \frac{d}{dX} \left[ \sum_{j=1}^{N} \gamma_j \exp(-z_j y(X)) \right] \frac{d}{dX} \left[ \sum_{j=1}^{N} \gamma_j \right]
\]

\[
\frac{d^2 y(X)}{dX^2} = \nu_i \rho_{en}(x) \frac{d}{dX} \left[ \sum_{j=1}^{N} \gamma_j \exp(-z_j y(X)) \right] \frac{d}{dX} \left[ \sum_{j=1}^{N} \gamma_j \right]
\]
\[ \mu_j(X) = \left[ 1 + 10^{-pK_a + \gamma \mu} \exp(-y(X)) \right]^{-1} \]  

(23)

The dimensionless flow velocity of electrolyte is defined with

\[ V(X) = \frac{v(x)}{(\Delta p)^2/\eta L_0) \text{ depending on position } x \text{ to the Brinkman equation} \]

\[ \frac{d^2V(X)}{dx^2} - \left[ \lambda(X)H \right]^2 V(X) = -1 \]

(24)

\[ 0 < X < \frac{d}{H}, \quad \frac{dV(X)}{dx} = -1 \]

(25)

\[ d / H < X < H / 2 \]

The boundary conditions are

\[ V(X) = 0 \text{ at } X=0 \]

(26)

\[ \frac{dV(X)}{dx} = 0 \text{ at } X=1/2 \]

(27)

On the interfaces of silane-PVA, PVA-PVAc the boundaries for layer

\[ V_i(X) = V_{i+1}(X) \]

(28)

\[ \frac{dV_i(X)}{dx} = \frac{dV_{i+1}(X)}{dx} \]

(29)

where

\[ \lambda = \lambda_0 \sqrt{\frac{n(X)}{\max(n(X))}} \]

(30)

The parameter \( n(x) \) is the volume concentration of silane, PVA and PVAc, \( \Delta p \) is the pressure difference between beginning and end of channel, \( L_0 \) is the length of channel, \( \eta \) is the viscosity of electrolyte. The term \( \lambda(X)^2 = \gamma \mu \) represents the frictional forces exerted on the liquid flow by the polymer segments in the polyelectrolyte layers and \( y \) is the frictional coefficient. Each resistance center is assumed to correspond to a polymer segment with radius \( a \). The polymer segments are distributed in the polyelectrolyte layers with the volume concentration \( n \). Each polymer segment exerts the Stokes resistance \( 6 \eta \pi n a \) on the liquid flow in the polyelectrolyte layers. Finally, the zeta potential can be computed using flow velocity and potential, where the surface is totally covered as

\[ \zeta_{\text{pH}} = -2F H^2 \left( \frac{\theta}{e} \right) \int V(X) \sum_{i=1}^{m} \exp(z_i y(X)) dX \]

(31)

Since the surface is not uniformly covered with PVA/PVAc microspheres, the zeta potential can be computed for the low order coverage as

\[ \zeta = \zeta_{\text{pH}} \left[ 1 - \frac{1}{\theta} \exp(-\frac{\pi \eta n a}{\sqrt{2}}) \right] \]

(32)

The number of particles \( p \) were set in the percentage values. The softness parameter \( \alpha \) was set to \( 10^{-8} \). The coverage simulation resulted in the value of 0.4, as listed in Tab. 3. This value in accord with the assumption of the low order coverage and indeed it is supported by the AFM scans as shown in Fig. 2 and Fig. 3 assigned as E3. These AFM scans clearly show not completely covered surface with the silane-PVA/PVAc complex film fully in agreement with simulated coverage of approximately 0.4.

Fig. 8 a, shows the dependence of the zeta potential intensity on the pH values. The circles are the data points and the line is a result of the soft layer model which both are in an excellent agreement. Fig. 8 b, shows the electric potential defined in Eq. 11 in a form of contour lines. The contour lines describe the distance from the surface of silane-PVA/PVAc complex film which is dependent of the pH value. The zero value of the distance on the x-axis corresponds to the interface, the positive values correspond to the solution space and the negative values correspond to the complex film space. The electric potential has clearly the lower gradient in the film than in the solution. In this case, the value of dimensionless potential \( y = e^{-\frac{\theta}{\gamma \mu}} \) is the charge corresponding to ionized segments of PVA.

**Conclusion**

In our contribution, the complex film formation, based on silane and PVA/PVAc microspheres on the glass fiber surface was determined by means of (i) the nano-scale by using AFM, and (ii) the macro-scale by using zeta potential. Since the details of interaction between the silane film and the PVA/PVAc
Hydrolyzed silane strongly binds through the Si-O-Si bond to the glass surface providing the attachment mechanism of PVA/PVAc microspheres at the surface. The silane on the glass fiber surface generates a structured topography forming islands on surfaces. Furthermore, the silane on the glass fiber surface seems to have distributions where besides the islands, the homogeneous film areas are also observed, as well as the empty sites might be considered. The value of average roughness, which is the arithmetic average of the absolute values of the surface height deviations, for silanized glass fiber surface after deposition of silane was 6.5 nm, while \( R_s \) for unsized glass fiber surface was only 0.6 nm.

The surface area value \( S_a \) represents an area of PVA/PVAc microspheres which is not affected by the silane penetration. The PVA/PVAc microspheres layer on the surface without silane film form hexagonal close pack structure with the \( S_a \) value of 0.2 \( \mu m \)^2. The increasing of silane concentration from 3.8 to 7.2 \( \mu g/ml \) silane might be removed some of PVA/PVAc microspheres in the hexagonal close pack structure. The penetration of initially prepared silane film providing the \( S_a \) value of 0.08 \( \mu m \)^2 and therefore the \( S_a \) value decreased to 0.03 \( \mu m \)^2. The \( S_a \) value of PVA/PVAc microspheres decreases with increasing silane concentration, due to the increasing vertical penetration of silane. The penetration reached a saturation providing even the overlayer of silane on the PVA/PVAc microspheres, for sample, where the concentration of silane was increased up to 14.3 \( \mu g/ml \). The silane film not only penetrates through the PVA/PVAc microspheres hexagonal close pack structure, but also deforms the PVA/PVAc microspheres from the spherical shape in a solution to a ellipsoidal shape, when they are adsorbed on the glass fiber. Due to surface interaction, the PVA/PVAc microspheres of approximately 600 nm size transform into the ellipsoids on the surface with an average dimensions of 300/600 nm. The size of PVA/PVAc ellipsoids on the glass fiber surface was approximately 320/570 nm. The silane concentration of 3.8 \( \mu g/ml \) resulted in the change of PVA/PVAc ellipsoids size to 7.2 \( \mu g/ml \), resulted in only slight increase of PVA/PVAc ellipsoids deformation, to the approximate size of 270/620 nm. Silane not only penetrates through the PVA/PVAc microspheres, deforms them, and eventually covers them with the overlayer, but silane also reacts with the surface of PVA/PVAc microspheres in the process of the complex film formation from the low silane concentration areas into the complex film area providing enough silane to stabilize the complex film structure. The values of residual silane honeycomb structure height \( H_\ell \) were 6.5, 7, and 12 nm for the silane increasing concentrations from 3.8, 7.2, and 14.3 \( \mu g/ml \), respectively.

The pH dependent zeta potential results suggest a specific role of the silane with effects on the glass fiber surface and also on the PVA/PVAc microspheres. The unsized glass fiber surface (A) and the silane film on the glass fiber (C) had similar pH dependent zeta potentials which increased from approximately -64 mV to -12 mV. The trend in pH range from 7 to 4 suggests that H\(^+\)K\(^+\) cations have higher affinity to unsized glass fiber surface than to silane film on the glass fiber surface. The zeta potentials for the PVA/PVAc microspheres on the glass fiber surface (D) and the PVA/PVAc microspheres within the silane film on the glass fiber surface (E\(_1\)) significantly decreased in comparison with A and C, to -25 mV and to approximately -5 mV at the pH range of 10.5 and 3, respectively. This less negative zeta potential is probably due to a chemical nature of silane-PVA/PVAc microspheres providing less negative charge in comparison with SiO groups. The D and E\(_1\) had also similar pH dependent values of the zeta potential. The shapes of the pH dependent zeta potentials for D and E\(_2\) are different also in the same pH range from 7 to 4. We suggest that in this pH range, H\(^+\)K\(^+\) cations have higher affinity to D, than to E\(_2\). The silane presence clearly lowers the affinity of H\(^+\)K\(^+\) cations, providing more neutral surface. This observation is in agreement with the AFM results, where the zeta potential measurements correlate with the presence of silane films on the surface. The opposite trends for pH dependent zeta potentials in the pH range from 7 to 4 are associated with the silane film.

The triple layer model was used to fit the unsized glass fiber surface and the silane film on the glass fiber surface. The complex film formation on the glass fiber surface. Concluding, the silane concentration was used as a base for the model utilizing a glass crystalline network of sites \( >\text{Al-O-Si}<_2 \) with a negative charge and an electro-neutral \( >\text{Al-OH-Si}_2 \) sites. The \( \Gamma_{\text{silane}} \), \( \Gamma_{\text{glass}} \), and \( \Gamma_{\text{PVA}} \) are the glass surface site densities of Al, Si, and Al-O-Si, respectively. The \( \Gamma_{\text{Alsilane}} \), \( \Gamma_{\text{SiSilane}} \), and \( \Gamma_{\text{Xsilane}} \) are the silane film on the glass surface site densities of Al, Si, and X, respectively. Note that \( \Gamma_{\text{PVA}} \) is sum of surface site densities AlOH and AlO\(_2\)\(_2\), for \( \Gamma_{\text{silane}} \) is sum of surface site densities SiOH, SiO\(_2\), for \( \Gamma_{\text{glass}} \) is sum of XH, XNa, X. The values of \( \Gamma_{\text{SiSilane}} \), \( \Gamma_{\text{SiSilane}} \), \( \Gamma_{\text{silane}} \), \( \Gamma_{\text{silane}} \), and \( \Gamma_{\text{PVA}} \) \( \Gamma_{\text{silane}} \) in the simulation resulted in relevant ratios of approximately 1, 1, and \( 10^{-4} \), respectively. The values of \( \Gamma_{\text{SiSilane}} \) and \( \Gamma_{\text{Xsilane}} \) differ significantly suggesting an effective alternation of the glass surface with the silane film as it was expected for the coupling agent.

The soft layer model was used to fit silane-PVA/PVAc complex film on the glass surface. Since the PVA/PVAc microspheres have the ellipsoidal shape within the silane film, this structure had to be transformed into the layer geometry. The simplification and compensation of the shape approximated the relevant lengths as the layer of silane with 10% of the total length (27 nm), the layer of first PVA shell with 30% (81 nm), the layer of PVA core with 30% (81 nm), and again the layer of second PVA shell with 30% (81 nm). The length distributions consider, simplify, and compensate the silane penetration in a honeycomb fashion from the glass surface through the PVA/PVAc microspheres forming a hexagonal close pack structure. The coverage simulation resulted in the value of 0.4, in accord with the assumption of the low order coverage and indeed it is supported by the AFM scans revealing not completely covered surface.

The interaction of the silane film with the PVA/PVAc microspheres is the base of a complex film formation. The silane film penetrates in a honeycomb fashion from the glass surface through the PVA/PVAc microspheres forming a hexagonal close pack structure. However the chemical interaction between the silane film and the PVA/PVAc microspheres is still of interest. Silane and PVA have unsaturated double bonds that might allow silane and PVA to react with each other, proposing a possible enhancement of silane-PVA/PVAc complex film interaction. One of interesting paths for further experiments might be a significantly increased temperature during the silane-PVA/PVAc complex film formation on the glass fiber surface. Concluding, the results of AFM, and zeta potential shed some light on the formation mechanism of the silane-PVA/PVAc complex film.

**Experimental Section**

Glass fibers were supplied (by Johns Manville Slovakia, a.s., Slovak Republic), Silane A 174 NT (3-(trimethoxysilyl) propyl methacrylate) (Silane) (by Sigma-Aldrich) was used as the coupling agent. PVA/PVAc microspheres (non-volatiles was 53%) (by Sigma-Aldrich) was used as the adjusting agent. All measurements were performed at room temperature. Glass fibers were dipped in solutions and suspensions of various compositions, as shown in Table 3.
were computed based on temperature by using calibration curve. The viscosity and permittivity of the electrolyte solution. The streaming potential at the measurement mode was set to 300 mBar. The viscosity and permittivity of the aqueous solution, which is forced by hydraulic pressure, over the electrochemical double layer disrupts a distribution of ions in solution, which is forced by hydraulic pressure, over the electrochemical double layer, and generates a potential difference, the streaming potential. The zeta potential was obtained from the streaming potential measurements based on the Smoluchowski equation as follows:

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

where $dU$ is the streaming potential, $p$ is the pressure drop across the streaming channel, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the dielectric constant of the aqueous solution, $\eta$ is the electrolyte solution viscosity and $\kappa$ is the electrical conductivity of the bulk solution. The streaming pressure at the rinse mode was set to 100 mBar. The streaming potential at the measurement mode was set to 300 mBar. The viscosity and permittivity of electrolyte were computed based on temperature by using calibration curve.

### Table 3. Composition of sizing solutions and suspensions.

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</tr>
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### Acknowledgements

The work was supported by APVV-0491-07, meta-QUTE and NANNOTE2. We acknowledge also the unlimited support of Peter Szepesi Plant Manager and Rastislav Krejci P&P Control leader of Johns Manville Slovakia, a.s.

### Keywords: glass fiber surface, silane, PVA/PVAc, AFM, zeta potential


Received: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

Figure 10. Schematics of single glass fiber for AFM surface topography.
The complex film formation, based on silane and PVA/PVAc microspheres on the glass fiber surface was determined by means of (i) the nano-scale by using AFM, and (ii) the macro-scale by using zeta potential. The silane film penetrates in a honeycomb fashion from the glass surface through the PVA/PVAc microspheres forming a hexagonal close pack structure.