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Adsorption of Silane Coupling Agents on Glass Fibre Surfaces

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Abbreviations

ESCA	Electron Spectroscopy for Chemical Analysis
XPS	X-ray Photoelectron Spectroscopy
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
SP	Streaming Potential
ZP	Zeta Potential
E-glass	Electrical Glass
A-glass	Alkali Glass
C-glass	Chemically Resistant Glass
S-glass	Special High Strength Glass
R-glass	Special High Strength Glass
CMC	Glass ceramic Composite
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
GC-MS	Gas Chromatography with mass-spectrometry
APTMS	γ-aminopropylmethoxysilane
OTMS	Octyltrimethoxysilane
APTES	γ-aminopropyltriethoxysilane
IEP	Isoelectric Point
EKA	Electro Kinetic Analyzer
PM-IRRAS	Polarization Modulation Infrared Reflection Absorption Spectroscopy
mfp	Mean free path
TOF-SIMS	Time-Of-Flight Secondary Ion Mass Spectroscopy

Symbols

L_{surf}	Liquid solvent molecule on an adsorbing surface
L_{sol}	Liquid solvent molecule in solution
A_{sol}	Adsorbate molecule in solution
A_{surf}	Adsorbate molecule on an adsorbing surface
θ_2	Fraction of the covered surface
V_p	Volume of adsorbed gas
V_{mon}	Volume of an adsorbed monolayer
k_a, k_b	Constants
p_G	Gas pressure
p^θ	100 kPa
w	Mass of adsorbate adsorbed per mass of adsorbent
$c_{2,B}$	Equilibrium concentration of anadsorbate in a solvent
c^θ	1 mol/dm^3
$n_{2,A}$	Amount of adsorbent
n_{nom}	Amount of adsorbed material in a monolayer
k_1	$1/n_{mon}$
k_0	k_1/K
m_A	Mass of an adsorbent
K	Measure of the strength of adsorption
f	Wetting force
γ_{lv}	Liquid-vapor surface tension
p	Perimeter of a plate
θ	Equilibrium contact angle at a solid-liquid interface
V	Volume of a liquid replaced by a plate
$\Delta\rho$	Difference in density between a liquid and a plate or another liquid
g	Gravitational acceleration

θ_a	Contact angle advancing
θ_r	Contact angle receding
ψ_0	Particle surface potential
ψ_s	Potential in the Stern plane
κ^{-1}	Debye thickness
ζ	Potential in the shear plane, electrokinetic potential, zeta potential
U	Electric potential difference
ε	Dielectric constant of a liquid
η	Viscosity of a liquid
Δp	Pressure difference over a plug
k_0	Conductivity of a liquid
δ	Solubility parameter
δ_d	Dispersive contribution to the total solubility parameter
δ_p	Polar contribution to the total solubility parameter
δ_h	Contribution of hydrogen bondings to the total solubility parameter
F_{AB}	Attraction force between different molecules A and B
F_{AA}	Attraction force between similar molecules A and A
G^m_p	Gibbs free energy
H^m_p	Enthalpy change
TS^m_p	Entropy change
$\Delta^g_l H_m$	Increase in enthalpy
R	Gas Constant (8.31441 J K^{-1} mol^{-1})
T	Temperature
V_m	Molar volume of a liquid
E_{kin}	Kinetic energy
E_b	Binding energy
$h\upsilon$	Exciting X-ray energy
Φ_s	Equipment work function

Abstract

Commercial glass fibres are commonly used in reinforced composites. The importance of such composites is apparent in a number of areas and applications. Composites have maintained their popularity during several decades, as the products offered give both strength and modulus at a reduced weight. Glass fibres used in composites are almost always pre-treated with coupling agents. Coupling agents are capable of interacting with both the organic polymer resin as well as the inorganic glass surface. These coupling agents play a key role in the strength of a composite.

The overall objective of this work was to characterize glass fibre surfaces after surface treatment with silane and to gain better understanding of surface processes at the silane-glass interface of a composite. Another goal was to investigate how the solvent used in the surface treatment process affected silane adsorption on the glass fibre surface.

Adsorption of silane coupling agents from water and organic media on a glass fibre surface were determined with several analysis methods. The results indicate that adsorption is dependent on different factors affecting the monomer dispersion and the formation of a polymer layer on the glass fibre surface. If the silane adsorbs only physically on the fibre surface it can lead to a break in the reinforced product. In order to avoid a breakage the silane treatment must be performed in a way, that only chemical adsorption of the silane can take place on the fibre surface.

In this study, adsorption mechanisms of silanes on both pure silica powders as well as glass fibre surfaces were examined. The experimental adsorption processes on a silica powder could be described by a combination of the Henry and Langmuir adsorption isotherms.

Important information on changes in electrokinetic parameters of heterogeneous glass fibre surfaces was obtained with streaming potential measurements. The changes introduced by silane adsorption on glass fibre surface affected the streaming potential and a clear change in the surface charge was detected. The adsorption was further confirmed by ESCA measurements by following the carbonyl C_3 signal. Information of the pH dependence of adsorption was detected by streaming potential measurements.

Furthermore, it was found that treatment of glass fibres with acids and bases resulted in leaching ions from both the fibre surface as well as from the fibre bulk. Part of the ions being leached out from the glass fibre surface were replaced by ions originating from the bulk of the fibre. This created an ion gradient from the fibre bulk to the surface.

Svensk sammanfattning

Glasfibrer används ofta i kommersiella kompositer med syfte av att förstärkta konstruktionen av dessa. Betydelsen av sådana kompositer kan ses inom flera områden och applikationer. Kompositer har behållit sin popularitet under flera decennier, eftersom de produkter som erbjuds ger konstruktionen både styrka och elasticitet kombinerat med minskad vikt. Glasfibrer som används i kompositer är nästan alltid förbehandlade med kopplingskemikalier. Kopplingskemikalierna kan interagera med både organisk polymerharts och oorganisk glasyta. Dessa kopplingskemikalier har en viktig roll i kompositens styrka.

Målet med detta arbete var att karakterisera glasfiberytorna efter ytbehandlingen med silan och därmed få en bättre förståelse av de ytkemiska processer som sker vid gränsytan silan-glas. Ett annat mål var att undersöka hur lösningsmedlet som använts i ytbehandlingsprocessen påverkar silanernas adsorption på glasfiberytan.

Adsorptionen av silaner på glasfiberyta från både vatten och organiska media bestämdes med hjälp av flera analysmetoder. Resultaten indikerar att adsorptionen är beroende av olika faktorer som påverkar monomerspridningen och bildandet av ett polymerskikt på glasfiberytan. Om silanet endast fysisorberar på fiberns yta kan det leda till en svag punkt i den förstärkta produkten. För att undvika brott måste silanbehandlingen utföras så att endast kemisk adsorption av silan kan äga rum på glasfiberytan. I denna studie undersöktes silanernas adsorptionsmekanismer på både rent kiseldioxidpulver och på glasfiberytor. De experimentella adsorptionsprocesserna på kvartspulver kunde beskrivas genom en kombination av Henrys' och Langmuir's adsorptionsisotermer.

Viktig information om förändringar i de elektrokinetiska parametrarna av glasfibrernas heterogena ytor samlades genom strömningspotentialmätningar. De ändringar som infördes genom adsorption av silan på glasfiberyta påverkade strömningspotentialen och identifierades som en tydlig förändring i glasfibrernas ytladdning. Silanadsorptionen bekräftades ytterligare med hjälp av ESCA mätningar genom uppföljning av karbonyl C3 signalens intensitet. Silan adsorptionens pH-beroende studerades med hjälp av strömningspotential-mätningar.

Slutligen konstaterades att behandling av glasfibrer med syror och baser resulterade i urlakning av joner från både glasfiberytan och från fiberns bulk. Den del av jonerna som lakats ut från glasfiberytan ersattes av joner med ursprung från den inre delen av fibern. Detta skapade en gradient från fiberns bulk till ytan och påverkade hållfastheten i glasfiberkompositerna.

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II. Treated glass fibers – Adsorption of an isocyanurate silane from CCl_4
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III. Adsorption of an isocyanurate silane on glassfibre surface from ethanol and toluene
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A. Norström, H. Watson, B. Engström and J.B. Rosenholm
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V. Investigation of the adsorption of mono- and bifunctional silanes from toluene onto porous silica particles and from aqueous solutions onto E-glass fibers
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VI. Modification of E-glass fibre surfaces with aqueous, non-ionic silane solutions.
A.E.E. Norström, H. Watson, P. Idman, J. Nuortila-Jokinen and J.B. Rosenholm
In "*Contact angle, Wettability and Adhesion*", K.L. Mittal Ed., VSP, Zeist, The Netherlands, Vol. 2 (2002) 125-146.

Contribution of the author

The author had main responsibility for design of experiments, analysis of the results and preparation of the manuscripts in publications I-IV. The author was responsible for the design of experiments and participated integrally in the analysis of the results and in the preparation of manuscripts in publications V and VI. ESCA measurements in all publications were performed by Heidi Fagerholm or Pasi Mikkola. Adsorption isotherms in paper V were made by Jan Bäckman or Tom Eklund.

Supporting publications

SI. Treated glass fibers, Part 1: Adsorption of an isocyanurate silane
J.G. Matisons, A.E. Jokinen and J.B. Rosenholm
Journal of Colloid and Interface Science, **194** (1997) 263-268.

SII. Treated glass fibres: Adsorption of an isocyanurate silane from ethanol
A.E.E. Jokinen, J.B. Rosenholm and J.G. Matisons
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SIII. Silanes that orientate glass fibres – Opportunities for new materials development
J.G. Matisons, A.E.E. Jokinen and J.B. Rosenholm
In "*Silicones in Coatings II*", International Centre for Coatings Technology, Florida, USA, Paper 9 (1998) 1-14.

SIV. Silane treated glass fibers, Part 4: Ureido silane deposited from ethanol
H. Watson, A.E.E. Jokinen, P.J. Mikkola, J.G. Matisons and J.B. Rosenholm
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SV. Aqueous amino silane modification of E-glass surfaces
H. Watson, A. Norström, Å. Torrkulla and J.B. Rosenholm
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SVI. Deposition of amine functional silanes onto E-glass fibres, an NMR study
H. Watson, A.E.E. Norström, J.G. Matisons, A. Root and J.B. Rosenholm
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1. Introduction

The surface of industrially manufactured glass fibres is routinely treated with silanes together with other components such as different film formers. Surface treatment with silanes, also referred to as sizing of fibres, is the key to success or failure of most reinforcement products. It is generally known that silane coupling agents enhance the reinforcement capacity of metal oxides and glass fibre armed composites. Sizing of a material is in a critical role regarding the price, processability and performance of the product [Plueddeman 1982, Rosen 1979].

Silanes are versatile materials used in a wide range of applications including adhesion promoters, coupling agents, crosslinking agents, dispersing agents, and surface modifiers. Silanes generate a water insoluble boundary between an organic polymer and an inorganic substrate [Angst 1991, Park 1991]. These chemicals react with either the polymer, metal oxide or the glass surface [Plueddeman 1982, Rosen 1979]. Based on the functionality, silanes are generally divided into two categories; functional silanes and non-functional silanes, also called coupling agents. Functional silanes are utilized in polymer composites, biomolecule immobilization, and adhesive technologies. Nonfunctional silanes are used in modification of the surface energy or wettability of substrates and are not intended to impact chemical reactivity of the substrate [Yang 2013].

The harmful effects, caused by water, on the mechanical properties of composite materials containing fibres or other fill materials are well documented [Matisons 2009, Plueddeman 1990, Plueddeman 1991]. The diffusion of water and the following chemical reactions at the fibre-polymer interface can be considered as the reason for delamination and thus failure of the composite. Silane coupling agents are used to prevent this problem. Research results reported in literature have confirmed that more than one monolayer of silane coupling agent on the oxide surface is needed in order to enhance the strength of the final product, the composite. An optimal thickness of the surface treatment material on the fibre surface is required to obtain increased strength properties. If this optimal thickness is not reached a composite with inadequate properties is obtained [Plueddeman 1982, Park 1991].

Characterization of the interface between the glass fibre and the surface treatment material is complicated as the fibre has a rough surface and since it is of isolating character. Analysis methods with special surface sensitivity are required because the amount of the adsorbate on the surface of the adsorbent is very small. Furthermore, the analysis methods should be suitable for analysis of the chemical structure. The high demands on the analysis methods have led to the fact that

surfaces like silicone oxides or quartz have generally been used to model adsorption on glass fibre surfaces. In this thesis, adsorption of silane coupling agents on glass surfaces has been studied with surface sensitive analysis methods like Electron Spectroscopy for Chemical Analysis (ESCA or XPS) and Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFT). The experimental work of this thesis, however, was performed about twenty years ago. During the summarization process of this thesis, the following observations were made.

The silane coupling agent literature has grown remarkably in the past 20 years. However, it can be considered that no real summarizing review articles have been published during that period. Most recent papers report the application of silanes with various functionalities onto surfaces without detailing the adsorption mechanisms. In addition, the glass fibre reinforcement field is today driven by large companies mostly working with end user specific or material specific applications. The majority of the research in the field is today performed in-house within these companies.

In the industry worldwide, glass fibre sizes are still dominated by amino silanes. In this thesis, results from research with two different amino silanes are published. Among the latest trends within sizing industry, the multi-silane approach is reported. Dipodal silanes in combination with conventional silanes have been shown to have a dramatic effect on adhesion to especially treated surfaces. The results on tripodal isocyanurate silane adsorption in this thesis are part of this multi-silane approach and can be considered to still be of current interest, justifying the publication of this thesis.

2. Review of literature

2.1. Glass fibres

The wide use of inorganic fibres in several structural composite applications demands enhanced performance on their chemical compatibility with different materials. Among the reinforced fibres used, glass fibres clearly dominate due to the combination of useful properties and low cost. The major ingredient in glass fibres is silica, SiO_2. Silica is typically mixed with other oxides, depending on the application. The silica-oxide mixture is melted, extruded through small holes (diameter 0,8 - 3,2 mm), drawn at velocities up to 60 m/s and finally sprayed with water. In order to protect the fiber a coating, or a size, can be applied on the surface of the fibres before they are chopped or wound onto forming packages. The process ends with drying of the fibres for 10-15 hours at 120-130 °C [Åström 1997].

Several types of glass grades have been developed. Alkali glass (A-glass) is commonly used for windows and bottles. Alkali glass has poor resistance to chemical attack and dissolves in acids and bases. Chemically resistant glass (C-glass) is used as laboratory ware, but is also used for glass fibre manufacture when the need of chemical resistance of the final product is greater than that of E-glass fibres. E-glass refers to electrical glass which is more resistant to chemical attack than A-glass but is still affected by strong acids and bases. The majority of all glass fibres is manufactured from E-glass. S-glass as well as R-glass are special high strength glass fibres manufactured for aerospatial industry [Prashanth 2017].

Strong acids and bases have been shown to leach ions from the E-glass fibre surface, resulting in brittle fibres and reduced physical and chemical resistance of the composite [Britcher 1998, Elmer 1984, Friedrich 2000, Kobayashi 1982, IV]. When E-glass fibres are exposed to deionized water, the ions have a tendency to leach out from the fibre surface. Pantano reported on the effect of leached ions on deposition, hydrolysis and condensation properties of the silanes using boron as an example [Pantano 1992]. Hydrolysis of the glass fibre surface results in micro-cracks, which reduce the physical strength of the fibres. Once hydrolysis of the surface has taken place, a physisorbed layer of water no more affects the physical properties of E-glass fibres [Watson 2001].

A new method to manufacture glass and ceramic fibres has evolved through a carefully designed sol–gel reaction of metal alkoxides and other oxide-bearing inorganic or organic metal salts. The sol-gel method has several benefits.

Relatively low production temperature is one of the benefits, as conventional manufacturing methods require melting of glass raw material at very high temperatures. High purity ceramics as well as different compositions of mixed ceramic oxides can be produced with the new method. This is not possible with conventional manufacturing techniques because e.g. phase separation and crystallization are problems that appear during cooling. One disadvantage with the sol-gel process is the relatively high cost of raw materials [Kanichi 2016].

2.2. Composites

Composite materials are composed of two or more materials with significantly different physical or chemical properties that, when combined, form a material with characteristics different from the individual components. The individual components are not miscible in each other and remain separate and distinct within the finished structure [Smith 1996]. The two constituents in a composite are a reinforcing component and a matrix. The reinforcing phase provides the strength, stiffness and hardness for the composite. Composite materials used in structural applications can be considered as high performance systems, but the manufacturing process of these composites needs highly controlled environments in order to obtain optimum performance [Prashanth 2017, Campbell 2010].

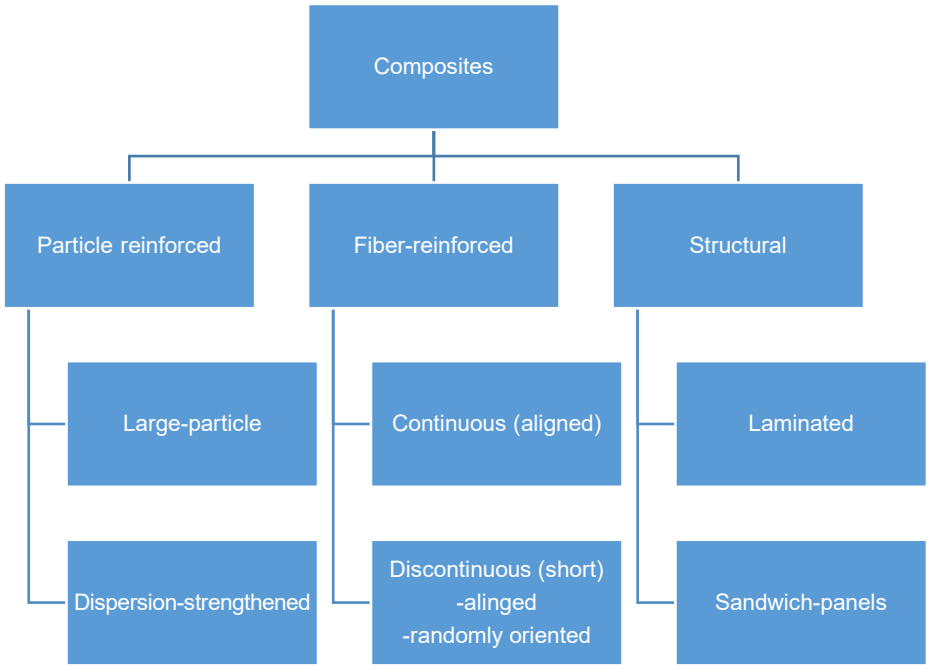


Figure 1. A classification scheme for various composite types [Callister 1987].

When a composite is formed, all constituents lend a degree of their own properties to the formed composite. Composites according to the filler type used can be classified into particulate, short fibre, long fibre, laminate and sandwich composites. In a particulate composite, the filler material is spherical. An example of a particulate composite is concrete where cement is the matrix and sand is the filler. In short and long fibre composites the filler material has a length-to-diameter ratio larger than 1. In long fibre composites, the ratio equals to infinity. In laminate composites, unidirectional fibres are impregnated with a matrix and is then formed as a sheet. These sheets or layers are piled on top of each other. The layers can be free fibres or woven mats placed in the same direction or in angles to each other. Increased stiffness is reached by placing the layers in angles to each other. In addition, the material of the reinforcing layer can vary depending on the application. Composites can also be formed as sandwiches. This type of composite is formed when the matrix is placed between two reinforcing plates. The sandwich form is lighter and more formable than the more traditional laminar composite. On the other hand, the manufacturing process of the sandwich composite contains several steps and is therefore more time consuming, complex and expensive than the process of the basic laminar composite. Different composite structures are classified in Figure 1 and examples are presented in Figure 2.

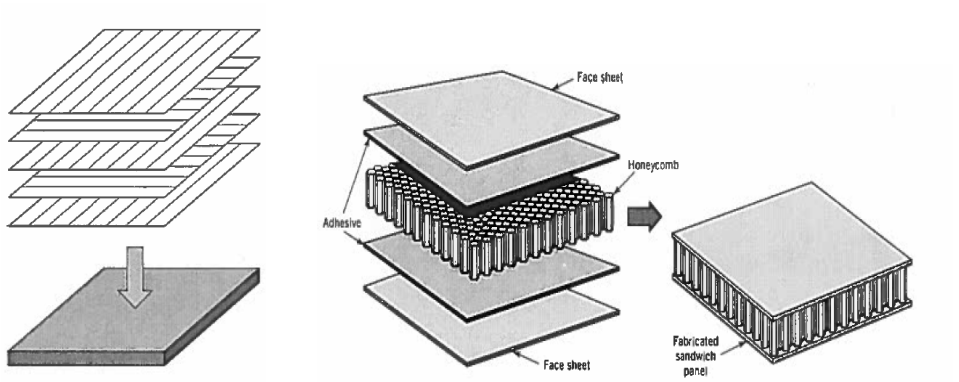


Figure 2. Schematic pictures of different composite structures. a) Laminar composite structure, the conventional model, b) Honeycomb core sandwich structure [Callister 1987].

The historical upswing of composites origins from the 1940's, when silicate glass reinforced composites became generally available. The importance of such products in various applications was soon realized, as these products offered high strength and modulus but were also remarkably light-weighted. Later it was discovered that these composites were very sensitive to the effects of humidity.

Another drawback in the use of glass fibre reinforced composites was the difference in the thermal expansion ability of these two components. This difference may in extreme environments result in stress at the interface of the components and may even exceed the strength of the composite [Gelest 2014, Matisons 2009]. Nearly 90 % of the fibre-reinforced polymers on the market today are made of glass fibres mostly due to their high strength-to-weight ratio and good fatigue resistance. The dominating position in the market is due to their recognized potential as high-tech, high-quality materials in electrical and military applications. In recent years, fibre-reinforced polymers have also been merely used within the building and construction industry [Roylance 2007, Prashanth 2017].

2.3. Silane coupling agents

Silanes are chemical compounds consisting of a silicon atom, which usually has three methoxy or ethoxy groups. The fourth end group is commonly an organic functional group. This functional group is determining the binding of silane to the polymer matrix. Silanes can be cationic, anionic or non-ionic depending on their functional group. Most commonly used silanes for surface treatment of glass fibres are trialkoxysilanes, which contain organic groups compatible with the polymer matrix [Kehoe 2007].

Silane coupling agents are commonly applied to fibres to improve the overall performance of reinforced composite materials by generating a water-resistant surface between an organic polymer and an inorganic substrate [Britcher 1995]. Silanes are mostly used in aqueous systems, as this is the general deposition process in industry. Water-based systems are used due to health, cost and environmental criteria. Generally, when diverse materials are combined, often at least one part is siliceous or has surface chemistry with siliceous properties involved; silicates, aluminates, borates, etc. A general formula of a silane coupling agent is as follows:

$$R\text{-}(CH_2)_n\text{–}Si\text{-}X_3$$

R = organofunctional group
$(CH_2)_n$ = hydrocarbon chain
Si = Silicon atom
X_3 = hydrolysable group, methoxy ($-OCH_3$) or ethoxy ($-OCH_2CH_3$)

Three alkoxy groups are attached to a silicon atom. The general formula for a silane coupling agent typically has two different functionalities, X and R. X is a reactive hydrolysable group, for example an alkoxy group. Silane coupling agents are applied either from dilute aqueous solutions partially hydrolyzed or from organic solvents, generally alcohol. Most of the coupling agents have undergone initial hydrolyzation and oligomerization before they interact with the chosen substrate [Britcher 1995]. It has been noted that lateral polymerization may occur without formation of bonds with the substrate [Tripp 1991]. The siloxane film formed on the surface consists of multiple layers [Plueddeman 1982, Park 1991, Allen 1992, Drown 1991].

When hydrolysis takes place, a reactive silanol group (SiOH) is formed. This silanol group is very reactive and can further condense with other silanol groups, for example, those on the surface of siliceous fillers and siloxane linkages. Stable condensation products are formed with other oxides such as aluminum, zirconium, tin, titanium and nickel. Less stable bonds are formed with oxides of boron, iron and carbon. Alkali metal oxides and carbonates do not form stable bonds with Si-O-. The other functionality of the coupling agent comes with the R group, which is a non-hydrolysable organic radical that brings the desired functionality for the end product [Gelest 2014].

In a theory according to Algar, silane coupling agents form a link between E-glass fibres and the polymer matrix. The functional groups in silane react specifically with either the glass or the polymer surface [Algar 2000]. However, in practice silanes have shown various ways of deposition on the surface. Plueddeman and Watson reported silane coupling agent depositions upside down on the glass fibre surface without leaving any free organic functionality for reaction with the polymer [Plueddeman 1991, Watson 2001].

2.4. Adsorption from solution

The amount of surfactant adsorbed on a solid surface can be experimentally monitored with adsorption isotherms. Adsorption from solution takes generally place as physisorption or chemisorption and the thickness of the adsorbed layer is either a monomolecular film or a multilayer. In a phase boundary between a solid surface and a solvent either the solvent or the solute molecules are adsorbing on the solid phase. Adsorption from a solution can be described as an exchange process, i.e.

$$L_{surf} + A_{sol} = L_{sol} + A_{surf} \quad ,$$

where A_{sol}, L_{sol} = the adsorbate (A) and liquid solvent (L) molecule in solution, A_{surf}, L_{surf} = the respective molecules on the adsorbing surface [V].

There are two standard isotherms that are frequently used for describing adsorption from solution; Freundlich's adsorption isotherm and Langmuir's adsorption isotherm.

Freundlich's adsorption isotherm is based on purely empirical data and does not presume that adsorption stops at a monolayer. Freundlich's adsorption isotherm for adsorption from solution is described by the following equation:

$$\ln w = \ln k_a + \frac{1}{k_b} \ln\left(\frac{c_{2,B}}{c^\theta}\right) \quad (1)$$

, where w is the mass of the adsorbate adsorbed per mass of the adsorbent, $c_{2,B}$ is the equilibrium concentration of the adsorbate in the solvent and c^θ is 1 mol dm^{-3}. Freundlich's adsorption isotherm is valid when ln w is a linear function of ln ($c_{2,B}$ /c^θ) with a slope $1/k_b$ and an intercept ln(k_a).

For comparison, Freundlich's adsorption isotherm for adsorption from gas describes the fraction of covered surface θ_2 as follows:

$$\theta_2 = \frac{V_p}{V_{mon}} = k_a \left(\frac{p_G}{p^\theta}\right)^{\frac{1}{k_b}} \quad (2)$$

, where V_p is the volume of the adsorbed gas related to a constant pressure per mass adsorbed material, p_G is the gas pressure, p^θ is 100 kPa and k_a, k_b are constants. When a monolayer has been adsorbed, $V_p = V_{mon}$.

Langmuir's adsorption isotherm can be applied to the fibre-surfactant system. In Langmuir's isotherm, the following assumptions are made: (i) adsorption takes place on a smooth surface, (ii) adsorption stops in a monolayer and (iii) all free places on the adsorbent are equally available. Langmuir's model describes the case where adsorption on the fibre surface can be considered competitive. The silane is immersed in the solvent and the solute and solvent are thereby competing of adsorption on the fibre surface. The solvent in the system is often preventing multilayer silane adsorption as either the solvent molecules or the silane/solute molecules are adsorbed on the solid glass fibre surface. In the adsorption process, the solvent molecules at the surface are replaced by the solute molecules. Langmuir's isotherm is often written as

$$\frac{c_{2,B}/c\theta}{n_{2,A}/m_A} = k_0 + k_1 \frac{c_{2,B}}{c\theta} \quad (3)$$

$$= \frac{1}{K\, n_{mon}} + \frac{1}{n_{mon}} \frac{c_{2,B}}{c^0} \quad (4)$$

, where $n_{2,A}$ is the amount of the adsorbent, c^{θ} is 1 mol/dm^3, $k_1 = 1/n_{mon}$, n_{mon}= the amount of adsorbed material in a monolayer, $k_0 = k_1/K$, $c_{2,B}$= equilibrium concentration of the adsorbate and m_A= the mass of the adsorbent. K is a constant related to the equilibrium constant of the adsorption reaction.

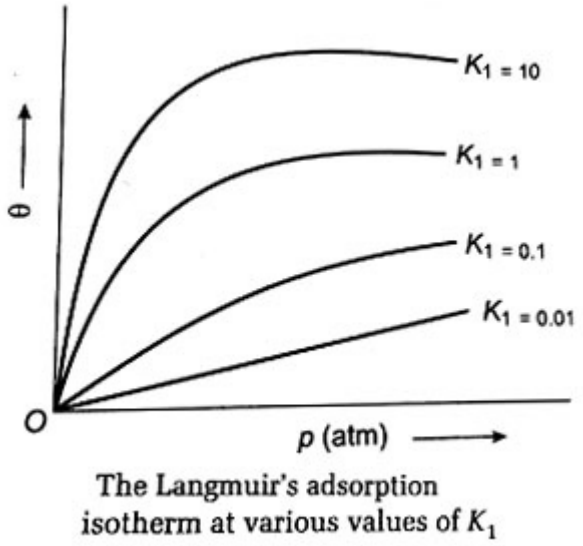


Figure 3. A schematic picture of Langmuir's adsorption isotherms for various values of K. Constant K is a measure of the strength of adsorption, θ is the fractional coverage of the surface and p is the pressure. The fractional coverage increases with increasing pressure. Different curves are obtained at different temperatures [Atkins 1998].

The initial linear part of the Langmuir isotherm can be presented as Henry's adsorption isotherm. The Henry's adsorption constant is the constant appearing in the linear adsorption isotherm, which originates from Henry's law. Henry's adsorption isotherm is the simplest adsorption isotherm where the amount of the surface adsorbate is interpreted to be proportional to the partial pressure of the adsorptive gas. The linear isotherm can be used to describe non-specific adsorption and the initial part of many practical isotherms [Atkins 1998].

The silanes are mostly applied from diluted aqueous solutions, where both hydrolysis and condensation of the silane coupling agent occur before adsorption onto the glass fibre surface. So part of the silanes have gone through the first stage of hydrolysis and oligomerization before interacting with the substrate used [Arkles 1991, Wang 1992]. The silane reaction with the glass fibre surface is described in Figure 4.

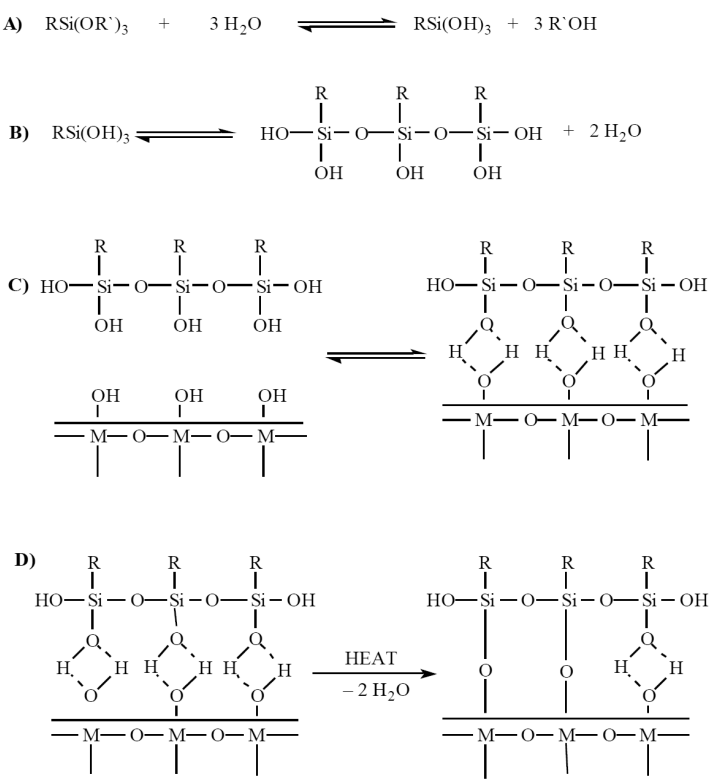


Figure 4. Reactions of silane on an E-glass surface. A) Hydrolysis of the alkoxy groups, B) condensation reaction, C) hydrogen bonding with the silanol groups of the E-glass fibre and D) formation of the bondings [Matisons 2012].

The alkoxy group of the silane is hydrolyzed as the silane is often applied on the fibre surface from an aqueous solution. (Figure 4, A.). This reaction is followed by the condensation and lateral reactions, where the polymeric structure of the silane is created. The hydrogen bonds of the silane then react with the silanol groups of the glass fibre surface. It is also possible that lateral reactions in some systems take place without a bonding to the surface [Tripp 1991].

2.5. Adhesion and cohesion

Adhesive forces are present in systems of dissimilar materials, such as glass fibre and water. Adhesive forces are caused by e.g. electrostatic and van der Waals interactions between two different materials. Cohesion, on the other hand, appears in systems of similar materials. Forces between atoms and molecules,

typically van der Waals forces, are effective only over very short distances i.e. parts of molecular dimensions. These forces are considered being short-range.

2.6. Wetting

Wetting plays an important role in many industrial processes such as printing, lubrication and surface treatment. The interest in study of superhydrophobic surfaces has in recent years increased, due to their potential use in e.g. nano-fluidics and electro-wetting. Wettability studies of materials are often carried out with contact angle measurements. The contact angle is by definition the angle formed at the solid-liquid-vapor contact line (three-phase contact line, tpcl). Contact angles less than 90° correspond to a wettable (hydrophilic) surface whereas contact angles over 90° refer to a nonwettable (hydrophobic) material [Yuan 2013]. Contact angles formed by a sessile drop are presented in Figure 5.

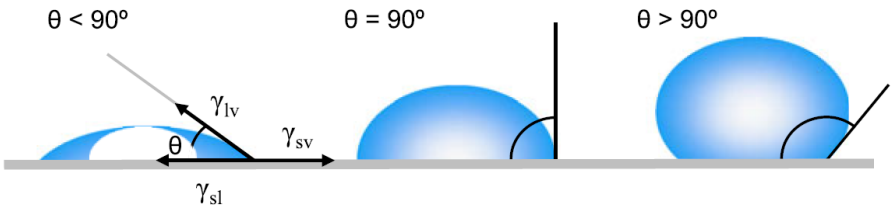


Figure 5. Schematic illustration of contact angles formed by a sessile drop on a smooth homogeneous solid surface [Yuan 2013].

Contact angle between a liquid and a solid sample can be measured by many different methods. A Wilhelmy balance method is presented in Figure 6. This method can also be applied for contact angle measurements of glass fibres. In this method, the vertical component of the force due to the surface tension of the liquid across the solid-liquid-gas interface is measured. Besides measuring the contact also the surface tension of an unknown liquid can be determined. The procedure is to pull the solid (i.e. plate or filament) slowly out of the liquid and to determine the maximum force generated. As a thin, vertical solid is put in contact with a liquid, a balance detects the change in the weight of the plate. This change in the weight is a combination of the buoyancy effect and the force of wetting. Wetting force *f* can be defined as:

$$f = \gamma_{lv} p \cos\theta \tag{5}$$

where γ_{lv} is the liquid-vapor surface tension, p the perimeter of the plate and θ is the equilibrium contact angle at the solid-liquid interface.

The total change in the force in the balance can be calculated from:

$$F = \gamma_{lv}\, p \cos\theta - V\, \Delta\rho\, g \qquad (6)$$

where V is the volume of the liquid replaced by the plate, $\Delta\rho$ the difference in density between the liquid and plate, or another liquid. The gravitational acceleration is expressed with g.

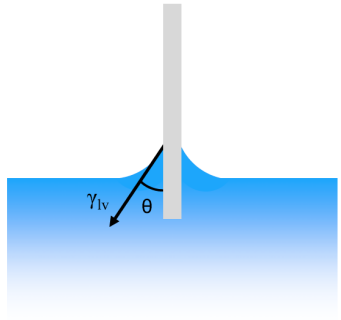


Figure 6. A schematic picture of the Wilhelmy balance method [Yuan 2013].

According to Miller the maximum wetting force is reached when the contact angle passes zero value during the withdrawal of the fibre from the solution [Miller1983]. From the measured advancing and receding contact angle values the following relationships can be calculated:

$$\cos\theta_a = F_w\,(a) / F_w\,(max) \qquad (7)$$

$$\cos\theta_r = F_w\,(r) / F_w\,(max) \qquad (8)$$

The wettability of a surface provides indirect information about the polarity and the average surface coverage on a macroscopic level of the surfaces [Fagerholm 1994].

2.6.1. Contact Angle Hysteresis

The contact angle of a surface-treated single fibre can be measured with the Wilhelmy balance method. Contact angle measurements provide information about the adsorption of silanes on the glass fibre surfaces. As discussed earlier, high contact angle gives an indication of a hydrophobic surface and a small contact angle refers to a hydrophilic surface.

In the Wilhelmy balance method a single fibre is mounted in the measuring device and the fibre is dipped into and lifted up from the wetting liquid at a constant speed. Contact angle is influenced by surface roughness, surface heterogeneity, solution impurities adsorbing on the surface, or swelling. An ideal surface is homogeneous, totally flat and the surface energy is constant all over the surface. In reality the surface is highly heterogeneous and contains impurities. The impurities affect both surface energy and surface roughness [Yuan 2013]. For real surfaces, advancing contact angle ($\theta_a > \theta_r$) is always higher than the receding contact angle. The difference between the two contact angles is called contact angle hysteresis indicating that the actual equilibrium contact angle is difficult to determine experimentally [Starov 2007].

The contact angle hysteresis is caused by several factors, such as variations in the fibre composition (e.g. fractions of different metal oxides in different parts of the fibre), variations in the fibre diameter originating from the manufacturing process and unevenly deposited silane patches on the fibre surface as well as the type of silane used [Sauer 1990, Dettre 1965, VI]. Also surface roughness influences contact angle hysteresis. Miller et al. reported that a lower receding contact angle for glass fibres can be explained by the presence of more higher surface energy components present on the fibre surface. The components tend to resist dewetting of the receding fluid front, thus lowering the receding angle. Higher wettability indicates that the work required to separate the glass fibre from water is higher. This means stronger polar interactions between the fibre and the liquid [Miller 1977, Van de Velde, 2000].

2.7. Characteristics of charged surfaces

In the boundary layer between a charged solid particle and a liquid, the potential energy varies with distance from the surface of the solid. The charge of particles may originate from ionization, ionic adsorption, orientation of polar molecules etc. Charged particles attract ions of opposite charge from the electrolyte leading in a distribution of counter ions at the solid-liquid phase boundary. The specific charge distribution formed at the interface is called the electrical double layer. The electrical double layer consists of two parts. The first part is a one-ion-thick layer, which sticks relatively tightly to the solid surface. The other part is the diffuse region, in which the electric potential decays with increasing distance from the particle surface. [Glasstone 1954, Bettlehem 1971, Atkins 1998].

In the Stern model the electrochemical double layer consists of a Stern layer of immobile ions on the surface and a mobile diffuse layer of counter ions(Figure 7) [Watson 2001].

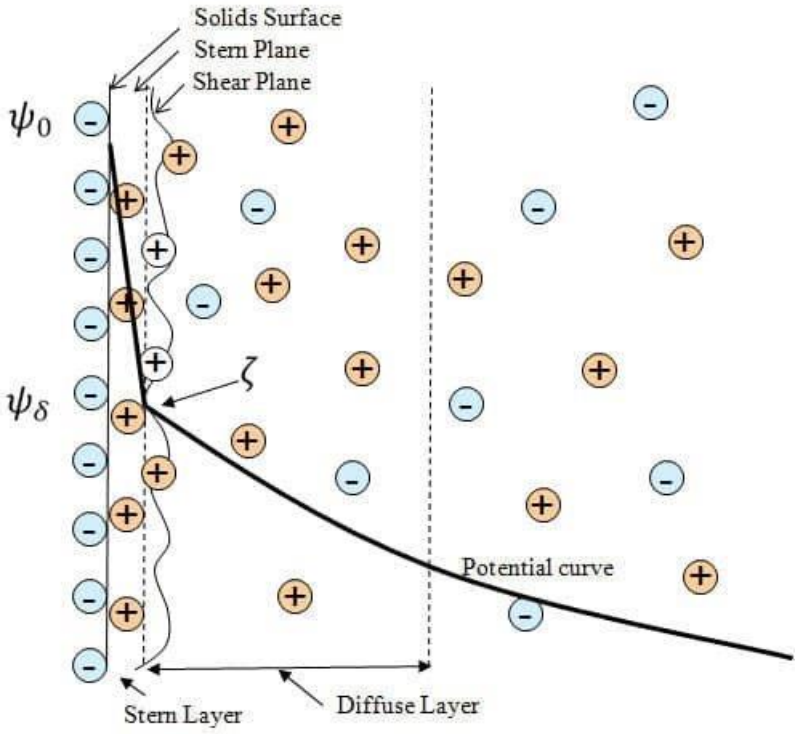


Figure 7. The electrical double layer according to the Stern model (after Shaw, 1969) [OnlineMBR 2018].

In the Stern model the electrical double layer is described as follows. ψ_0 is the symbol for the particle surface potential. ψ_δ describes the potential in the Stern plane. The potential in the shear plane is called the electrokinetic potential or the zeta potential, ζ. It is not possible to exactly determine the location of the surface of shear and it is therefore assumed that it is located in the Stern plane, so as an approximation, $\zeta = \psi_\delta$. According to the Debye-Hückel approximation the potential ψ decreases exponentially with distance x from the Stern plane. The distance $x= 1/\kappa$ is used as a measure for the thickness of the diffuse layer. The distance κ^{-1} is called the Debye thickness.

Parameters of the Stern layer such as the zeta potential and the thickness of the double layer are affected by the ionic strength of the electrolyte used. The value of the zeta potential is generally used as a measure of the effective surface charge of a particle. By changing the pH at which the streaming potential is measured, the effect of acid and base on the surface charge of the material can be determined [Gu 1998, Jacobash 1985, Anton Paar 1999, Idman 1998]. The Stern layer has an associated charge due to the dissociation of groups on the solid surface such as

SiO- H+ or by adsorption of ions OH-, H+, K+, Cl- [Jacobash 1985, Anton Paar 1999, Idman 1998].

In colloid chemistry, the main interest in electrokinetics is on the movement of charged particles in an electric field. The experimental measurements characterizing properties of the electric double layer aim at determining the zeta potential value (ζ-potential) of the system. An electrical field is deforming the electrical double layer. Alternatively, if mechanical forces affect different parts of the electrical double layer, an electrical field is created. The four different electrokinetic phenomena that can take place are a) electrophoresis, b) electro-osmosis, c) sedimentation potential and d) streaming potential. Streaming potential measurements can be utilized for determination of the surface charge of glass fibres. This technique will be discussed in chapter 5.3.5.

2.8. Solubility

Hildebrand introduced solubility parameters (δ) in 1924. Hildebrand's ideas were followed by Scott and later by Flory and Huggins. The work of Flory and Huggins involved a lattice upon which the solvent and solute were placed, resulting in a theory proposing an explanation to the inability of some solvents to dissolve given polymers [Hildebrand 1924, Watson 2001]. The theory proposes that a material with a high δ value requires more energy to dispense in a material with a low δ value, than would be gained by mixing the two materials. This results in immiscibility of these two materials. To be able to mix or to solvate two liquids with each other the Gibbs free energy G^m_p of the mixture at constant pressure needs to be negative. Mixing will occur if enthalpy change H^m_p is less than the change in the entropy term TS^m_p.

$$G^m_p = H^m_p - TS^m_p < 0 \tag{9}$$

Solubility parameter can be estimated from

$$\delta = [(\Delta^g_t H_m - RT)/V_m]^{1/2} \tag{10}$$

This assumption is a simplification and not applicable to all mixtures. The use of δ simplifies the system too much and does not apply to systems with polar and hydrogen-bonded materials. The solubility parameter was further divided to three components relating to dispersion forces, hydrogen bonding and polar interactions [Barton 1983]. In this theory, dispersion forces originate from fluctuating dipoles that have a positive nuclei and a negative electron cloud in all atoms of every molecule. Barton defined the hydrogen bonds to have

donor/acceptor associations or "secondary bonds formed to another atom by a covalently bound hydrogen atom" [Barton 1983]. Hydrogen bonding materials can be divided into three classes: proton donors, proton acceptors and proton donor/acceptors.

The total solubility parameter δ_t can be expressed as the sum of all components:

$$\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} \quad (11)$$

2.9. Silane desorption from a glass fibre surface

To be able to control desorption of the adsorbed silane from the glass fibre surface, the fibres can be washed with different solvents. Desorption of silane can be estimated based on the solubility parameters of the solvents used in the washing procedure. The solubility parameters used are defined by Hansen [Barton 1983]. Hildebrand [Brydson 1978] explained the usage of solubility parameters. The smaller the difference between the solubility parameters between the polymer and the solvent, the more soluble is the polymer in the solvent. If the variations between the solubility parameters are within ± 2 units, the solvent can be considered suitable for the solute investigated.

Consider the attraction force between the different molecules A and B being F_{AB}, and the attraction between similar molecules A be F_{AA} and between similar molecules B be F_{BB}. When $F_{AB}>F_{BB}$ and $F_{AB}>F_{AA}$, the mixture is compatible and no phase separation takes place. If F_{AA} or F_{BB} is bigger than F_{AB}, the mixture is incompatible. This is schematically presented in Figure 8 [Brydson 1978].

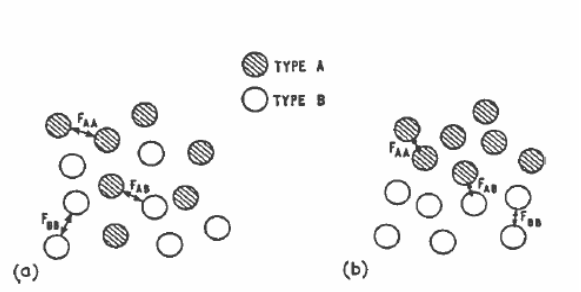


Figure 8. Schematic presentation of compatible and incompatible systems according to Hildebrand, a) If $F_{AB}>F_{AA}$ or $F_{AB}>F_{BB}$, the mixture is compatible; b) If $F_{AA}>F_{AB}$ or $F_{BB}>F_{AB}$, phase separation of molecules occurs [Brydson 1978].

In many surface reinforcement applications, the system consists of two or more different compounds competing of the free sites on the substrate surface. This competitive adsorption leads generally to varying adsorption mechanisms for the different components. The component, which preferentially best wets the fibre surface, determines the adsorption tendency. When the system consists of molecules adsorbing on the surface followed by polymerization, it is not possible for the solvent to remove the polymerized material from the surface anymore. In this case, it is the solvent that is adsorbing on the polymer surface.

3. Recent trends and modifications in glass fibre composites

The modern trends, developments and applications in the field of glass fibre composites are several. Glass fibres are known to be excellent at handling high tensile stress but are weak in terms of enduring compression depending on their brittle nature. Plastics have the ability to handle compression loading well but cannot endure high tension. A combination of these two components gives a material that resists both compressive and tensile forces well [Erhard 2006]. Chemical modifications of glass fibres as components in various glass fibre reinforced composites are of great importance when striving to achieve the required strength values at various applications. Chemical modifications of glass fibre reinforced plastics have helped to achieve enhanced mechanical properties in matrix rich regions. Nanoclay-glass fibre hybrid composites are the latest development in elevated erosion resistant materials [Pirzada 2015]. Recent fields of application where surface-treated glass fibres are components in reinforced glass fibre composites are presented in this chapter.

Applications of fibre-reinforced plastics are still limited to smaller parts made of reinforced plastics, such as parts of bridge deck, griders, reinforcement bars, stay cables or handrails. However, the development in the field of silane coupling agents has during the last ten years been considerable. Large companies have R&D departments doing in-house research and apply silanes with various functionalities onto surfaces on customer demand and the field is mostly applications and materials driven. It is generally accepted that the adsorption mechanism of silanes onto E-glass fibres (presented in Figure 4) follows the traditional model of hydrolytic deposition of silanes.

Coupling agents available on the market have for the last twenty years been dominated by aminosilanes [Gelest 2017]. The latest development in the field are the synergistic multi-silanes. The multi-silane approach, where tripodal or dipodal silanes are combined with conventional silanes, have shown dramatic effects on adhesion to treated surfaces. Silane combinations offer an advantage over conventional silanes in terms of maintaining the integrity of surface coatings and composites in aqueous and aggressive environments. The improved durability is associated with increased cross-link density of the interphase and the resistance to hydrolysis. This is due to the possibility to form not only three but five or six oxane bonds [Arkles, 2014].

In this thesis, the tripodal isocyanurate silane was one of the studied silanes. One of the developments in the field of silane-treated-surfaces is in the analysis of

coated fibres and especially in the development of analytical techniques and equipment. As an example, streaming potential devices are commercially available and used in companies as everyday quality control instruments [Plonka 2004].

3.1. Multipodal silanes

Multipodal, i.e. di- or tripodal silanes are newly developed adhesion promoters that have a hydrolytic stability up to 10 000 times higher than that of conventional silanes. The challenge with conventional silanes has always been that silanols self-condense to form siloxanes resulting in phase separation or gelation. Through addition of multipodal silanes, the enhanced hydrolytic stability has significant impact on shelf life, substrate bonding and improved mechanical strength of composites [Gelest 2014].

Functional di- and tripodal silanes as well as combinations of non-functional di- or tripodal silanes and functional conventional silanes have a significant impact on substrate bonding and possess enabling activity in many adhesive systems, particularly primer and aqueous immersion applications [Gelest 2014]. Di- or tripodal silanes have two or three silicon atoms that can covalently bond to a surface unlike conventional silanes, which have only one such silicon atom for surface attachment (Figure 9.) [Singh 2014].

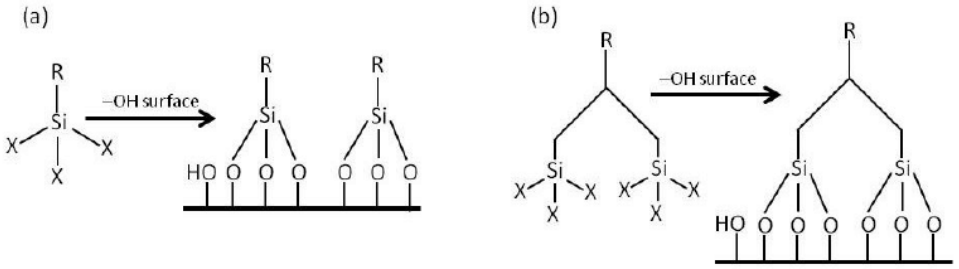


Figure 9. Covalent bonding to a hydroxylated surface by a) a conventional and b) a dipodal silane [Singh 2014]

With several silicon atoms available for surface atoms to bond offers higher wet durability in the end product. In this thesis, surface treatment with tripodal silane was studied.

3.2. Self-Healing composites

Functional repair components stored inside hollow reinforcement fibres is considered as a self-repair system for future composite structures. Self-repair can take place in two ways; intrinsic, where the polymers are able to heal cracks by themselves, or extrinsic where the healing agent has to be pre-embedded [Trask 2006, Yuan 2008]. Intrinsic self-healing is based on physical interactions in the composite. The healing process has five steps: 1) surface rearrangement, affecting the initial diffusion function and topological feature, 2) surface approach, 3) wetting, 4) diffusion, the main factor controlling the recovery of the mechanical properties and 5) randomization, ensuring disappearance of the cracking interface. The core issue in the extrinsic healing technique is the filling of the brittle-walled vessels with polymerizable medium. The chemical floats to the crack, polymerizes and eliminates the crack and weakness. Hollow fibres embedded within the composite have been investigated at different length scales and in various materials, such as bulk concrete [Dry 1996, Kessler 2001, Trask 2006].

3.3. Glass-ceramic composites

Glass fibre reinforced composites or glass-ceramic composites are materials that are suitable for industrial applications requiring a combination of lightweight, strength and toughness such as wings, luggage racks, doors and bulkheads. The mechanical properties of ceramics can be significantly improved by use of the fibre reinforcement concept, which has led to a new class of composite materials referred to as ceramic matrix composites (CMC). The research in this field has led to promising results in achieving lightweight structural materials where high temperature strength is combined with improved fracture toughness, damage tolerance and thermal shock resistance. Aluminosilicate glass fibres and borosilicate glass fibres have been found as good and suitable reinforcing fibres for this application. The processing can be done in three ways; simple slurry infiltration for loosely packed fibre weaves, chemical vapor infiltration or electrophoretic vapor deposition [Chavla 1993, Boccacini 2001].

3.4. Glass fibre reinforced concrete

Modern architecture puts continuously increasing requirements on the construction materials and technologies. Glass fibre reinforced concrete is lighter than natural stone and solid concrete and can therefore meet the expectations of

especially shape building facades in high quality. With this non-metallic high performance material, it is possible to construct lightweight, thin, single- and double-curved elements [Ferrira 2012, Funkea 2013]. The innovative material is made of two-dimensional bi-directional wrap-knit alkali-resistant glass fibre reinforced concrete. This construction allows for degrees of freedom by increasing the material strength and by improving the material durability. The glass fibre composites have superior thermal insulation capability and seismic shear strength. These features make them interesting and essential ingredients in modern building materials [Brameshuber 2006, Priestely 1994].

3.5. Nanoclay-glass fibre hybrid composites

Glass fibre composite materials have good properties along the fibre direction, but severe problems are faced in matrix-rich regions where stress transfer to reinforcing fibres is not effective and only polymer properties dominate. This common problem is handled with hybrid composites, where nanofillers are incorporated into the matrix phase. Incorporation of nanomaterial to the composite can provide increased stiffness, strength and thereby increased toughness. Depending on the nanoparticle, chosen enhanced electrical and thermal conductivity or barrier properties can be added. Multi-scale composites can be manufactured by two methods; independent dispersion of the nanofiller throughout the polymer matrix or chemical linking of the nanofillers to the fibres. Chemical linking of the nanoparticles to the fibres strengthens the fibre-matrix interface and transfers stress more efficiently, overcoming thereby the problems of traditional glass fibre composite systems [Wood 2012, Kinloch 1983, Feng 2011].

3.6. Recycling of glass fibre composites

For a long time, glass fibres have been the most applied reinforcement material in composites within the construction industry. Glass fibre reinforced materials, both end-of-life and manufacturing waste, are difficult to recycle in a cost-effective way. This type of material has traditionally been disposed in landfills, which due to the legislative and landfill-pricing development has today become impossible. The awareness of this problem is reflected in the extent of recent research around glass fibre recycling especially as the use of glass fibre reinforced composites is currently growing particularly within the transportation and the wind energy sectors. Several industrial processes are available for recycling

composites but the biggest challenge within this field is remaining. When glass fibre composites are recycled the performance drops by 80 – 90 % [Thomason 2016, Derosa 2005, Goodship 2012].

In recent papers of Yang et al. and Thomason et al. the potential of strength recovery through HF treatment of glass fibres has been reported. Yang et al. reported that the fibre strength was dependent on the HF treatment time and the conditioning temperature. Heat-treated fibres with HF treatment showed high levels of fibre recovery, but only minor improvements in composite performance [Yang 2015]. Thomason et al. presented results based on research following a similar protocol as that of the HF work by Yang et al. The authors presented the use of a combination of thermal conditioning, hot NaOH treatment and silanization on the average strength of single fibres, the interfacial shear strength between the fibres and the performance of random in-plane glass fibre laminates. The results indicated that 80 % of the glass fibre strength was lost when exposed to temperatures typically used in thermal recycling processes. These methods are not suitable for composite reinforcement. However, the single fibre strength recovery showed more promising results. According to the data on single fibre tensile testing up to 75 % of the strength loss can be recovered by a short treatment with NaOH. The fibre strength recovery was further enforced by application of silane sizing. The silane layer also ensures further composite compatibility in a polymer composite matrix. The recent development of a non-HF-based glass fibre strength regeneration treatment technology is a step in the right direction towards cost-effective closed-loop glass fibre reinforced products [Thomason 2016].

4. Objectives

In this thesis silane adsorption and desorption on industrial E-glass fibres was studied. The aim of the research was to characterize the fibre surface before and after surface treatment with silane and to gain better understanding of the surface processes at the silane-glass interface of the composite. Another objective was to investigate how the solvent used affected silane adsorption on the glass fibre surface.

Surface modification of glass fibres was performed chemically and the modified surfaces were characterized by using both wet and dry analysis techniques.

In paper I, the aim of the study was to examine the performance of glass fibres treated with a variety of silanes in both aqueous and organic liquids. Three silanes (aminosilane, anhydride silane and epoxysilane) were used as coating chemicals.

In papers II and III, the aim was to investigate the influence of the relative affinity of a tripodal isocyanurate silane to the fibre surface and the solvent, respectively. Adsorption on fibre surface from three organic solvents was monitored.

The aim of paper IV was to examine in detail the effect of strong acids and bases on E-glass fibres. The silanes used in this work were isocyanurate silane, aminosilane and ureidosilane. In addition, the deposition characteristics of silanes from acid solution as well as the effect of acid/silane solution upon the E-glass fibres was examined.

In paper V, the influence of surface modification on a porous silica powder with mono- and bifunctional silanes from toluene was investigated. The influence of the bifunctional silane treatment on glass fibre surface from aqueous solution was also reported.

Paper VI discusses the orientation of adsorbed epoxy and metacrylate silanes on E-glass fibre surfaces especially in low concentrations. In addition, formation of aggregates was examined.

5. Experimental methods

E-glass fibres were treated in aqueous or organic solutions according to the procedures described in publications I-VI. A summary of the treatment procedures are presented in Figure 11.

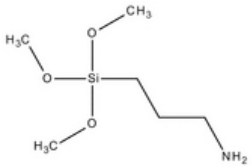
5.1. Materials

E-glass fibres from Ahlström Glassfibre in Karhula were used as substrates. Glass fibres were untreated and drawn from molten glass mass with only clean water as lubricant. Glass fibres were manufactured according to a standard procedure described in details in the literature [Lowenstein 1973]. The mean diameter of the fibres was measured to be 10.8 μm and they were cut to a length of 8 mm. The density was measured to be 2.50 g/cm^3 and the specific surface area 0.7 m^2/g.

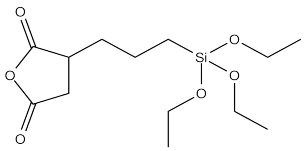
All chemicals used were at least of laboratory grade and were used without further purification. As surface treatment materials in the adsorption studies, ten different silanes were used, of which one was applied on glass fibres from both aqueous and organic solvents. The rest were applied from an aqueous solution. The silane coupling agents were chosen because they differ chemically from each other and were the best available products to each test. The chemical names and structures of the used silanes are presented in Table 1.

Table 1. Silanes used in the thesis.

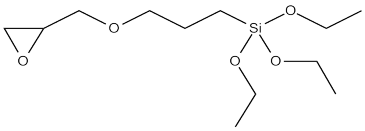
Chemical	Commercial
N,N-bis-(3-trimethoxysilylpropyl)amine	Amino
(3-triethoxysilylpropyl)succinic acid anhydride	Anhydride
3-glycidoxypropyltriethoxysilane	Epoxy
Tris(3-(tri-methoxysilyl)propyl)isocyanurate silane	Y11597, Isocyanurate
Aminofunctional silane ester	Y9708, Amino
γ-Ureidopropyltrimethoxy silane	Y11542, Ureido
Octyltrimethoxysilane	Octyl silane
γ-Aminopropyltrimethoxysilane	Amino
γ-Methacrylpropyltrimethoxysilane	Methacrylate
γ-Glycidoxypropyltrimethoxysilane	Epoxy



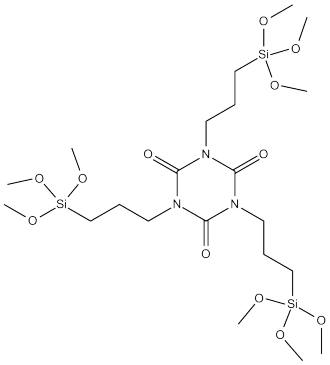
3-trimetoxysilylpropyl) amine [I]



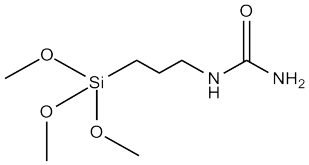
(3-triethoxysilylpropyl) succinic acid anhydride [I]



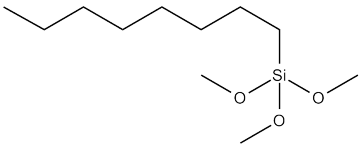
3-glycidoxypropyltriethoxysilane [I]



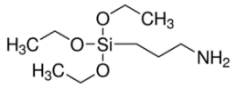
tris(3-(trimethoxysilyl)propyl) isocyanurate [II,III,IV]



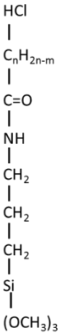
γ-ureidopropyltrimethoxy silane [IV]



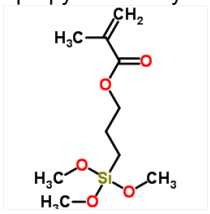
octyltrimethoxysilane [V]



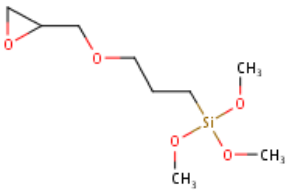
γ-aminopropyltrimethoxysilane [V]



aminofunctional ester [IV]



γ-methacryloxypropyltrimethoxysilane [VI]



γ-glycidoxypropyltrimethoxysilane [VI]

Figure 10. Chemical formulas of the silanes used in the thesis.

Water used in the tests was distilled and deionized and the pH of water was measured to be 5.5-5.8. Surface tension of water was 71.97 mN/m at 25°C and conductivity was $5.56*10^{-8}$ S/cm at 25°C.

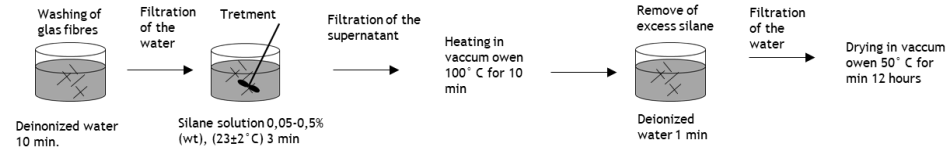
5.2. Silane treatment of the E-glass fibres

Silane treatment concentrations and the treatment procedures are presented in Table 2. and Figure 11.

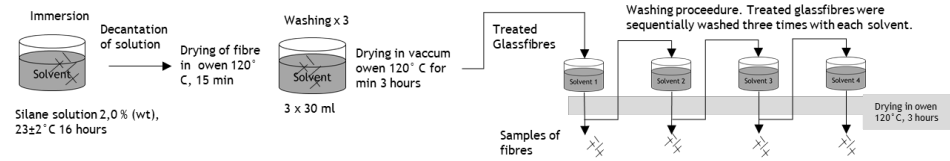
Table 2. Silane concetrations, solvents and pH's used in this thesis.

Paper	Silane	Conc. wt%	Solution	pH
I	N,N.bis-(3-trimethoxysilylpropyl)amine	0.05, 0.2, 0.5	aqua	5.5-5.8
I	(3-triethoxysilylpropyl)succinic acid anhydride	0.05, 0.2, 0.5	aqua	5.5-5.8
I	3-glycidoxypropyltriethoxysilane	0.05, 0.2, 0.5	aqua	5.5-5.8
II,III,IV	tris(3-(trimethoxysilyl)propyl)isocyanurate	0.05, 0.1, 0.5, 1, 2	aqua, CCl_4, ethanol, toluene	2, 4, 5.8, 7,9,12
IV	γ-ureidopropyltrimethoxy silane	0.05, 0.1, 0.5, 1	aqua	2, 4, 5.8, 7,9,12
V	octyltrimethoxysilane	0.005, 0.01, 0.1, 0.15	toluene	4,5,6,7
V	γ-aminopropyltrimethoxysilane	0.005, 0.01, 0.1, 0.15	toluene	4,5,6,7
IV	aminofunctional ester	0.05, 0.1, 0.5, 1	aqua	2, 4, 5.8, 7,9,12
VI	γ-methacryloxypropyltrimethoxysilane	0.005, 0.01, 0.2, 0.15	aqua	4,5,6,7
VI	γ-glycidoxypropyltrimethoxysilane	0.005, 0.01, 0.2, 0.15	aqua	4,5,6,7

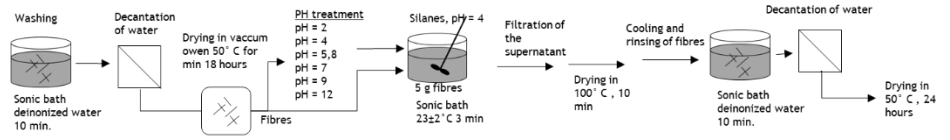
Paper I



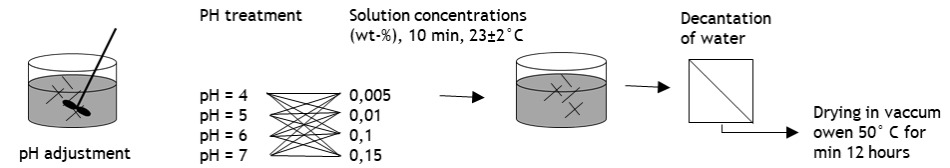
Paper II & III



Paper IV



Paper V



Paper VI

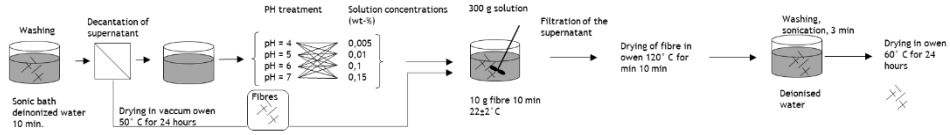


Figure 11. Surface treatment procedures per papers I-VI.

5.3. Characterization methods

5.3.1. Adsorption isotherms

An increased concentration of solute, compared to the bulk concentration, close to an interface, is called adsorption. Adsorption of surface active agents onto solids are commonly described by adsorption isotherms. Experimental adsorption results obtained can be interpreted by the classical Langmuir, Freundlich or Henry equations, or combinations of these [Parfitt 1981, Bäckman 2000,V]. The adsorbed amount on the surface can be achieved by direct methods like optical

reflectometry, among others, or by indirect methods. The direct method measures the adsorbed amount on the solid surface, while the indirect method, more used, measures the amount of the non-adsorbed adsorbate in the supernatant. In order to measure the non-adsorbed amount in the supernatant, the solid and the solution phase have to be separated. The adsorbed amount, Γ, is calculated according to equation [Fleer 1993]:

$$\Gamma = \frac{\Delta c_p V}{A_s} \tag{12}$$

where Δc_p is the difference between the added amount of polymer, and the amount detected in the supernatant at equilibrium, V the volume of the solution, and A_s the specific area available for adsorption.

5.3.2. Electron Spectroscopy for Chemical Analysis (ESCA)

Electron spectroscopy for Chemical Analysis (ESCA) or X-ray Photoelectron Spectroscopy (XPS) is an analytical technique for chemical characterization of surfaces. In this technique, the sample is placed in a sample chamber in vacuum. The sample is bombarded with soft x-rays and core-level photoelectrons are emitted. The schematic picture of an ESCA device and the principle of ESCA technique are presented in Figures 12 and 13. ESCA is an instrument with high surface sensitivity and it provides information of the outermost surface. Detection limits in ESCA are of the order 0.1 - 1 at-% and a typical sampling depth is about 5 nm [Brewis 1997, Briggs 1990].

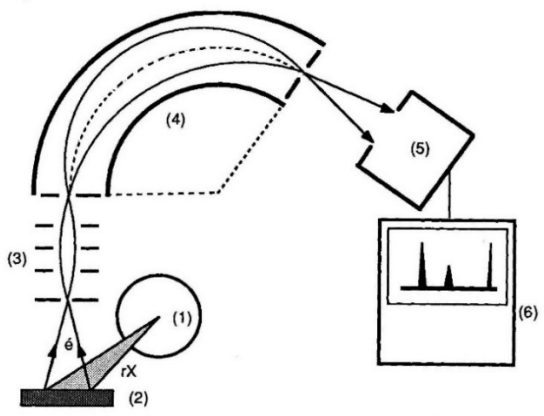


Figure 12. Schematic picture of a XPS analyzer with the following components and units: 1) X-ray tube, 2) Sample, 3) Electronic focusing system, 4) Spectrometer, 5) Electron detector (channeltron) and 6) Data acquisition unit [Iramis 2017].

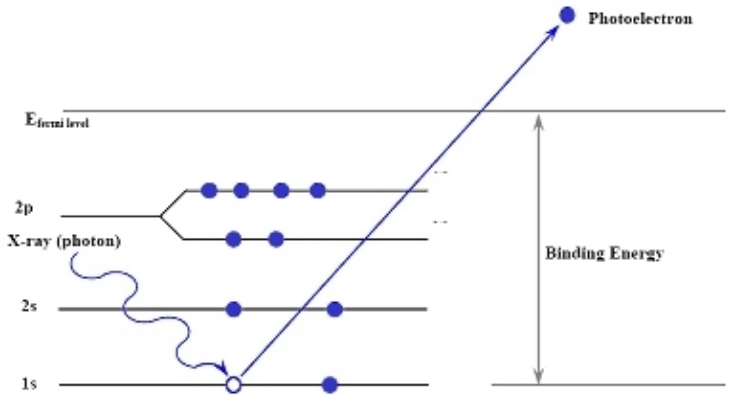


Figure 13. Principle of ESCA technique [CoreTech Integrated Limited 2018].

Information about elemental composition of solid surfaces, e.g. fibres, can be achieved with XPS by registration of kinetic energies of the emitted photoelectrons. This results in a spectrum of electron intensity as a function of kinetic energy (E_{kin}). The kinetic energy is replotted using a binding energy (E_b) scale. The relation between the kinetic and the binding energy is presented in equation 13, where

$$E_b = h\upsilon - E_{kin} - \Phi_s \quad (13)$$

$h\upsilon$ is the exciting X-ray energy and Φ_s the work function of the equipment. The most common X-ray sources used are Al Kα ($h\upsilon$=1486,6 eV) or Mg Kα ($h\upsilon$=1253,6 eV). All elements except helium and hydrogen can be detected with ESCA. High surface sensitivity is achieved by a limited depth of escape of the emitted photoelectrons. The average distance that a photoelectron travels, i.e. the mean free path (mfp) is mainly a function of its kinetic energy and the density of the solid.

The inelastically emitted scattered electrons become part of the electron background of the spectrum. In this spectrum, the intensity increases with increasing intensity E_b. The excited core holes resulting from photoelectron emission relax, either by X-ray emission (fluorescence), or by Auger electron emission. During this relaxation, the core hole is filled by another electron from a higher energy level. The energy difference between these two levels results in the emission of an Auger electron. Auger electrons show up in ESCA spectrum as broad peaks and have characteristic energies. However, these peak energies are independent of the exciting X-ray energy ($h\upsilon$) and can easily be distinguished

from the photoelectron peaks by switching the X-ray source [Brewis 1997, Briggs 1990]. The Auger phenomenon is schematically presented in Figure 14.

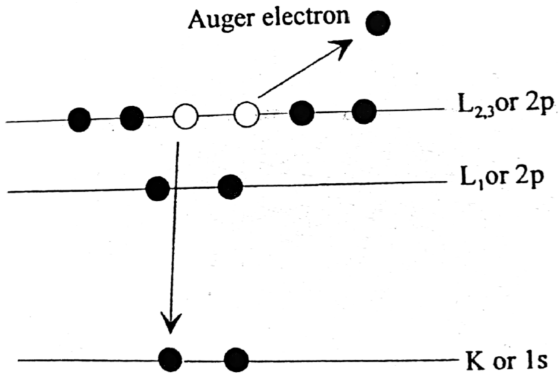


Figure 14. A schematic picture of the Auger process [ESCA System manual 1988].

ESCA can be used to obtain information about the chemical characteristics of a solid as it is possible to relate the binding energies of e.g. C (1s) or Si (2p) peaks to the chemical binding state of these elements. For practical purposes, ESCA has been shown to provide direct valuable elemental information about the solids and about adsorption of surface-active agents on solid surfaces. Adsorption of surfactants can in some cases directly be confirmed by using ESCA by analysis of chemical binding states of elements present on the surface. Semi-quantitative information about the amount of surfactant adsorbed can also be obtained. Due to the high surface sensitivity of ESCA surface coverage of even sub-monolayers can be recorded. A more detailed description of the ESCA technique is found e.g. in Briggs et al. [Briggs 1990]. The incident angle between the x-ray source and the apparatus has in this work been set to 45°. In Paper I, the angle was set to 30°. XPS can also be used for quantitative measurements. However, only values of atomic surface concentrations can usually be achieved for homogeneous samples and the accuracy is normally not better than 10 %.

5.3.3. ESCA signals

In this work, typical ESCA signals for silica surfaces, glass fibres and silanes were examined. The elements and their peaks analyzed were C (1s), O (1s), Si (2p), Al (2p), Ca (2p), Na (1s), N (1s) and B (1s). Atomic concentrations (%) of different binding states of i.e. carbon and silicon determined from high-resolution C (1s) spectra were also reported.

5.3.4. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

Several spectroscopic analysis techniques have been applied in order to analyze surfaces modified with filler materials. Besides ESCA, infrared spectroscopy has turned out to be an effective method.

The strong scattered light from glass fibres has caused the biggest problems in IR technique [Ishida 1978]. Diffuse reflectance infrared Fourier transform spectroscopy, DRIFTS, is working with the scattered light from the material itself and can thereby be successfully used for analysis of surface-modified glass fibres [Culler 1984]. A schematic picture of DRIFTS is presented in Figure 15. As the infrared beam is penetrating the surface to a depth of ca. 1 μm it can be considered to detect the bulk of the sample. A special DRIFTS unit is placed into the IR chamber and the sample itself is placed in a measuring cup inside the DRIFTS unit.

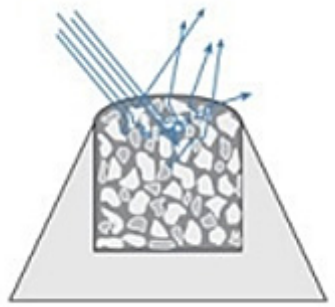


Figure 15. A schematic picture of the IR beam interacting with the sample in a diffuse reflectance experiment [ThermoFisher Scientific 2018].

Wavelengths between 3100 cm^{-1} and 2700 cm^{-1} were analyzed. In this area signals from C-H groups can be detected. Signals from the C-H groups originate from the surface modification solution used, i.e. the silane, and are thereby an excellent indicator for possible silane adsorption. It should also be mentioned that DRIFTS as a technique is suppressing weak signals and strengthening strong signals.

5.3.5. Streaming Potential/Zeta Potential (SP/ZP)

Streaming potential can be measured for a material packed in unorganized capillars or for a material that can be formed as porous plugs. The method is reflecting the processability of fibres in a realistic way [Fagerholm 1992]. The solid

phase (in this case glass fibres) is held stationary by a porous plug. An electrolyte solution is compressed through the fibre plug with a constant pressure and the potential difference between the electrodes on both sides of the plug is registered as a function of time. This gives an electric potential difference U between the ends of the fibre plug. A schematic picture of streaming potential is presented in Figure 16.

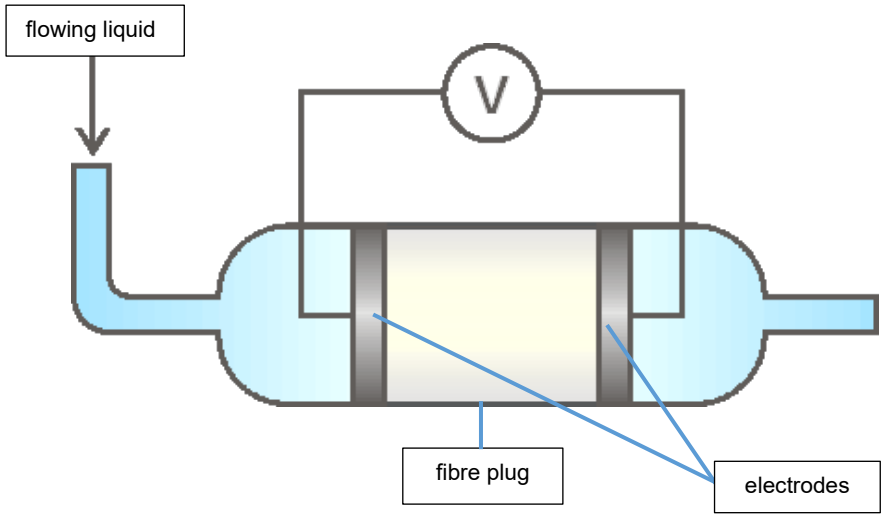


Figure 16. Schematic picture of a streaming potential measurement.

The zeta potential, ξ, can be calculated from

$$\xi = \eta \, k_0 \, U / \varepsilon \, \Delta p \qquad (14)$$

, where η is the viscosity of the liquid, k_0 is the conductivity of the liquid, U is the difference in the electrical potential, ε is the dielectric constant of the liquid and Δp is the pressure difference over the plug, i.e. the pressure which drives the liquid through the fibre plug.

The streaming potential device used in Paper I was built in-house according to the principle described by Jacobash et al. [Jacobash 1985]. The measurement chamber of the streaming potential apparatus consisted of a cylindrical cell with a silver-coated electrode at each end. Between the two electrodes, the glass fibres were packed to form a plug with a certain pre-selected porosity [Schurtz 1985]. In Papers V and VI, the streaming potential device used was a commercial Anton Paar Electrokinetic Analyzer (EKA), equipped with a pH titration apparatus [Anton Paar 1991].

In EKA a pressure difference between the inlet and the outlet of the capillary system is generated using a pump [Anton Paar 1999]. The current (mV) and the streaming potential (Up) are measured with silver chloride coated circular silver electrodes. The solution is pumped under pressure through the system back and forth. The method requires that both streaming potential and specific electrical conductivity are measured [Anton Paar 1999].

Börner and Schurtz have reported that the packing of the fibre plug in streaming potential measurements is of great importance. The electrolyte solution has to be able to be pumped through the system without affecting the pressure gradient over the glass fibre plug [Börner 1994, Schurtz 1985]. The increase in the pressure gradient in the EKA system needs to be held linear. Non-linear increases in the pressure may result in non-laminar flow affecting the flow of the electrolyte solution and this would result in non-reliable results.

In the measurements it was noticed that as the pH of the electrolyte solution became more acidic the zeta potential rose to more positive values. The isoelectric point (iep) is the pH value where the measured zeta potential value is zero. It can be stated that if the pH of the electrolyte solution is higher than the pH of the iep, the fixed surface of the double layer is anionic. If the pH is lower than the iep, the fixed surface of the double layer is cationic [Watson 2001].

The iep of the surface (anionic or cationic) is of great importance. At basic pH the surface of the E-glass fibres is anionic with OH^- groups dominating. This may result in "upside down" orientation of the silane. If the pH of the surface is acidic the glass fibre surface is repelling amino groups and attracts the acidic silanol groups. This results in "rightway-up" orientation [Torrkulla 1998]. Both glass fibre surface pH as well as the silane deposition pH affect adsorption of the silane.

5.4. Other characterization methods used

The main characterization methods used in this work are presented above. In addition, several other characterization methods were utilized in this thesis work. The complementing characterization methods used were: conductivity measurements (I, IV), scanning electron microscopy (SEM) (II, III), thermogravimetric analysis (TGA) (II,III), Raman spectroscopy (IV), Plasma emission spectroscopy (IV) and gas chromatography combined with mass-spectrometry (GC-MS) (V).

All characterization methods used have been described in detail in papers I – VI.

6. Results and discussion

In this chapter the main results from Papers I-VI are summarized.

6.1. Adsorption of mono- and bifunctional silane on porous silica particles [V]

Considering the adsorption process in general, the most important parameters in the process are the following: (i) the surface chemistry of the solid; (ii) the nature of the solute as well as the chemical structure and the interactions with the solvent; (iii) the nature of the solvent; (iv) the nature of the interactions between the surface and the adsorbed species; (v) the structure of the adsorbed layer; and (vi) temperature. Adsorption isotherms can be utilized in characterizing adsorption on powder surfaces. The system should however be designed so that the parameters (i) and (iv) dominate the adsorption isotherm [V].

Adsorption of the monofunctional silane octyltrimethoxysilane (OTMS) and the bifunctional silane γ-aminopropyltrimethoxysilane (APTMS) on silica powder was analyzed with the Langmuir adsorption isotherm. The procedure has been described in literature [Bäckman 2000, Hiementz 1986]. It is possible to calculate the area occupied per adsorbed molecule, if the specific surface area of the substrate is known. However, in this study the mean molecular area concept was found not to have real physical significance, even though the cross-sectional area of APTMS was found to be 0.28 nm^2, corresponding to a fully compressed monolayer of octadecyltrimethoxysilane at the air/water interface [Linde´n 1996]. The concept does not take into account aggregation into large aggregates and eventual two-dimensional structures. It was concluded that the bifunctional silane APTMS was adsorbed mainly with its amine group attached onto the silanol groups of the silica powder.

The cross-sectional area of OTMS, 1.21 nm^2, indicated incomplete initial adsorption and did not indicate monolayer formation. The results indicated that adsorption did not reach a plateau value for OTMS within the concentration range investigated. It was therefore not possible to fit a Langmuir-type of isotherm, which presumes that a monolayer or monosite adsorption would take place. The experimental data was fitted to the Freundlich isotherm. The plot in Figure 17.a indicates that the Freundlich isotherm is satisfactory (R=0.9921) in representing experimental data. The Freundlich type of adsorption implies a multilayer adsorption induced by (i) hydrogen bonding to or condensation with the silanol groups or by (ii) secondary OTMS surface aggregation on the surface monomers.

However, Larsson and Stenius have in their adsorption studies of small probe molecules onto wood found two adsorption mechanisms taking place simultaneously [Larsson 1987]. They observed fast specific adsorption onto surface hydroxyl groups and slow nonspecific adsorption into the porous wood matrix. These adsorption processes could be described by two overlaid adsorption isotherms, a Henry-Langmuir isotherm. The resulting general appearance of their isotherm was very similar to the adsorption process of OTMS. The combined isotherm fitted well to the experimentally determined adsorption of OTMS (Figure 17.b).

It can be stated that OTMS is initially weakly adsorbed onto a few silanol groups. At higher concentrations, OTMS forms aggregates and seems to adsorb onto the surface quite non-specifically. The adsorption process can be described by the multisite Freundlich isotherm or more accurately by overlaid Langmuir and Henry isotherms. The Freundlich isotherm describes the specific adsorption of OTMS onto surface silanol groups and the Langmuir-Henry isotherm describes the non-specific adsorption of formed silane aggregates.

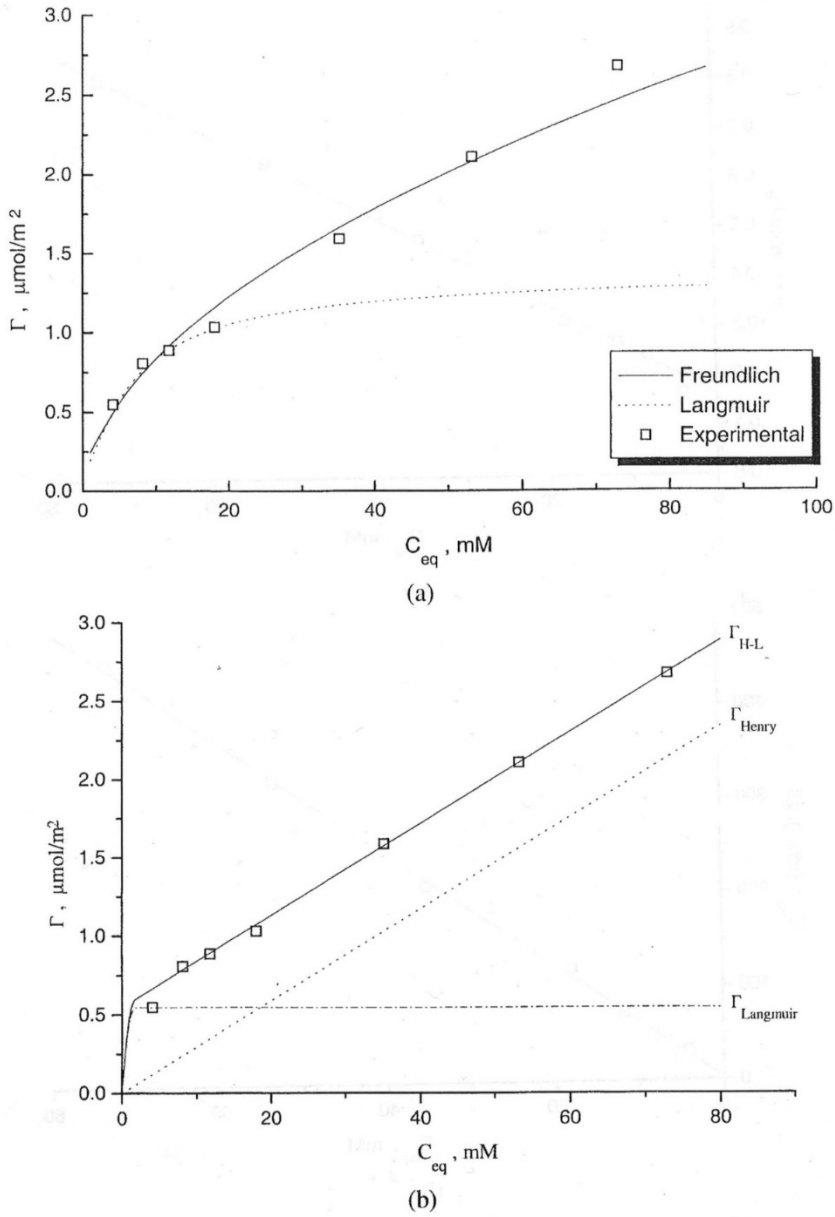


Figure 17. The fit of the Langmuir and Freundlich isotherms (a, upper curves) and the Henry-Langmuir isotherms (b, lower curves) to the experimental surface excess values (squares) for octyltrimethoxysilane (OTMS) adsorbed onto silica from toluene at 25ºC.

6.2. Effects of acid and base treatment on E-glass fibres [IV, V]

Treatment of E-glass fibres with acids, bases and deionized water typically results in leaching ions from both the surface and the bulk of the E-glass fibres [Elmer 1984, Friedrich 2000, Kobayashi 1982, Pantano, Martin 1978, Tettamanzi 1983, IV]. When the E-glass fibres in this work were exposed to these solvents, similar results as reported in the literature were seen. Anions and cations leached out from the untreated glass fibre surface by both acidic and basic solutions (Figure 18). This phenomenon was confirmed by ESCA (Table 3.)

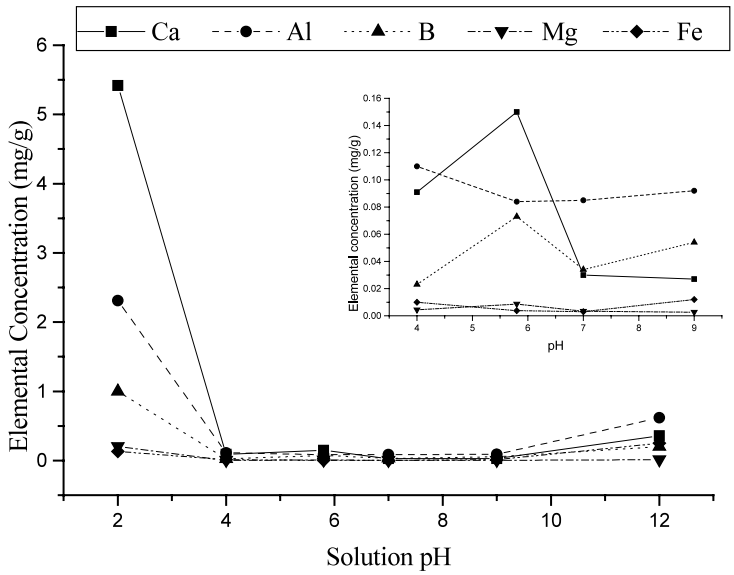


Figure 18. Effect of pH on the quantity and type of ions leached from E-glass fibres from pH = 2 to pH = 12. Insert: Effect of pH on the quantity and type of ions leached from E-glass fibres from pH = 4 to pH = 9.

The strong acid solution (pH 2) removed large quantities of aluminum, boron and calcium. The leakage of aluminum and calcium from the fibre surface led to a breakdown of the fibre surface and left a network consisting mainly of silica and boron oxides on the fibre surface. The surface breakdown included an ion exchange mechanism between the hydrogen ions of the acid and the aluminum, boron and calcium ions originating from the glass fibre surface. This has also been reported in the literature [Kobayashi 1982]. In the treatment with strong basic solutions (pH 12) the SiO_2 and B_2O_3 networks of the glass fibre surface were hydrolyzed and the hydroxides formed dissolved from the fibre surface to the solvent. An ion exchange mechanism was observed. Treatment with strong bases, where pH is above 10, remove ions from the glass fibre surface by hydrolyzing the

Si-O-Si network [Friedrich 2000]. Hydrogen ions were replaced by sodium on the glass fibre surface and formed a Si-O-Na bond, leading to a large amount of sodium detected on the fibre surface after surface treatment in pH 12 [Elmer 1984]. This weakening of the whole fibre structure can explain the poor physical properties of the treated fibres [Britcher 1998, Elmer 1984]. Calcium was leached from the fibre surface both at low and high pH.

Table 3. Elemental analysis (ESCA) of the E-glass fibre surface before and after treatment with acid and base solutions. (nd = not detected). The results are presented in At%.

	Ca	Al	B	Na	Si	O
untreated	3.4	5.6	0.4	0.4	17.4	44.4
pH = 2	0.6	1.4	1.0	nd	24.5	72.5
pH = 7	3.1	5.7	nd	nd	24.2	67.1
pH = 12	3.2	4.7	0.6	11.2	17.2	63.3

Adsorption of γ-aminopropyltriethoxysilane (APTES) from water was dependent on the pH and concentration of the solution in which the E-glass fibres were treated. When the pH of the treatment solution exceeded the pH_{iep} (4.2) of the untreated glass fibres, the free silane became oppositely charged. A greater adsorption of APTES was detected at increasing pH. This could be seen as a positive zeta potential and as a shift upward of the isoelectric point (Table 4). An excess of silane produced a phase-separated, hydrolyzed silane network, which was mechanically bound around the glass fibres. In acidic solutions, the properties of the silane-treated glass fibres as well as those covered with an excess polymer skin could be detected. In alkaline solutions, the diminished silane adsorption or the enhanced influence of washing was detected, indicating a linear relation between the surface charge and surface wetting [V].

Table 4. The isoelectric points in 0.001 mol dm^{-3} KCl solution of E-glass fibres treated with APTES at different pH and with different concentrations of the silane.

Conc. of silane (wt%)	pH = 4	pH = 5	pH = 6	pH = 7
0.005	5.2	5.3	5.5	5.3
0.01	4.6	6.2	6.8	7.9
0.10	8.6	8.9	8.9	8.8
0.15	8.5	9.0	9.3	8.9

Treatment with deionized water resulted in leached ions throughout the whole pH scale. Aluminum and calcium leached out in largest quantities. These both ions have a strong complex building ability and are capable of forming organometallic complexes with silanes.

6.3. Effect of surface treatment on E-glass fibre surface charge and silane adsorption [I, V, VI]

The streaming potential technique has been used for characterizing changes in electrokinetic parameters of heterogeneous surfaces, for example, due to silane adsorption on a glass fibre surface. The streaming potential technique gives information on the anionicity or cationicity of the surface [Jacobasch 1985, Schurtz 1985, Jednacak 1974, Garcia 1997]. Recalculated to zeta potential, a negative potential indicated that the glass fibre surface was anionic and a positive potential indicated a cationic surface [Jednacak 1974].

Aminosilane adsorption on the E-glass fibre surface reported in Paper I changed the fibre surface from a negatively charged surface via neutralization to a highly positively charged surface due to the excess adsorption of the cationic silane. The surface treatments with anhydride and epoxy silanes changed the glass fibre surface to even more anionic, due to the negative charge of the silanes. Adsorption of the anhydride silane was confirmed by taking a closer look at the carbonyl C_3 peak in the ESCA spectrum. Anhydride silane may react with water and produces two carboxylic acid groups. The carbonyl C_3 signal was increasing with increasing concentration of the silane and indicated that the anhydride silane was partially oxidized to carboxylic acid (Table 5). The calculated atomic concentrations for the different binding states of carbon were determined from the deconvoluted high-resolution C (1s) spectra. C_1 refers to the hydrocarbon contamination, C_2 to carbon bonded to a single oxygen, and C_3 to a carbonyl-type carbon. By plotting the recorded zeta potential values against the amount of adsorbed nitrogen (N (1s) peak), a rough linearity between the surface charge and the concentration of the silane was observed (Figure 19).

Table 5. Atomic concentrations of different binding states of carbon determined from high-resolution C (1*s*) ESCA spectra of E-glass fibres treated with epoxysilane and anhydride silane.

Epoxysilane (wt%)	C_1 (285.0 eV)	C_2 (286.7 eV)	C_3 (289.0 eV)
0.05	29.9	3.9	1.6
0.2	32.2	6.6	1.7
0.5	40.5	9.9	2.1
Anhydride silane (wt%)	**C_1 (285.0 eV)**	**C_2 (286.7 eV)**	**C_3 (289.0 eV)**
0.05	26.8	3.8	2.8
0.2	33.4	6.7	2.5
0.5	37.6	7.5	3.2

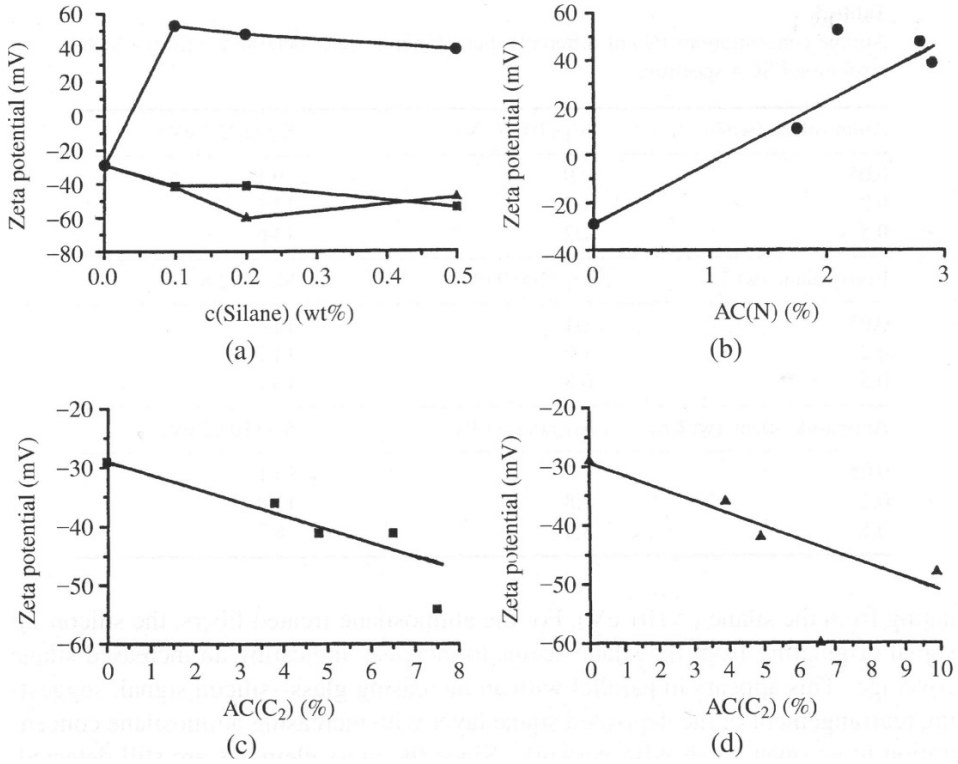


Figure 19. (a) Zeta potential of E-glass fibres treated with aminosilane (spheres), anhydride silane (squares) and epoxysilane (triangles) plotted as a function of the wt% of silane in the treatment solution. (b - d) Dependence of the zeta potential on the atomic concentration of N in aminosilane (b, circles), the atomic concentration of C_2 in anhydride silane (c, squares), and epoxysilane (d, triangles) [I].

The dependency of zeta potential on the silane treatment solution pH was presented in Paper V. E-glass fibres were treated at four different pH levels with four different APTES concentrations. The results indicated that the amino silane did not influence the surface charge extensively when the fibres were treated at low silane concentrations. However, when the pH of the treatment solution exceeded the pH_{iep} (4.2) of the untreated E-glass the free silane became oppositely charged. Increasing pH indicated enhanced adsorption detected as enhanced zeta potential and with an upward shift of the isoelectric point. When fibres were treated with an excess of APTES a remarkable shift in zeta potential was registered. Excess amino silane formed a silane polymer film around the fibres. These fibres being isolated by this polymer film were not affected by the properties of the E-glass fibres.

Adsorption of APTES on E-glass fibres produced opposite effects on two sides of the isoelectric point. In alkaline solutions a small enhancement of the negative charge was found. In the alkaline pH range, the protonation of the amine group

was small. A larger enhancement in the negative charge was detected for the partly hydrolyzed APTES polymer. The small increase in the negative zeta potential as compared with untreated glass fibres originated from the hydrolyzed silanol groups, as the silane was attached on the fibre surface through their amine groups. The zeta potential of the fibres as a function of pH is presented in Figure 20.

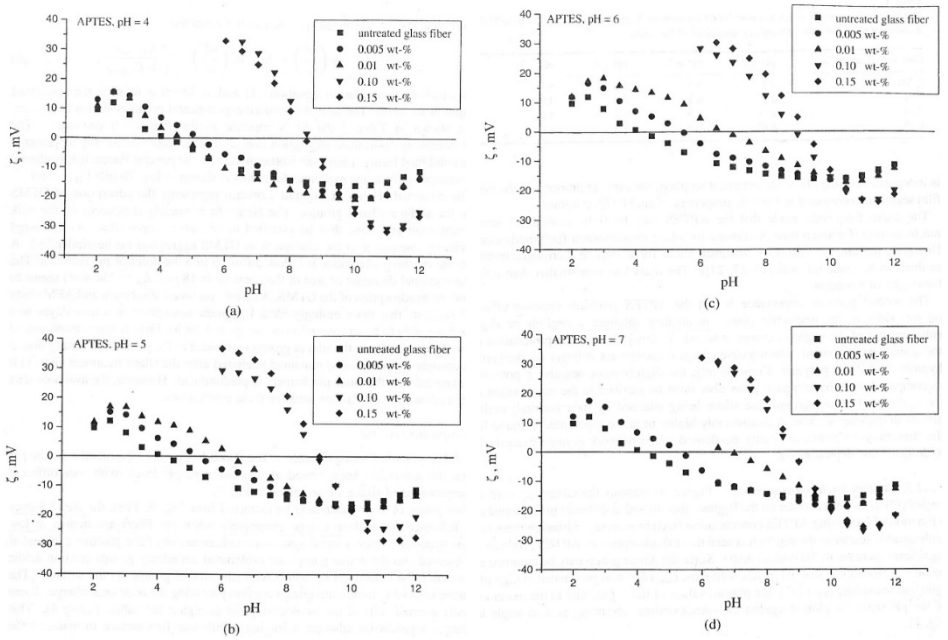


Figure 20. The zeta potential of E-glass fibres as a function of pH of the aqueous 10^{-3} mol dm^{-3} KCl solution. The fibres were treated at four different pH (a, b, c, d) with four different concentrations of amino silane (APTES) as indicated in the figure.

In Paper VI the E-glass fibre surface was treated with two silanes: methacrylate silane and epoxy silane. ESCA results in this study indicated that adsorption of the silanes was determined by pH. When the glass fibres were treated with methacrylate silane at low concentration (0.05 wt-% silane) and low pH of the silane solution the surface of the treated E-glass fibres was acidified due to ionization of the aluminum hydroxide groups and silica silanols. A second region at higher concentrations (0.01 – 0.15 wt-% silane) consisted of a condensed Si-O-Si network. This can be seen in Figures 21 and 22 as high contact angle (decreased hydrophilicity) and stable iep and zeta potential.

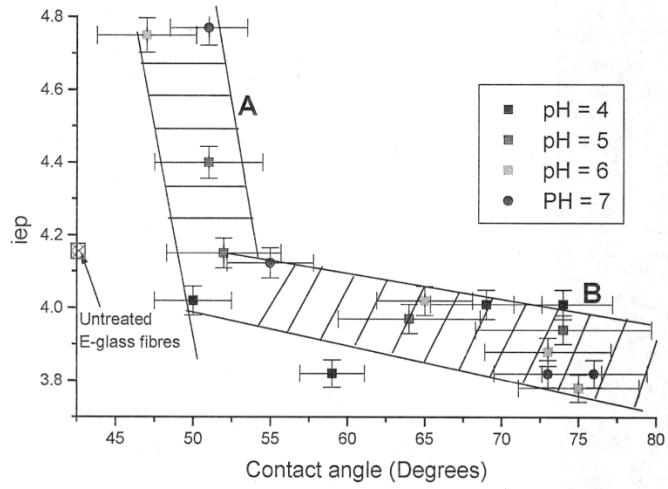


Figure 21. Isoelectric points (iep) plotted against advancing dynamic contact angles (test liquid deionized water, pH = 5.8) for E-glass fibres treated with methacrylate silane. The low concentration area for all deposition solutions used is marked with A and the high concentration area is marked with B. In the region A, the deposition solution pH had a significant effect upon the iep but had a minimal effect upon the contact angle [VI].

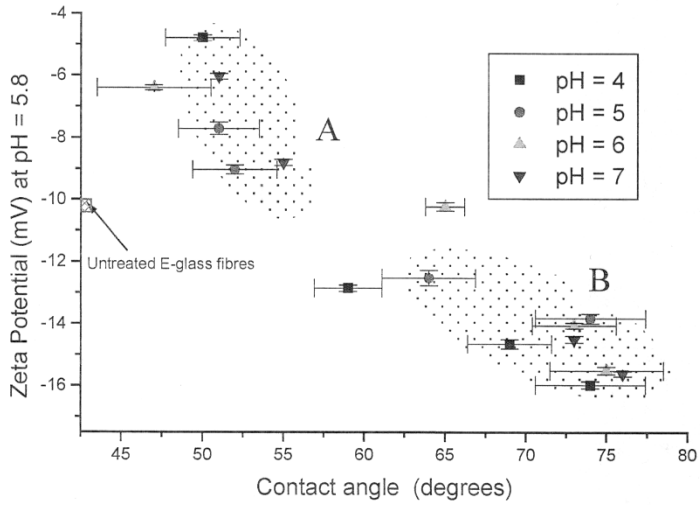


Figure 22. Zeta potential plotted against the dynamic contact angle (test liquid: deionized water, pH = 5.8) for E-glass fibres treated with methacrylate silane. The low concentration area for all deposition solutions used is marked with A and the high concentration area is marked with B. In the region A, the deposition solution pH had a significant effect upon the zeta potential but had a minimal effect upon the contact angle [VI].

Epoxysilane was present on the glass fibre surface in two forms: at low silane concentrations as a hydrolyzed diol and at higher concentrations as oxidized acid and as unreacted epoxy groups. The iep of the epoxy silane treated glass fibre

surface indicated a surface consisting mainly of acidic sites. This implies that the silane was adsorbed on the glass fibre surface in patches. At the highest silane solution concentration the condensed or polymerized Si-O-Si surfaces were the dominant phenomena resulting in a high contact angle and low iep [VI].

6.4. Effect of the solvent washing sequence on silane adsorption [II, III]

Solubility parameter is a useful tool for determining the affinity of a deposition solvent for a specific polymer. Washing the silane-coated E-glass fibres sequentially with various organic solvents probes the relative affinity of the silane and solvents to the surface. The relative affinity of the silane and the solvents with the surface was evaluated by looking at the relative solubility parameters. The hypothesis was that the smaller the difference in the solubility parameter ($\Delta\delta$) the better is the solubility and the interaction between the silane and the solvent.

Isocyanurate silane deposited from carbon tetrachloride was adsorbed on the E-glass fibre surface but was partially washed off with carbon tetrachloride and ethanol, leaving patches of silane on the glass fibre surface. Tetrahydrofurane adsorbed on the fibre surface, or was mixed with the remaining silane/siloxane and together formed a more extended coverage on the fibre surface. This mixing mechanism can be explained by the solubility parameters. The differences in solubility parameters indicated a maximal interaction between isocyanurate silane, acetone and THF. With the methanol wash the excess solvent bound on the surface was largely removed and the siloxane layer was partly reoriented. The methanol wash left the nitrogen groups more exposed. This can be verified by the increased N/O ratio in the ESCA analysis results. Signals from nitrogen and oxygen originate from surface treatment. Methanol had the highest cohesion because of the rich hydrogen bonds. This explains the special behavior of methanol. The fibre surface remained patchy with the chemisorbed silane/siloxane at the surface [II].

However, the adsorption results were contradictory when isocyanurate silane was deposited on the E-glass fibre surface from ethanol and toluene. The trends relying on the solubility parameters in Paper II could not be fully applied in Paper III. Toluene and ethanol originally adsorbed on the fibre surface and were partially washed off the surface. Some washing solvent seemed to absorb into or mix with the silane/siloxane surface polymer. The physico-chemical processes taking place during the deposition and washing procedures are complex and difficult to explain with existing theories, with references to the values of the solubility parameters of the pure substances alone [III].

6.5. Silane adsorption from aqueous media [I, V, VI]

Interactions between silane coupling agents and inorganic oxides are well studied and different factors affecting the monomer dispersion and the polymer formation on surfaces are well documented in the literature [Cohen 1986, Kawaguchi 1992, Hariharan 1990, Van de Ven 1993]. Out of these factors, the following can be mentioned: solvent used, substrate used, molecular mass of the polymer and the polydispersity index, concentration, treatment time, amount reactive sites per molecule and the functionality for chemisorption of the reactive groups, reaction temperature, type of post treatment and especially for aquatic systems, the pH. If the silane used for surface modification adsorbs only physically on the fibre surface it can lead to a break in the glass fibre reinforced final product. The break takes typically place where a reorientation of the silane on the surface of the product forms. In order to avoid this problem the surface treatment must be performed in a way where only chemical adsorption of the silane on the fibre surface can be ensured.

Adsorption of silane coupling agents from water on a glass fibre surface could be determined with the analysis methods chosen. ESCA results verified a traditional silane adsorption on the glass fibre surface. The "traditional adsorption" refers to a normal orientation of the silane, with the silanol groups oriented towards the surface forming a carbon and nitrogen-enriched surface layer shielding the constituent elements of the glass fibre and silanol oxygen. This was seen in the ESCA spectra as enhanced carbon concentration and suppressed oxygen concentration with increasing amino silane concentration. The enhanced surface nitrogen was shielding Al and Ca originating from the glass fibre. At higher amino silane concentrations less shielding of Al and Ca was detected. This indicated a rearrangement of the silane surface towards an open surface film structure. Enhanced signals from N and Si_1 confirmed the overall silane adsorption. Mielczarski et al. [I, Mielczarski 1989] reported a similar adsorption mechanism, accompanied by partial carbon removal. Amino silane and anhydride silane showed a better coverage of the glass fibre surface than the epoxy silane. The conductivity measurements [I] revealed that only a small fraction of the total surface was covered by epoxy silane, or that the free-standing partially condensed surface formed at higher concentrations was very porous. Better coverage was obtained with both amino silane and anhydride silane [I].

In paper VI, the E-glass fibre surface was treated with two silanes: methacrylate silane and epoxysilane. The study revealed that both silanes deposited in two distinct layers on the fibre surface. This depended mainly on the deposition solution concentration. ESCA results indicated that the deposition was also affected by pH. At low concentrations and low pH of the silane solution, the

surface of the methacrylate-treated E-glass fibres was acidified due to the ionization of the aluminum hydroxide groups and silica silanols.

The two deposited layers on the glass fibre surface are clearly presented in Figure 23. The plot of zeta potential versus CH_2/BO at the acid plateau (electrolyte pH = 2.4) revealed that glass fibres treated with low concentration methacrylate silane solutions had a less acidic surface (Figure 23, line A). The glass fibres treated with methacrylate silane had a higher concentration of silane deposited and indicated a more acidic surface due to Si-O-Si groups (Figure 23, line B).

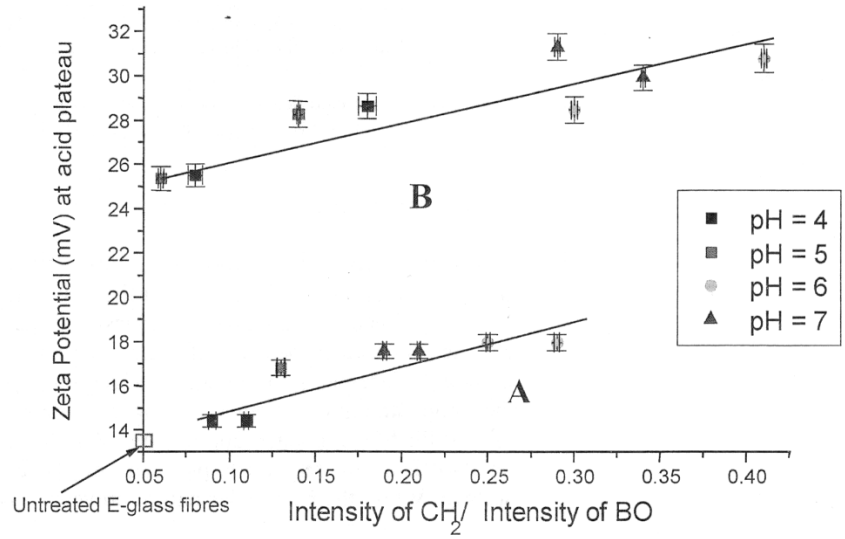


Figure 23. Zeta potential of E-glass fibres treated with methacrylate silane at the acid plateau (pH = 2.4) versus CH_2/BO intensity. The CH_2 signal originates from the silane and the BO (boron-oxygen) signal originates from the glass fibre [VI].

The epoxy silane adsorbed on the glass fibre surface in two forms: as a hydrolyzed diol in outermost layers as unoxidised acid, and as unreacted epoxy groups. The amount of C1s and the $Ca2p_T/Ca2p_U$ ratio in the ESCA spectrum indicated that adsorption and condensation of the epoxy silane on the glass fibre surface was dependent on both solution concentration and pH. Treatment at low silane concentration (< 0,01 wt-%) made the glass fibres more hydrophilic. This was due to the diol and the acid groups on the surface. At higher silane concentrations, the condensed Si-O-Si surface turned more hydrophobic [VI].

Silane adsorption on a glass fibre surface depends on several factors. In this chapter the effects of silane concentration and pH of the silane solution on silane adsorption from aqueous solution were reported. The surface charge of the silane-treated glass fibres depends on the charge of the silane. The variations in the deposition solution concentration as well as variations in the pH led to changes in

orientation of the deposited silane, deposition in two distinct layers or silane adsorption in two different chemical forms.

6.6. Silane adsorption from organic solvents [II, III]

SEM has been widely used for resolving the surface morphology of silane-treated glass fibre surfaces [Dwight 1990, Ooi 1990]. A treatment of E-glass fibres with an isocyanurate silane in organic solutions resulted in interactions between the silane and the fibres not presented earlier. SEM pictures of the surface-treated fibres did not only indicate a relatively smooth surface but also formation of silane bridges between single parallel fibres. Earlier only bridges between crossing fibres had been presented [Park 1991]. In the earlier presented cases, the bridges had been formed in the middle of two crossing glass fibres. For the silane to be able to build bridges between parallel fibres, the silane must be in hydrolyzed form. In organic solvents, the humidity on the fibre surface is the only source for hydrolysis. This humidity on the glass fibre surface is water diffusing from the bulk of the glass fibre and is originating from the manufacturing process.

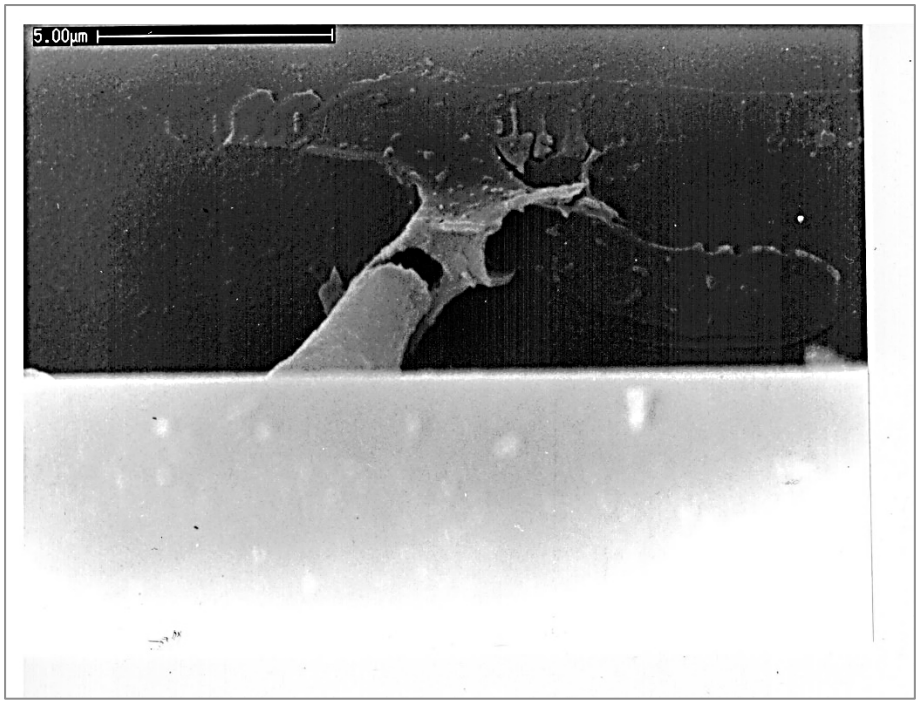


Figure 24. E-glass fibres treated with 2% (w/w) isocyanurate silane from carbon tetrachloride. The image reveals that silane structures formed bridges between two fibres. Previously SEM pictures of silane-coated glass fibres have typically revealed a smooth surface morphology [II, Ooi 1990].

DRIFTS results indicated that the isocyanurate silane had adsorbed on the E-glass fibre surface from all solvents used. This was confirmed with the signals from the DRIFTS spectra in the C-H stretching region. The silane signals in the C-H region provide a rough indicator of the adsorption. The subtraction technique, where B-O overtone was subtracted from the total spectrum gave a possibility to investigate the important spectral area between 3100 cm^{-1} and 2700 cm^{-1} on a normalized scale [Jokinen 1998]. A (semi-)quantitative measure of how well the surface is covered can be calculated from the ratios between B-O and C-H signals. Signals in the C-H area originated from the isocyanurate silane and could thereby be used as a reliable adsorption indicator.

Table 6. –BO/-CH_3 and –BO/-CH_2 ratios of the glass fibres coated with 2.0 % silane in CCl_4.

Treatment	-BO/-CH_2 (2930 cm^{-1})	-BO/-CH_3 (2876 cm-1)
Untreated fibres	0	0
Treated, CCl_4 washed fibres	1.4	2.0
CH_2Cl_2 washed fibres	1.5	1.9
Acetone washed fibres	0.9	1.4
THF washed fibres	0.9	1.2
MeOH washed fibres	1.5	2.0

Table 6 indicates that two levels of -BO/-CH_2 and -BO/-CH_3 can be seen. The higher level is given by the treated, CCl_4, CH_2Cl_2, and MeOH washed fibres. The lower level is given by the acetone and THF washed fibres. This indicates that acetone and THF seem to be bound to the silane polymer surface forming a more extended coverage on the surface.

TGA was used for analyzing the amount of silane coating on the fibre surface. TGA results for the silane-treated E-glass fibres from organic solvent showed mass losses consistent with adsorption from the different solvents. The weight loss refers directly to the amount removed from the surface. Analyses performed with TGA after the washing procedure with different solvents gave directly the amount of silane that had been removed from the fibre surface. An increase in the amount of removed silane indicated a co-adsorption of the solvent on the fibre surface.

When a silane-treated glass fibre surface was analyzed with ESCA, an increase in the carbon signal and a decrease in the signals originating from the base element, the glass fibre, was observed. The adsorbing silane covered the base elements and increased the carbon concentration of the surface. As a new element, originating from the silane, nitrogen was detected. Nitrogen can be considered as a valuable indicator of adsorption. When the fibres were washed with various organic solvents a decrease in the carbon signal was observed, as expected, as the

physically adsorbed silane was removed from the surface. The same phenomena were registered for oxygen. An increase of the silicone signal originating from the bulk glass further confirmed the removal of the physically adsorbed silane.

Comparing the results from silane adsorption studies in aqueous and organic media, certain similarities were revealed. ESCA results verified silane adsorption on the glass fibre surface in both media. This was apparent as increasing carbon and nitrogen signals and a decreasing oxygen signal as a function of the surface treatment medium concentration. The basic elements originating from the glass fibre were suppressed in the spectra as the fibre surface was covered with adsorbed silane. Other analysis methods such as conductivity measurements, DRIFTS and the washing procedure confirmed the adsorption process in both aqueous and organic media.

7. Conclusions

7.1. Main findings

In this chapter the main findings of this thesis are summarized according to the studied topics listed in Table 7.

Table 7. A list of the main topics studied in this thesis

Topic	Paper
Ion leaching, orientation of the adsorbed silane on glass fibre surface; amino silane, anhydride silane and epoxy silane	I
Relative affinity of silane to glass fibre surface, influence of solvents; isocyanurate silane	II & III
Effect of pH on silane adsorption on glass fibre surfaces; isocyanurate silane, amino silane and ureido silane	IV
Comparison of adsorption isotherms, influence of silane concentration on adsorption; octyl silane, amino silane, methacrylate silane and epoxy silane	V & VI

7.1.1. Ion leaching

In paper I the deposition of three silanes (amino, anhydride and epoxy) on the glass fibre surface was monitored. The main interest in paper I was the amount of ions leaching from the silane-treated surface. In addition, the orientation of the adsorbed silane was examined. The effect of the deposited silane layer on ion leaching was measured by comparing the concentration of ions removed from silane-coated and uncoated fibres. Silane orientation was examined on molecular level following the variation of the surface composition on the glass fibre. The tests were performed in aqueous solution. ESCA, streaming potential and conductivity measurements were applied. In ESCA analysis several take-off angles were applied.

If a silane polymerizes on the glass fibre surface a complete siloxane network is formed. This network prevents ions from leaching from the fibre surface. On the other hand, an incomplete network allows ions or the silane itself to dissolve from the surface.

The conductivity measurements revealed that both amino silane and anhydride silane covered the surface well (Figure Paper I/Figure 3). The strongly reduced conductivity to one third of the reference supernatant indicated that both silanes produced an efficient barrier against ion dissolution. For amino silane, this

finding was supported by ESCA N 1s peak as the conductivity was linearly related to the atomic nitrogen concentration. For anhydride silane, a similar linearity was observed between conductivity and the atomic concentration of C_2. Epoxy silane behaved differently on the fibre surface. The conductivity of the supernatant remained much higher than for amino and anhydride silanes. The surface network formed by epoxy silane seemed to be porous allowing a large amount of ions to leach out from the surface. The large ion desorption was not supported by ESCA and zeta potential results. However, the epoxy silane seemed to form a porous patch-wise siloxane network and no protection against ion leaching was detected. This was confirmed by increasing C peaks and Si peaks as well as gradual reductions of the atomic concentration levels of Ca 2p and Al 2p signals, both originating from the glass fibre surface.

Zeta potential analysis confirmed that both anhydride and epoxy silanes increased the anionicity of the glass fibre surface. The amino silane made the surface more cationic. However, all silanes deposited on the surface linearly to the deposition concentration. This was confirmed by ESCA.

The orientation of the adsorbed silane on the glass fibre surface was examined with ESCA. A take-off angle of 30° was chosen because at small angles the contribution from the surface roughness increases and thus the chosen take-off angle is representative of the outermost surface layers. At low deposition concentration, amino silane adsorption followed a normal adsorption orientation pattern where the silanol groups oriented towards the glass surface. The silanol formed a carbon and nitrogen rich surface layer shielding the constituent elements of the glass fibre. At higher concentration the shielding of constituent elements of glass, Al and Ca, were less shielded. This was due to a rearrangement to an open surface film structure, as the signals N and Si_1 enhanced and verified that adsorption had taken place.

ESCA analysis of surface-treated glass fibres with anhydride and epoxy silanes showed a continuously increased contribution of carbon and a decrease of oxygen percentage with increased silane concentration. This indicated silane adsorption with the silanol groups attached to the glass surface. The constitutional elements from the glass fibres were shielded by the silane coating. This was especially evident with Ca and Al signals as they were decreasing with the increased silane coupling agent concentration. The adsorption of both epoxy and anhydride silanes was further confirmed by analysis of the ESCA C_1 signal as the carbon-oxygen functional group originating from the silane could be detected.

7.1.2. Relative affinity of silane to glass fibre surface, influence of solvents

The influence of the relative affinity of silane (isocyanurate) for the glass fibre surface and for the solvent (CCl_4), respectively was monitored in paper II. The silane-glass interaction was related to the relative affinity of the silane. The relative affinity was assessed by examining the modified glass fibre surface before and after it was washed with a series of organic solvents, characterized e.g. by their solubility parameters. In addition, the influence of solvent on the orientation of the silane on the glass fibre surface was examined. Glass fibre surface was characterized with DRIFTS, ESCA, TGA and SEM.

Silanes interact with both an inorganic surface and the solvent. In order to monitor the relative affinity of the silane and the solvents with the surface the relative solubility parameter of the the silane and the different solvents can be compared. If a solvent is classified as primary solvent for a monomer, polymer or oligomer the solubility parameter should differ only by ± 2 $MPa^{½}$ from that of the used chemical. Carbon tetrachloride as well as the other solvents were according to the solubility parameter classification considered as good solvents for the isocyanurate silane. The exception was methanol with a solubility parameter outside the range and could only be classified as a good dilutant of the silane.

DRIFTS results showed that adsorption of isocyanurate silane could be confirmed by the signals in the C-H stretching region. In addition, two different levels of -BO/-CH_2 and -BO/-CH_3 were apparent in the DRIFTS spectra. The higher level was found for the treated, CCl_4, CH_2Cl_2, and MeOH washed fibres. The lower level was observed for the acetone and THF washed fibres. The lower level results indicated that acetone and THF seemed to bind to the silane polymer surface, but no conclusion of the relative washing-off power of any of the solvents relative to CCl_4 could be drawn.

Silane-treated and sequentially washed glass fibres where further analyzed by ESCA. Atomic concentrations of calcium, sodium and aluminum provided good information about the surface coverage of silane onto glass surface, as the elements were not present in the silane. The decreasing signal of these elements was in line with the increasing silane deposition on the fibre. The appearance of nitrogen signal confirmed the silane deposition as no nitrogen was present in the glass fibres. The increase in nitrogen concentration throughout the washing sequence can be due to silane reorientation on the surface. The washing sequence may have exposed the nitrogen signal from the head down silane more clearly. By observing the differences in binding energies between O 1s and Si 2p signals the nature of the fibre surface was further examined. Binding energy differences between 429 and 429,62 eV indicate a silicate nature and no coupling agent was detected. A

binding energy difference within 429,82 to 430,9 eV indicated a silane-coated surface. A binding energy value between these indicated a patchwise covered surface. Even though the CCl_4 and CH_2CH_2 washed surfaces had binding energy differences indicating a silane/siloxane covered surface, the silane seemed to adsorb in patches on the surface. As the washing procedure continued, the differences in binding energies increased, indicating a more covered surface. After the final washing step (MeOH) the difference in binding energies was reduced indicating a patchwise adsorption. It can be considered more of a dissolution and re-adsorption effect rather than a wash off effect as the nitrogen group from the silane is more exposed.

In paper III the discussion about the relative affinity of silane (isocyanurate) for the glass fibre surface and for the solvent was continued. The results in this paper complemented the research in paper II. The organic solvents studied were ethanol and toluene. The relative affinity of the silane was assessed by examining the modified glass fibre surface before and after it had been washed with a series of organic solvents characterized, e.g. by their solubility parameters. Glass fibre surfaces were monitored with DRIFTS, ESCA, TGA and SEM.

An empirical method to investigate the binding to a surface is to treat the silane-coated fibres with i) dichloromethane, ii) acetone, iii) THF and iv) methanol, respectively. The increasing washing power assumed is fully empirical, but is expected to probe the relative affinity between the silane and solvents with the surface and the bonding of the silane to the surface. The smaller the difference of the absolute solubility parameters ($|\Delta\delta|$) is, the better the interaction between the silane and solvents. A good solvency leads to a poor adsorption on the glass fibre. Examining the solubility parameters of ethanol and methanol it can be stated that they behave as diluents and not as true solvents for the silane. The other deposition and washing solvents dichloromethane, acetone, THF and toluene are within the range of ± 1-2 $MPa^{½}$ and can be considered as good solvents. The $|\Delta\delta|$ suggests the following order of solubility capacity: THF<toluene<acetone<CH_2Cl_2<<EtOH<MeOH, the smallest being the best solvent. This sequence is not in line with the empirically estimated washing power of the liquids applied.

DRIFTS technique is applied for qualitative and semi-quantitative analysis of surface layers with a thickness of several micrometers. This is a common range for polymers adsorbed to surfaces. The DRIFTS results showed that adsorption of isocyanurate silane could be confirmed by the peaks in the C-H stretching region. As the signals were weak a subtraction technique was needed to remove the background signal from the glass fibre in order to examine the spectral region 3100^{-1} cm and 2700 cm^{-1} in detail. The semi-quantitative results of surface

coverage were given by the ratios between B-O and the C-H signals. The DRIFTS results suggested that a distinctive solvent effect on silane adsorption on surface could be seen only after the silane-treated fiber had been washed with THF. The difference in the solubility parameters between THF and the isocyanurate silane was only 0.56, and THF was thereby considered as a good solvent for the silane. The overall differences in the effect of the washing sequence applied suggested that the isocyanurate silane formed different surface layer structures when adsorbed from a good solvent (toluene) and a poor solvent (EtOH).

The adsorption of the isocyanurate silane on the fibre surface was confirmed since the nitrogen N1 signal was present in the spectrum and could only arise from the silane. The signal was reducing in line with the washing sequence. However, controversial resultswere observed by ESCA results. The small increase in N1s signal as well as the increase in carbon and oxygen signals after the CH_2Cl_2 wash indicated a partial rearrangement following the solvent absorption into the thick silane surface layer. In addition, a rearrangement during the acetone wash was confirmed by enhanced oxygen, Ca and Al signals. Al signal is a component from the glass fiber only. Surfaces washed by toluene as well as those washed by ethanol showed patchwise adsorption of silane as both silane-related signals and signals originating from glass were detected. This was considered to be attributed to both a washout and rearrangement mechanism.

7.1.3. The effect of pH on silane adsorption on glass fibre surfaces

The adverse effects of pH on glass fibres were discussed in paper IV. Previous work in the field revealed that acids and bases affect the glass fibre surface adversely. In addition, also the well-known fact that most of the silanes are applied from acidic solutions on the fibre surface was of interest. Three issues of interest were considered: the effect of strong acids and bases on glass fibres, the deposition characteristics of silanes from acid solution, and the effect of acid/silane solution upon glass fibres. Three different silanes were used (amino, ureido, isocyanurate). The effects of acid base treatments on the glass fibre surface were characterized by Raman spectrometry, plasma emission spectrometry, ESCA and conductivity measurements.

Strong acids and bases (pH = 2 and pH = 12) leached large quantities of ions from the glass fibre surface. Strong acid solutions removed large quantities of aluminum, boron and calcium. The acid solutions tend to cause a breakdown of the surface network, inducing an ion change mechanism between H of the acid and Al, B and Ca ions from the glass surface. Strong basic solutions removed iron and sodium from the glass fibre surface. In basic solutions, the surface SiO_2 and

B_2O_3 networks hydrolyzed, and the hydroxides dissolved from the surface. Large amounts of sodium was detected with ESCA at pH = 12. There are two possible sources for this finding. The first is that sodium had leached out from the bulk of the fibre and the second is that it had adsorbed on the surface in an ion-exchange reaction as the sodium hydroxide was used for adjustment of the solution pH. Between pH = 4 and pH = 9, the quantities of ions leached remained relatively constant.

All three silanes studied were applied similarly to water which had been adjusted to pH = 4 within a minute of application. All silanes were unhydrolyzed within this short time. The poorly deposited amino silane was removed from the fibre surface by washing of the fibres with deionized water. The washing off was verified by the high conductivity of the washing solution as well as the Raman analysis of the unhydrolyzed silane (-OCH_3 signal) in the supernatant solution. For unhydrolyzed silane to stay in the solution, the silane methoxy group must be shielded from the aqueous phase, possibly by micelle formation. Reduction in the Raman peak intensities demonstrated the removal of silane from solution. This removed silane was deposited on the fibre surface. This adsorption was verified by ESCA analysis. The ureido silane deposited on the fibre surface in relatively large quantities, as measured by elemental analysis for carbon and nitrogen. The conductivity measurements of the washing solution indicated that only small amounts of deposited silane was removed from the fibre surface. Ureido silane was most effective in shielding the fibre surface, allowing fewer leached ions in to the silane solution supernatant and washing solution in line with the increasing concentration. The isocyanurate silane was only partially soluble in water, but sufficient silane was dissolved to adsorb on the fibre surface at all concentrations. Adsorption of the silane was verified by a correlation between increased carbon content and decreased oxygen content.

7.1.4. Influence of the silane concentration on adsorption

In paper V the adsorption of the monofunctional octyl silane (OTMS) and the bifunctional amino silane (APTMS) on porous silica powder was examined. Octyl silane adsorption on glass fibre surface was also of interest. The silane adsorption investigation on porous silica was performed from toluene as the adsorption study on glass fibre surface was made from water. In addition, the orientation of the adsorbed silanes was monitored. The silane adsorption was monitored by DRIFTS, GC-MS, SP and ESCA.

In adsorption studies on porous silica, low concentrations of octyl silane (OTMS) adsorbed weakly onto a few silanol groups. At higher concentrations

OTMS-aggregates were found to adsorb on the surface quite non-specifically. The adsorption was described by overlaid Langmuir and Henry isotherms. The first part of the combined isotherms described specific adsorption of the octyl silane onto surface silanol groups whereas the second isotherm described non-specific adsorption of the silane aggregates forming hemi-micelles. The amino silane (APTMS) adsorbed mainly with its amine group onto the silanol groups of the silica surface. This phenomenon was described by the fit of the Langmuir isotherm.

Adsorption of APTMS from water on glass fibres was examined as well. The streaming potential measurements revealed important findings. ATMS did not influence the surface charge much when the fibres were treated at low concentrations. Only a small enhancement of the positive ζ-potential was observed as the amine groups were protonated and the ethoxy groups were reacting with silanol groups on the surface and there was only a small shift in the iep to higher pH values. This indicated a patchwise adsorption. As the pH of the deposition solution exceeded the iep of the fibres, the free silane became oppositely charged. In an aqueous solution both silane and amine groups may be bound to the fibre surface, depending on the pH. Higher pH gives also enhanced adsorption, which can be verified by an enhanced positive ζ-potential. However, an excess treatment of APTMS formed a silane polymer film, polymer network, around the fibres which was phase-separated and hydrolyzed and only mechanically bound to the glass fibre and was largely independent of the glass fibres. The ζ-potential results could linearly be related to contact angle results. In acidic solutions the properties of a silanized glass fibre surface and that covered by an excess polymer skin was revealed. In alkaline solutions a rough relationship between diminished APTMS adsorption and the zeta potential and the advancing contact angle was observed.

Paper VI discussed the orientation of the adsorbed silane on the glass fibre surface. The silanes examined were epoxy and methacrylate silanes. The silanes were deposited from an aqueous solution and the pH of the solution varied between 4 and 7. The fibre surface and adsorption of silanes were analyzed by ESCA, SP, Contact angle measurements and DRIFTS.

Methacrylate silane was deposited on the fibre surface in two distinct layers. ESCA results indicated that the deposition also was dependent on the pH. Examination of the C1s signals indicated that a larger amount of silane was deposited on the surface at pH = 6 than at pH = 4. As the deposition pH increased the number of Ca sites, originating from the glass, decreased. This indicated shielding of the Ca sites by the adsorbed silane and preferential adsorption of the

silane on Ca sites. The increase of the solution concentration followed the same trend.

Epoxysilane was present on the fibre surface in two forms: both as a hydrolyzed diol in the outer layers and oxidized as epoxy hydrolyses to a diol followed by an oxidation to an acid. In addition, unreacted epoxy groups were detected on the surface. Adsorption of the epoxy silane on the glass fibre surface was verified by ESCA. The variations in the amounts of C1s and Ca2p signals indicated that the deposition of the silane was depending on both pH and the concentration of the silane solution. The iep of the epoxy silane indicated that the fibre surface had an acidic nature. This implies a patchwise deposition of the silane. At low concentrations, the glass fibre surface became more hydrophilic, due to diol and acid groups on the surface. At higher concentrations, the surface turned more hydrophobic as the polymerized Si-O-Si network was formed. At highest concentrations the polymerized Si-O-Si surface was the dominant feature.

7.2. Citation analysis 2011-2018

The experimental work in this thesis was made twenty years ago and published in four papers and two book chapters. While summarizing the thesis, the question about the importance of the findings reported in the published papers arose. One indication of the impact of the research findings comes through the number of citations these publications have gained. The following gives a review over selected citations made to the publications of this thesis during 2011-2018.

Paper I:
The citations made to paper I are altogether eleven and have been made during 2005-2017.

Thompson et al. cited the findings in surface charge of the glass fibres produced by adsorption of amine and epoxy silanes. The results were utilized in their studies within the field of mineral engineering [Thompson 2017]. The surface charge of the glass fibre surface was of main interest in the research of Chen et al. who cited the results of streaming potential investigations where glass fibres have negative potential in neutral water and indicates a negatively charges surface. The surface treatment with cationic film forming agents where prioritized in their work based on the results of paper I. The work is in the field of fiber-reinforced polymers and the fiber used in the composite was basalt fiber [Chen 2016]. Baranowska et al. cited surface charge findings within the field of modification of porous silicon surface with proteins [Baranowska 2015]. The

usability of the Si 2p peak as an accurate technique for monitoring surface coverage was cited by Schircliff et al. in their ESCA studies of mixed silane monolayers for DNA attachment [Schircliff, 2011]. They reported curve fitted results that indicated that Si 2p could be considered as a reliable indicator of silane coverage.

Paper II:
The citations made to paper II are in total thirteen and have been made between 1999 and 2018. The majority of the citations were made before 2011.

Xing et al. studied monolayer formation of an organosilane on magnetite nanoparticles. The shape of the adsorption isotherm of the silane on magnetit was discussed. They cited that the shape of the isotherm indicated that the silane adsorption proceeded through monolayer formation, followed by multilayer deposition [Xing 2018].

Abdel-Halim, in their work involving water absorbency of cellulosic fibres by removing water repellent components from the fibres, cited the importance of the physicochemical properties of the fiber surface as they govern the degree of adhesion of the reinforcing fiber to the polymer matrix [Abdel-Halim 2012].

Paper III:
The citations made to paper III are altogether five and have been made between 2005 and 2016.

Reis et al. discussed the silane connection to a silica surface. The presence of protic solvents may lead to an inhomogeneous surface modification. They cited the use of aprotic solvent which might be an alternative for the improvement of the homogeneity of the glass surface modification [Reis 2016]. Reis et al. are working in the field of vibrational spectroscopy. Liu et al. cited our finding, where the solvent used in a modification process and the washing process after the modification would make a huge difference to the silane film deposited on a modified surface in terms of their structure [Liu 2015]. Liu et al. are doing research within the field of modification of glass fiber surfaces and glass fiber reinforced polymer composites.

Paper IV:
Paper IV has been cited altogether fifteen times during 2002-2018.

Gaillard et al. discussed in their research adsorption of chlorotrimethylsilane (CTMS) on glass. The silane adsorption was found to be enhanced by NaOH treatment. They cited to our comparable results where e-glass fibres had been etched in NaOH and exposed to silanes. The authors' field of interest was isotherm

analysis of the solution-based uptake of CTMS on a photosensitive glass [Gaillard 2018].

Vallittu et el. cited that it is known that good quality and surface purified glass fibres exhibit stability in pH between 3 and 10. Glass fibres can be considered a bio-stable material in vivo in that area [Vallittu 2017]. In another publication, Vallittu et al. cited the reported importance of good quality and stability of surface purified E-glass fibers in solutions with pH between 4 and 10. In addition, they discussed that the hydrolytic stability is dependent on the stability of the polymer matrix, stability of fillers, and stability of the interface between fillers and polymer matrix. The field of application was fiber glass-bioactive glass composites for bone replacing and bone anchoring implants [Vallittu 2015]. Mosquera discussed fiber-reinforced composite-fixed dental prostheses in her thesis. In her field of research, E-glass and S-glass fibers are the most frequently used types of fibers. The reported finding of glass fibre chemical stability in the pH range of 4-11 was cited [Mosquera 2015].

The chemical and thermal resistance of basalt fibres in inclement environments was studied in a paper by Shuni et al.. In the mechanical stability tests the basalt fibres were leached in acid solution and in high temperature for several hours and differences were registered. Basalt fibres remained well whereas the mechanical properties of glass fibres decreased dramatically in acid solutions both in room temperature and at high temperature. The effects of strong acids on glass fibres were cited in that publication [Shuni 2013]. Manikandan et al. cited paper IV with the statement "Surface modifications enhance the mechanical properties of fibres". In the work the effect of surface modifications on the mechanical properties of basalt fibres reinforced polymer composites was reported [Manikandan 2012].

Paper V:

The citations made to paper V are altogether seven, during 2007-2018.

Garoushi et al. studied in two papers the reinforcing effect of discontinuous glass fibers on mechanical properties of ionomer cement. In these studies the result from paper V utilized. When fibre surface silane was esterified with polyacrylic acid a polymer with functional double bond was established. The other cited finding was that silanol groups can react with the OH- groups and form a siloxane bond as well as react with metal ions and form a metal-siloxane bond [Garoushi 2018, Garoushi 2018]. A similar citation by Garoushi et al. was made earlier in a report involving hollow glass fibres used as reinforcement in glass ionomer cements [Garoushi 2017].

Kaya et al. aimed in their work to syntehsize and produce novel and thermally stable polyimines containing methylsilane in the backbones. The results from paper V were cited in the discussion about the nature of organofunctional silanes and the utilization of the silanes in glass fibre reinforced polymeric composites [Kaya 2017].

7.3. Summary

In this work, E-glass fibres treated with different silanes were thoroughly characterized. The aim was to gain better understanding of the surface processes at the silane-glass interface of the composite.

The ion leaching studies indicated that an even coating of the glass fibre surface protects the fibre surface from leaching ions. The adsorbed silane layer formed a shield towards ion leaching. The shielding effect however varied with silane concentration and pH. Strong acids and strong bases (pH = 2 and pH = 12) leached large quantities of ions from the fibre surface. The ion leaching from a treated glass fibre surface was the lowest and constant between pH = 4 and pH = 9.

The orientation studies of the silanes on the glass fibre surface indicated in several cases a dependency between deposition concentration and pH. Adsorption in low concentrations followed a normal orientation pattern, where the silanol groups were oriented towards the glass surface. At higher concentrations, the silane often seemed to form a silane polymer network and adsorbed only mechanically in a ring structure on the fibre surface. Some of the silanes were present on the fibre surface in two distinct layers or in two forms.

The relative affinity of the silane to the fibre surface could be assessed by examining the modified fibre surface after it had been washed with a series of organic solvents characterized by their solubility parameters. The results obtained gave information about the actual nature of the solvent used in silane applications. Some solvents could be considered to contribute more as a dissolution and re-adsorption solvent than washing off the silane from the surface.

7.4. Perspectives

The following is a list of experiments and investigations that could lead to further understanding of adsorption and the glass fibre strength properties:

- An extraction investigation concerning time and solvent; To study how much silane can be extracted and during what time.

- Improved control of the surface treatment procedure to possibly obtain a more even distribution of the silane.
- GC-MS and ToF-SIMS analyses on silane extracts and glass fibres to obtain more precise information about the functional groups present.
- Strength studies of the composites involving surface-treated reinforcing glass fibres.
- PM-IRRAS studies of the silane orientation on the glass fibre surface.
- Aging studies of the glass-polymer interface since the kinetic properties of the composite are of great practical importance.

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