

# Faculty of Biology, Chemistry and Earth Sciences Department of Physical Chemistry II

**BIO-INSPIRED (GLASS) FIBRE-COMPOSITES** 

# **Diploma Thesis**

submitted in partial fulfillment of the requirement for the Diploma degree in chemistry

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# Affidavit

I hereby confirm with a clear conscience that I prepared this thesis independently, by exclusive reliance on the literature and tools indicated therein. This thesis has not been submitted to any other examination authority in its current or an altered form; and it has not been published.

Location, Date

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# Acronyms and constants

BC	Before Christ	PB-b-Px	Block-copolymer with	
BSE	Back-scattered electrons	PDMS	Poly(dimethyl siloxane)	
CCD	Charge-coupled device	PE	Poly(ethylene)	
CLSM	Confocal laser scanning microscopy	PEO	Poly(ethylene glycol)	
DCM	Dichoromethane	PP	Poly(propylene)	
DI	Distilled	$\mathbf{PS}$	Poly(styrene)	
DMSO	Dimethyl sulfoxide	PSD	Position sensitive diode	
DOF	Depth of field	R	Universal gas constant	
DSA	Drop shape analysis	RCA	Cleaning procedure by W. Kern	
e	Elementary charge	RT	Room temperature	
FT-IR	Fourier transformed	$\mathbf{SC}$	Standard clean	
	infrared spectroscopy	SE	Secondary electron, or	
h	Plank constant		Spectroscopic ellipsometry	
m <sub>e</sub>	Mass of electron	SEM	Scanning electron microscopy	
MPI	Max Plank Institude	SFM	Scanning force microscopy	
MPTMS	(3-Mercaptopropyl)trimetoxysilane	THF	Tetrahydrofuran	
NIR	Near infrared,	UV	Ultra violet, $\lambda \leq 380\mathrm{nm}$	
	$780\mathrm{nm} \le \lambda \le 3000\mathrm{nm}$	VASE	Variable angle	
NMP	N-Methyl-2-pyrrolidone		spectroscopic ellipsometry	
P4VP	Poly(4-vinyl pyridine)	VD	Vapour-phase deposition	
PA	Polyamide	VIS	Visible light,	
PAN	Poly(acrylonitrile)		$380\mathrm{nm} \le \lambda \le 800\mathrm{nm}$	
PB	Poly(butadiene)	WET	Wet-chemical deposition	

# Chapter

# Introduction

## 1.0 Motivation

Engineering composite materials are required and expected to exhibit high mechanical performance. Natural fibre-composites outperform most common synthetic composites, ceramics, polymers, metals and alloys in respect to their ratio of elastic modulus to density. Most loadbearing biological structures are found to be based on a hierarchical construction: *clever* highlysophisticated compositions of flexible and rigid components. The mechanical advantages are expected to arise from functional adaptations of the structure at all levels of hierarchy. [1] Plant materials like wood, bamboo or giant reed combine high elasticity with high elastic modulus and good shock absorbance. These properties result at least partly from a fibre-gradient-matrix structure of the material. Plant cell walls consist of inflexible fibrillar cellulose and soft matrix. The proposition to adapt the principle of gradient structures to improve mechanical properties including vibration damping, fracture behaviour, stiffness, strength and toughness (at low weight) have been honoured by the *German Federal Ministry for Education and Research* (BMBF). The task is not only to recognise nature's principles but to realise a materialistic adaptation: fundamentally, development goes hand in hand with evaluation. The work presented in this thesis is based on the evaluation of plant cell wall inspired material.

# 1.1 Status of the field

Conceptional inspiration from nature is not new, and many engineering approaches can be considered to be stimulated from observations of natural systems. [2] The prior art of bio-inspired composite materials have to be distinguished from bio-composite materials. The latter are composites combining natural and synthetic components. Cellulose microfibrils, the fibrous structures in the wood cell wall, show high mechanical properties along the longitudinal direction, such as a elastic modulus close to 138 GPa and an estimated strength of at least 2 GPa. [3] Cellulose pulp extracted from wood powder is used as fibrous bio-component in composites. Additionally natural fibres find application embedded in synthetic matrices. Natural fibres do not have clear advantages over conventional synthetic fibres in terms of strength and stiffness, but their advantages appear when they are considered on the basis of strength per unit weight (specific strength) or modulus per unit weight (specific modulus) focused on their reinforcing effect. [4] The field of bio-inspired composites utilises natural concepts to functionalise synthetic components. The modification of fibres to promote adhesion to the matrix is most common. Therefore synthetic fibres are coated with a textile sizing after fabrication. But the optimisation of component adhesion is only a first step towards better material properties of composites. More sophisticated is the adaptation of the hierarchical gradient substructure, reported for numerous natural composites. [1] Materials with periodically varying elastic modulus exhibit a hindered crack propagation. [5] The combination of adhesion promotion and a gradual array of rigid and ductile material domains can result in advanced materials. Many questions arise from the conceptions of bio-inspired materials:

Can the biological (gradient-based) structure be transferred to synthetic composites?

What is the dominant effect yielding mechanical synergy?

What is the failure mechanism of the composite?

How to improve the adhesion of the individual components?

## 1.2 Concept

This thesis presents the concept of (glass) fibre-composite materials inspired by the primary cell wall assembly of plants. The fibre-matrix interaction and the stability of this interphase are crucial for the mechanical performance of the composite. The introduction of a bio-inspired gradient phase based on a two-step chemical approach developed by A. BERTIN is expected to yield mechanical synergy. The modification of fibreglass based on silicon oxide model substrates is evaluated. Samples were prepared at MPI Golm and Bayreuth University and partly provided by A. BERTIN. The performed two-step modification is presented and mechanistically discussed. The main emphasis in this work is not the preparation of samples but the characterisation of the surface. The morphology of the model substrates were analysed to improve the mechanistic understanding of the treatment and yielded surface structure. Four polybutadiene based polymers and polyacryolonitrile were used for polymer-grafting. SFM topography was applied to evaluate the surface modification of both steps of the treatment. Contact angle measurements were performed to check the homogeneity and wettability of the surface coatings. A methodology to evaluate film thickness of the introduced surface coating on glass using VASE was elaborated. The surface of modified and unmodified fibreglass subjected to a pull-out tensile test were analysed with SEM for structural differences.

This thesis is part of the project of *fibre composite material with gradual matrix transitions*, a cooperation of MPI Golm (biomaterials and colloidal chemistry), ITV Denkendorf, Freiburg University (plant biomechanics groups) and Bayreuth University. This project originated from an idea contest in the framework of the BMBF *bionic competition* on an improvement of technical composites with a new concept for the embedding of glass fibres based on the primary cell wall assembly.

# Chapter 2

# Theory

# 2.0 Composite materials

A composite can be descriped as a "multiphase material which is artificially made of chemically dissimilar materials seperated by a distinct interface". Evolution of modern fibre-composite materials is closely linked to the development of plastics since synthetic resins are idealy suited as matrix components. The aim was and still is to yield mechanical synergy by compensation of deficiencies of the individual component. Beneficial properties are high strength and rigidity at low density (lightweight), corrosion-resistance, specific energy-intake capability (at low densities), low cost processability, recyclability, low maintenance, dimensional stability and prestige (*high-tech* material). Disfavourable is the increased material cost and developmental effort. A composite material has to account for the additional costs by a distinct advantage in material properties. Most important applications are in the construction of aircrafts, water-crafts, vehicles, architectures (buildings) as well as mechanical and electrical engineering. [6]

**Fibre-composite material:** The term *fibre-composite* replaces the old expression *fibre-reinforced plastic*, since it is emphasising a one-sided contribution of the fibre. Both phases contribute to the physical properties, as described in the following.

### 2.0.1 Fibre

As the main task is to bear load, the reinforcing component has to exhibit high strength and rigidity. Therefore strong atomic bonds together with a low density are expected. Both is true for substances based on the elements boron, carbon and silicon. Even though glass and carbon are not classical construction materials they have gained great importance as reinforcing fibrous components. Table 2.1 presents natural and synthetic fibres commonly used individually and/or in composites. The aim is to translate the theoretical high strength and rigidity to the composite. Characteristic contributions of the dispersed phase: fibre concentration, size, shape, distribution and orientation.

Table 2.1: Classification of fibres. Natural fibres are available in short and limited length. Therefore they are labeled as *staple fibres*. Synthetic fibres are generally unlimited in length and therefore called *filament*. Compared to synthetic fibres, natural fibres are usually easier to recycle and are based on renewable raw materials. [7]

Natural fibres		flax, hemp, sisal, silk, wool, cotton, hair, burlap
Synthetic	organic fibres inorganic fibres metal fibres	PE, PP, PA, PAN, aramid, carbon glass, quartz, SiC, basalt, Al <sub>2</sub> O <sub>3</sub> , boron, asbestos steel, aluminium, copper, nickel, beryllium, tungsten

**Size and shape:** The fibre can be modelled as a chain, whereas the strength is determined by the weakest link. With an increasing number of links the probability of finding a new even weaker link increases. Therefore, large volumina exhibit more strength-reducing defects. A single fibre with a rather small volume can bear higher loads than a compact material. By introducing fibres to the composite the total volume becomes partitioned into many small volumina. This assumption, made by WEIBULL, is known as the *theory of the brittle fracture*. [8] Another aspect is that by reducing the diameter of the fibre, the size of possible defect sites decreases as well.

**Defects and notches:** Usually it can be expected that the distribution and orientation of defects is statistically in a material volume. Even minimal notches and cracks may contribute significantly to the strength. Since fibres will not be free of defects, the strength will be less than the theoretical value based on the atomic bonds. Most critical are defects lateral (perpendicular) to the direction of stress. At the borders of defects even small loads can induce stress high enough to start the fracture mechanism. A crack (fissure) is formed and grows locally. The extension of the crack along the fibre becomes inhibited due to the elongated nature of the fibre. Therefore the growth of a crack needs higher loads compared to compact materials. Nevertheless, it is crucial that the amount of defects in the raw fibre as well as those introduced by processing are minimised.

**Internal stress:** The production of fibreglass introduces internal stress. This is a beneficial effect because the strength-reducing influence of surface defects is decreased. Promoted by the weak thermal conductivity the surface of glassfibres, spun from melt, cools faster than the inside. The slowly quenched core shrinks and creates internal stress at the surface. This stress is counteracting the propagation of defects.

#### 2.0.2 Fibreglass

Fibreglass is probably the first synthetic fibre produced by man. Egyptians have been able to prepare fibreglass from melt, dating back to 3500 BC. In 1938 the USA started the first industrial manufacturing of infinite textile glass as insulation material for electric applications. In 1942 these fibres have been added to a matrix of unsaturated polyester resin to construct

	Characteristic	$\mathrm{SiO}_2$	$(\mathrm{Al}_2\mathrm{O}_3 + \mathrm{Fe}_2\mathrm{O}_3)$	CaO	MgO	Na <sub>2</sub> O	$K_2O$	$B_2O_3$	$\rm ZrO_2$
A	Common soda-lime silica	72	<1	10		14			
AR	Alkali resistant	61	<1	5	<1	14	3		10
С	Chemical corrosion resistant	65	4	13	3	8	2	5	
Е	Electrical composition	54	15	17	5	<1	<1	8	
$\mathbf{S}$	High strength and modulus	65	25		10				

Table 2.2: Approximate compositions of reinforcing fibreglass. All values are given in weight % and do not represent various impurities. [7]

aircraft components. Beneficial mechanical properties are high strength, elastic modulus and stiffness at low weight.

Glass fibres are inorganic fibres of high strength. Their strength is based on the strong covalent bonds of silicon and oxygen. The basic building unit SiO<sub>2</sub> is capable to form tough networks. Crystallised quartz is based on a short- and long-ranged ordered state. Addition of metalloxides inhibits the formation of Si–O–Si links and thus an ordered state. Figure 2.1 presents the order states of SiO<sub>2</sub>. By fast quenching the melt is unable to crystallise and the material remains in an amourphous state. While solidification the high viscosity of the supercooled liquid inhibits the formation of a long-ranged ordered state. This glassy structure is metastable. Due to the lack of order and orientation of this three-dimensional atomic network, (fibre)glass exhibits isotropic properties. The composition of fibreglass determines its properties and application. Typical compositions and designations are presented in Table 2.2. E-glass is most popular and inexpensive. The content of SiO<sub>2</sub> is approximately 54 weight %, which is relatively low compared



Figure 2.1: Order of SiO<sub>2</sub> building units: **a** crystallised quartz (*Bergkristall*) with short- and long-ranged order; **b** fused silica (*Kieselglas*) without long-ranged order; **c** soda-lime glass (*Natron-Kalkglas*) with a disturbed network. [6]

	Ŷ	<u> </u>
Polymer		Characteristics and applications
Thermosetting:	Epoxies Polyesters Phenolics Silicones	<ul><li>High strength (for filiament-wound vessels)</li><li>For general structures (usually fabric reinforced)</li><li>High-temperature applications</li><li>Electrical applications (e.g. printed-circuit panels)</li></ul>
Thermoplastic:	Nylon/Perlon Polycarbonate Polysytrene	Less common, especially good ductility, recyclability "

Table 2.3: Polymeric matrix materials for fibreglass. [9]

to other fibre glasses. S-glass is stronger than E-glass. It consists mainly of silica, a lumina and magnesia.

**Manufacture of fibreglass:** Melted glass  $(1400 \,^{\circ}\text{C})$  is extruded through a spinneret of 1 to 2 mm opening size. Extruded high viscous material is stretched at high speeds to a diameter of 5 to 24  $\mu$ m and solidifies instantly. Nozzles apply a fine coating called *sizing* to increase both abrasion resistance and promote adhesion to the matrix. (Textile) sizings consist of plasticiser, film-forming substances and lubricants. In further production steps this coating is removed by heat cleaning and a *finish sizing* is applied. The final coating usually consists of 5 to 10% additives (lubricants, antistatics), 80 to 90% foam-forming substances and 5 to 10% adhesion promoters. Numerous compositions of sizings are available whereas the composition has to be optimised for the distinct application. Yielded single fibres are collected to bundles and coiled onto reels.

#### 2.0.3 Matrix

Various materials may be used for a composite material: metals, ceramics, glasses, cement or synthetic materials like polymers or resins. The matrix is basically an embedding compound containing an addition compound (reinforcement). It is mostly the weaker and less rigid but ductile component of the composite. Externally applied stress is transmitted and distributed to the reinforcement. One main task is to bind the reinforcements together and protect them from surface damage due to abraison or chemicals. Additionally it seperates the single fibres material and prevents the propagation of brittle cracks from fibre to fibre.

Polymer matrices can be divided into thermoplastics and thermosets. Thermoplastics are noncross-linked polymers that melt to a liquid when heated and freeze to a very brittle, glassy state when cooled sufficiently. Polymer chains associate through weak VAN DER WAALS forces (polyaliphates), stronger dipole-dipole interactions and hydrogen-bonding (polyamides), or stacking of aromatic rings (polystyrene). Thermoplastics are elastic and flexible above glass transition temperature.



Figure 2.2: Tensile strength: the stress-strain response  $\sigma_{\epsilon}(\epsilon)$  of the fibre-composite is a synergy of both components. The rigid fibre deforms linear-elastically up to high strains. The matix is more ductile and changes from linear-elastic to a plastic deformation at a critical strain. The composite response can be divided in two stages: at first both components deform elastically; above a critical strain, only the fibre deforms elastically, since the matrix is in the plastic regime. The combination of fibre and matrix is improving the stress-strain response of the matrix. [9]

Quite contrary thermosets are polymeric systems that develop a covalent-bonded threedimensional network upon curing. The network is based on irreversible cross-linking, initiated by elevated temperatures, irradiation or curing agents. Prior to curing, thermosetting materials are liquid or malleable. Remelting or remolding is not possible after curing. Uncontrolled reheating of the material results in reaching the decomposition temperature before the melting point is obtained. Most commonly unsaturated polyester or epoxy resins are used.

#### 2.0.4 Mechanical properties

The mechanical properties of a composite are a result of its components and mechanical synergy. Figure 2.2 present a tensile strength comparison of fibre, matrix and composite. The addition of fibres reinforces the matrix. Matrix and composite both exhibit two regimes: elastic and plastic deformation.

Fundamentally one can distinguish micro- from macromechanics. The macroscopic mechanical properties of a composite specimen result from various factors like concentration, distribution and orientation of the fibre. Micromechanics concentrate on the primary interaction of a single fibre and matrix. Pull-out tests on embedded fibres yield insight to the interfacial stability of the composite. The pull-out experiment is presented in Section 3.8.

#### 2.0.5 Fibre-matrix interface

The interphase is crucial to the performance of the composite: a steep gradient in local properties of the system yields reduced adhesion of reinforcement and matrix. Weak interactions provide a good energy adsorption but compromised strength and stiffness. Strong interactions result in strong and stiff, but brittle composites. A prolonged gradient combines adequate energy adsorption and strength. The adhesion between fibre and matrix is fundamentally influenced by adsorption and wetting. Liquid matrix material with a surface tension below the



Figure 2.3: ASHBY map: elastic modulus E versus density  $\rho$  for different materials. Data of similar materials is summarised by regions in this plot. "Wood" refers to the properties of wood along the fibre direction. Wood combines a high elastic modulus and with a low weight. Metals and alloys with comparable modulus are considerably heavier. Even tough wood itself is a polymeric material, its mechanical properties outperform polymeric materials used in engineering. [1, p. 1282]

surface tension of the fibre will wet the surface. For higher surface tensions de-wetting takes place. A gradient can be established by surface-bound molecules sticking out into the matrix. Even though, no covalent bonds are formed, *inter*diffusion may promote adhesive interactions or yield entanglement of molecules. This *autohesion* is an important mechanism. Natural fibre-composites stand reference for beneficial use of gradients.

# 2.1 Bio-inspiration

The architecture of fibre-composites has neither been invented by mankind, nor is it valid to declare it as an outcome of our modern understanding of technology. Hierarchical structures have been developed by an evolutionary process of adaption and selection in the timeframe of a several hundred million years. Compensation of forces by high-strength fibres is only one prosperous principle of nature and depicts a scaffold of modern lightweight construction. Fibrous constructions outperform compact complements in many respects like rigidity, stress-resistance and (light)weight. Bio-fibre-composites can be found in many load-bearing constructions like the skeleton, stems or the musculature. In the following section wood is presented as an example of a natural fibre-composite. Moreover the hierarchical structure of the plant cell wall is discussed. [1, 10]

#### 2.1.1 Wood: a natural fibre-composite

Wood is one of the oldest and most commonly used building materials. It offers exceptional elasto-static properties at a minimum weight. Figure 2.3 presents a comparison of wood to typical engineering materials. This natural lightweight-material allowed the construction of



Figure 2.4: Illustration of a plant cell wall: rigid cellulose fibrils are embedded into a ductile matrix of pectin; hemicellusoses link the cellulose fibrils. [11]

houses, tools, (surface)vehicles, water- and aircrafts. Even nowadays many applications cannot abandon wooden components due to a lack of a convenient substitute. Even tough wood has been displaced by metals and synthetic (fibre-)composites in many fields, modern materials cannot deny their natural descent (e.g. identical nomenclature, principles of construction and processing). The reason for the exceptional mechanical properties can be found in the design of the plant cell wall. Because of that cell wall, plant cells posses a higher rigidity in comparison to animal cells. Since plants are sendentary and not dependent on locomotion, the lack of flexibility for a higher structural support is a fair trade.

Figure 2.4 shows an illustration of the primary cell wall of plants. The intermediate space of the middle lamella and the plasma membrane consists of cellulose, hemicelluloses and pectin. Crystalline cellulose microfibrils are linked via hemicellulosic tethers. This cellulose-hemicellulose-network is embedded in a matrix of branched polysaccharides: pectins and cross-linking glycans. The coextensiv network of pectins provides elasticity and increases the resist-ance to compressions. The cross-linking glycans increase the tensile strength of the cellulose -hemicellulose structure. Additionally, soluble proteins are expected to contribute to the mechanical strength. This hierarchical structure combines high elasticity with high elastic modulus and good shock absorbance. These properties result at least partly from a fibre-gradient-matrix structure. [1, 10, 12]

#### 2.1.2 Bionic adaptaion

Based on the mechanically beneficial concept of the plant cell wall high performance polymer/fibreglass composites are desirable. In this work the inflexible fibrillar cellulose is substituted by fibreglass, which is also crystalline, strong, and resistant to hydrolysis. A polymer can form a random, amorphous structure with lower strength similar to hemicelluloses. Instead of pectin, a thermosetting polymer resin (e.g. epoxy) can be used to embedd the fibrous network. Mechanical properties such as vibration damping, strength, toughness, fracture behaviour and stiffness have to be optimised.

## 2.2 Scientific background

Since the performance of a composite depends on the fibre-matrix interface (ref. Section 2.0.5), the theory of wetting, cohesion and adhesion are briefly discussed in the following.

#### 2.2.1 Wetting tension

Wetting is a process by which a solid-gas-interface is replaced by an interface between the same solid and a liquid. When a liquid phase is exposed to a solid substrate and unable to spread, a contact angle  $\theta$  is formed.  $\theta$  depicts the angle between the interfaces along the contact line of three adjacent phases (*line of wetting*). Figure 2.5 presents an illustration of the contact angle of a lenticular drop of liquid. The GIBBS free energy  $\mathcal{G}$  depends on temperature T, pressure p, number of particles n and interfacial area  $\mathcal{A}$ .

$$d\mathcal{G} = \left(\frac{\partial \mathcal{G}}{\partial T}\right) dT + \left(\frac{\partial \mathcal{G}}{\partial p}\right) dp + \sum_{i} \left(\frac{\partial \mathcal{G}}{\partial n_{i}}\right) dn_{i} + \left(\frac{\partial \mathcal{G}}{\partial \mathcal{A}}\right) d\mathcal{A}$$
(2.1)

$$= -\mathcal{S} dT + V dp + \sum_{i} \mu_{i} dn_{i} + \gamma d\mathcal{A}$$
(2.2)

Solving equation 2.1 yields equation 2.2, presenting the influence of entropy  $\mathcal{S}$ , volume V, chemical potential  $\mu$  and the interfacial tension  $\gamma$ . The formation of an interface is based on intermolecular forces. In contrast to the bulk phase, molecules situated at the interface exert unidirectional forces. In a system of constant temperature, pressure and number of particles, the energy/work  $\Delta \mathcal{G}$  is required to form and maintain a surface area  $\Delta \mathcal{A}$  to vapour, is the surface tension  $\sigma$ . The interfacial tension  $\gamma$ , by contrast, is depicting an interface area, but is often used equivalently. Both are two-dimensional tensions.

$$\left(\frac{\partial \mathcal{G}}{\partial \mathcal{A}}\right)_{T,p,n} = \begin{cases} \sigma \\ \gamma \end{cases}$$
(2.3)

The geometry of a drop depends on the surface tension and gravitation. While the surface tension is dependent of the contact area  $\mathcal{A}$ , gravitation is a function of the volume. If the surface tensions are viewed as forces acting on a tangent to the corresponding interfaces and applied perpendicular to the unit length of the permeter of wetting, the force balance is given





by the YOUNG equation (Eq. 2.4), as depicted by Figure 2.5.

$$\sigma_{\text{solid}} = \gamma_{\text{solid,liquid}} + \sigma_{\text{liquid}} \cdot \cos\theta \quad \text{or} \quad \cos\theta = \frac{\sigma_{\text{solid}} - \gamma_{\text{solid,liquid}}}{\sigma_{\text{liquid}}} \tag{2.4}$$

By the transfer of substance from the liquid phase via vapour, or due to the migration (diffusion) of molecules of a liquid along the solid surface, a thin film is formed. FRUMKIN suggested that while examining wetting, the formation of the adsorption layer in equilibrium with the macroscopic liquid must be accounted. With the two-dimensional pressure  $\Pi$  of the equilibrium adsorption layer, Young's equation (Eq. 2.4) reads as

$$\sigma_{\text{solid}} - \Pi = \gamma_{\text{solid,liquid}} + \sigma_{\text{liquid}} \cdot \cos\theta \quad \text{or} \quad \cos\theta = \frac{(\sigma_{\text{solid}} - \Pi) - \gamma_{\text{solid,liquid}}}{\sigma_{\text{liquid}}}.$$
 (2.5)

The adsorption layer reduces the surface tension at the gas-solid interface as accounted in Eq. 2.5. For low energy surfaces the effect of  $\Pi$  can be neglected. Based on the magnitude of the contact angle the wettability can be described:  $\theta = 0^{\circ}$  absolute wetting;  $0^{\circ} < \theta < 90^{\circ}$  good wetting;  $90^{\circ} \leq \theta < 180^{\circ}$  poor wetting;  $\theta = 180^{\circ}$  absolute non-wetting. The value of  $\theta$  can also be used to describe the degree of similarity between the solid surface and the liquid (*liophilicity*). Surfaces with a high wettability of water are designated as *hydrophilic*, while those poorly wetted are *hydrophobic*. The polar character of the surface can be concluded from the hydrophilicity. [13]

#### 2.2.2 Cohesion and adhesion

The wetting is determined by a force balance of adhesive and cohesive forces. [14] Figure 2.6 illustrates the principles of cohesion and adhesion. The work of cohesion  $W_{\text{cohesion}}$  of a single pure liquid or solid phase (A), is the work done on the system when a column A of unit area

is split, reversibly, normal to the axis of the column to form two new surfaces, each of unit area, in contact with the equilibrium vapour phase. The work of cohesion is therefore twice the surface tension  $\sigma_A$  of phase A.

$$W_{\text{cohesion}} = 2 \cdot \sigma_{\text{A}} \tag{2.6}$$

When two condensed phases A and B, forming an interface of unit area are separated reversibly, to form interfaces of unit area, the work of adhesion  $W_{\text{adhesion}}$  is required (Eq. 2.7).

$$W_{\rm adhesion} = \sigma_{\rm A} + \sigma_{\rm B} - \gamma_{\rm AB} \tag{2.7}$$

The work of cohesion (Eq. 2.7) can be derived from the work of adhesion (Eq. 2.6), since there is no interfacial tension for identical phases (A=B). A comparison of YOUNG's equation (Eq. 2.4) with the definition of  $W_{\text{adhesion}}$  (Eq. 2.6) yields the YOUNG-DUPRÉ equation (Eq. 2.8). The work of adhesion, at the solid-liquid interface, can be determined experimentally in reference to a unit area.

$$W_{\text{adhesion}} = \sigma_{\text{liquid}} \cdot (1 + \cos \theta) \quad \text{or} \quad \cos \theta = \frac{W_{\text{adhesion}} - \sigma_{\text{liquid}}}{\sigma_{\text{liquid}}}$$
(2.8)

By substitution of the surface tension of the liquid by its work of cohesion (Eq. 2.7) the YOUNG's equation shows the balance of adhesive and cohesive forces (Eq. 2.9).



Figure 2.6: Principles of cohesion (left) and adhesion (right): Cohesion is based on the separation of a phase (A) by creating new interfaces. Adhesion describes the separation of two phases (A and B). The initial interface is substituted by two new ones.

# Chapter 3

# Methods

In this chapter the methods used in this thesis are briefly explained.

# 3.0 Microscopy

The term *microscopy* derived from the greek  $\mu\iota\kappa\rho\delta\varsigma$  (*mikros*)  $\sigma\kappa\sigma\pi\varepsilon\iota\nu$  (*skopein*), which means to inspect/observe something small. What is regarded as small depends on the actual ages and their technological progression. Nowadays, the limit of resolution has shifted to magnitudes in the order of nanometres. Advanced *nanoscopy* techniques offer higher resolutions and enhanced constrast in comparison to classical optical microscopy. In the following the applied microscopy techniques with their respective resolving capacities are described.

## 3.1 Optical microscopy

The classical optical microscope is based on two components: a condenser lens, which focalises light to a limited area of the sample; and a lens collecting the backscattered light thus projecting a real image in the focus plane of the eyepiece. The eyepiece serves as a loupe creating a magnified virtual image on a detector. The total magnification is the product of the respective magnifications of lens and eyepiece. Based on Köhler, two apertures control the illumination in the optical path: a field diaphragm restricts the light passing the collector lens and preventing the intrusion of stray light; an adjacent condenser diaphragm limits the backscattered light passing the condesor lens. Contrast and resolution depend on the condenser diaphragm: by closing the diaphragm the image gains contrast but loses resolution. The resolution can be described as the capacity to resolve two individual points distanced at  $d_{\min}$ .

$$d_{\min} \approx 0.61 \cdot \frac{\lambda}{NA}$$
 and  $NA = n_{\text{medium}} \cdot \sin \alpha$  (3.1)

NA marks the numerical aperture, which quantifies the influence of the condensor diaphragm by  $\alpha$ , the half-angle of the maximum cone of light that can enter or exit the condensor. Additionally, the resolving capacity depends on the light wavelength  $\lambda$  and the refractive index of the medium  $n_{\text{medium}}$  to traverse. For visible light the maximal resovable details are typically in the range of 0.5 to 1  $\mu$ m, depending on the lens, illumination and numerical aperture. [15] This resolution suffices for inspections and manipulations in the micrometre domain.

## 3.2 Confocal laser scanning microscopy

Confocal Laser Scanning Microscopy (CLSM) has become a versatile tool for three dimensional microscopic imaging. Image acquisition is realised by sequential scanning of the sample with a laser beam. A spatial pinhole eliminates out-of-focus light or flare in specimens that are thicker than the focal plane. Another benefit is the spatially limited illumination. The detected intensity at positions of (x, y, z) layers is captured. This signal represents the light intensity but not the actual wavelength/colour of the specimen. No optical picture is recorded. Height information is obtained by optical slicing. The stacking of layers creates a three dimensional picture. The resolving capacity in the x, y-plane is according to Eq. 3.1 given by

$$d_{\min}(x,y) = [0.37, 0.61] \cdot \frac{\lambda}{NA}$$
 and  $NA = n_{\text{medium}} \cdot \sin \alpha$  (3.2)

with the RAYLEIGH coefficient being 0.37 for strictly confocal and 0.61 for classical imaging. The resolution in z reads as

$$d_{\min}(z) = [0.45, 0.71] \cdot \frac{\lambda}{n - \sqrt{n^2 - NA^2}}.$$
(3.3)

The coefficient 0.45 designates reflection mode and 0.71 (auto)fluorescence. Therefore the resolution in z is reduced  $(d_{\min}(z) \approx 3 \cdot d_{\min}(x, y))$ . Confocal imaging is possible in reflection mode and fluorescence mode. Reflection mode enables the evaluation of non-fluorescent specimen. Further information about the theory of CLSM can be found in literature.

## 3.3 Scanning electron microscopy

SEM is a microscopy technique based on an electron beam scanning the sample in ultra high vacuum. Since the resolving capacity is dependent on the wavelength, as described by Eq. 3.1, lower wavelengths grant higher resolutions. Beyond the spectrum of visible light an electron beam can serve as light. According to DE BROGLIE the wavelength of an electron is related to the momentum p (mass m, velocity v) and the PLANK constant h.

$$h = p \cdot \lambda$$
 and  $p = m \cdot v$  (3.4)



Figure 3.1: Operating principle of a field emission SEM: an electron source emits an electron beam; electromagnetic and electrostatic lenses are controlling the beam focusing it at a specific plane; the position is direct by scan coils; the sample is scanned point-topoint; BSE and SE are registered at the respective detectors. [18]

The velocity of the emitted beam from an electron gun depends on the plate-supply voltage U.

$$E_{\rm kin} = \frac{1}{2} \cdot {\rm m}_{\rm e} \cdot v^2 = {\rm e} \cdot U = E_{\rm pot} \qquad \text{hence} \qquad v = \sqrt{\frac{2 \cdot {\rm e} \cdot U}{{\rm m}_{\rm e}}} \tag{3.5}$$

At a voltage of 1 kV emitted primary electrons should have a velocity of  $1.88 \times 10^7 \text{ m s}^{-1}$  what correlates to  $\lambda(1 \text{ kV}) = 0.039 \text{ nm}$ . The wavelength is approximately four orders of magnitude smaller than visible light. For ideal conditions  $d_{\min}(1 \text{ kV})$  is approximately 2.5 nm. The resolution is inversely proportional to the applied voltage:  $d_{\min}(0.2 \text{ kV}) \approx 5 \text{ nm}$  and  $d_{\min}(30 \text{ kV}) \approx 0.4 \text{ nm}^1$ . Even though, low voltages are preferable because they produce a clearer surface structure, due to less damage, less charge-up and less edge effect.

The spatial resolution of the SEM is limited by the size of the electron spot, which depends on both the wavelength and the electron-optical system producing the scanning beam. The resolution is also limited by the size of the interaction volume, or the extent to which the material interacts with the primary electron beam. [16, 17] The operating principle of a field emission SEM is presented in Figure 3.1.

**Detection:** Backscattered electrons BSE are primary electrons which are scattered by elastic collision with the nuclei of the sample atoms. They originate from a large escape depth. In addition primary electrons may activate the emission of secondary electrons SE. Ejected at the impact point of the primary electron beam, these electrons (of low energy < 50 eV) are intercepted by the weak electrical field at the sample surface. They are then accelerated to a high energy by the field of the electrostatic lens and focused on the annular IN-LENS detector

<sup>&</sup>lt;sup>1</sup>obtained with HITACHI S-5500

inside the beam booster located above the objective lens. While the IN-LENS detector provides the best high resolution information, a lateral SE detector (EVERHART-THORNLEY) in the specimen chamber provides optimum topographical information. Signals from both detectors may be mixed to deliver optimum image quality.

Contrast is generated by differences in the number of emitted electrons and the possibility of their detection. Topographic contrast is possible if both factors depend on surface topography. Compositional contrast is based on the difference in emission of BSE from domains of different atomic numbers. For larger nuclei the probability of backscatter is higher, whereas the yield of SE will not vary significantly.

Apart from resolution and contrast, the depth of field DOF is an important variable. Depending on the orientation of the sample surface and the plane of best focus, the region in effective focus varies. The DOF can be influenced by the working distance WD and the aperture size. Small WD grants high resolutions but compromise the depth of field and vice versa. High resolutions and great DOF can be adchieved at small aperture sizes but may result in grainy images.

## 3.4 Scanning force microscopy

Scanning force microscopy was invented by BINNING, QUATE and GERBER in 1986 [19] and found application in force spectroscopy and topographic imaging. The setup consists of a probe scanning the sample with its position being controlled by an opto-electronical feedback. [20]

**Principle of function:** The probe (tip) is mounted to a cantilever spring. Cantilever displacements are registered via the *optical lever technique*: a laser reflected on a position-sensitive diode PSD. Changes in the PSD current correspond to deflections:

$$\Delta I_{\text{vertical}} = (I_{\text{A}} + I_{\text{B}}) - (I_{\text{C}} + I_{\text{D}}) \qquad \text{vertical deflection} \tag{3.6}$$

$$\Delta I_{\text{lateral}} = (I_{\text{A}} + I_{\text{C}}) - (I_{\text{B}} + I_{\text{D}}) \qquad \text{lateral deflection} \tag{3.7}$$

The cantilever deflection  $z_{\text{cant}}$  depends on the PSD signal  $I_{\text{vertical}}$  and the sensitivity S.

$$z_{\text{cant}} = I_{\text{vertical}} \cdot S \tag{3.8}$$

The sensitivity is the correspondence of the piezoelectric translator  $z_{\text{piezo}}$  to the photodiode current. Both topography and force measurement are based on the detection of the laser deflection on the position sensitive diode  $I_{\text{PSD}}(z_{\text{piezo}})$ . For topography the determination of the absolute force F is not required.

**Topography:** A topographic image is obtained by plotting the deflection of the cantilever (or the height position of the translation stage) versus its position (x, y) on the sample. To avoid

alterations of the surface due to the permanent tip contact while scanning, an alternative mode with less/no shear forces is preferable. The *tapping mode* relates to the tip/cantilever acting as a harmonic oscillator (Eq. 3.9).

$$F_{\text{external}} = m \cdot \frac{\partial^2 x}{\partial t^2} + k \cdot x = A(\omega) \cdot \sin(\omega \cdot t + \phi(\omega)) \quad \text{with} \quad \omega_{\text{res}} = \sqrt{\frac{k_{\text{cant}}}{m}} \quad (3.9)$$

The probe is excited at its resonance frequency  $\omega_{\rm res}$ . Due to vibration the probe is in intermitted contact to the surface. When interacting with the surface the vibration, described by amplitude A and phase  $\phi$ , changes. The feedback enables the representation of the topography. The phase signal may reveal information about the sample the height signal is unable to show. Material contrast can cause characteristic shifts in the phase, even though the amplitude is the same. The resolution is limited by the size of the probe/tip used for scanning. The topography is always a *convolution* of sample topography and tip topography. The minimal curvature possible in the height signal is the tip curvature radius (usually less than 10 nm). The tip sharpness may change during measurement due to wear or material pick-up. The surface roughness can be calculated from the topography z(x, y). Eq. 3.10 presents the average mean  $R_{\rm av}$  and the quadratic mean roughness  $R_{\rm q}$ . Both are statistical representations of the magnitude of a varying topographic height, but the  $R_{\rm q}$  value is more representative.

$$R_{\rm av} = \frac{1}{n} \cdot \sum_{i=1}^{n} |z_i|$$
 and  $R_{\rm q} = \sqrt{\frac{1}{n} \cdot \sum_{i=1}^{n} z_i^2}$  (3.10)

**Force measurement:** By HOOKE's law (Eq.3.11) the force F is given by the spring constant k and the displacement z.  $\alpha$  is the angle of the deflected cantilever to its original position (approx. 10%).

$$F = -\left(k \cdot \frac{z}{\cos^2 \alpha}\right)_{\text{cant}} \approx -(k \cdot z)_{\text{cant}}$$
(3.11)

The knowledge of the cantilever spring constant  $k_{\text{cant}}$  is essential for the conversion of the  $I_{\text{PSD}}(z_{\text{piezo}})$  to force-distance curves F(D). Coarse values are given by the manufacturer, but a separate determination yields more precise values. The spring constant depends on the YOUNG's modulus  $E_{\text{Young}}$  and the geometry: width w, length l and thickness th.

$$k_{\rm cant} = E_{\rm Young} \cdot \frac{w \cdot th^3}{4 \cdot l^3} \tag{3.12}$$

Since a precise determination of the modulus and the thickness is laborious and alternative method is preferable: HUTTER and BECHHOFER introduced the *thermal noise method* in 1993. [21]



Figure 3.2: Force curve: a non-contact approach is followed by a jump-to contact; further approaching yields a deflection (repulsive force) of the cantilever; the successional retraction exhibits a prolonged contact, due to adhesion (attractive force); the cantilever is extended until a jump-off contact occurs; the cantilver regains its distance in the non-contact regime (e.g. baseline). The hysteresis of approach and retraction represents the work of adhesion. [20]

The interaction of tip and sample, an attractive or repulsive force F(D), depends on the interaction potential  $U_{\text{interaction}}$  and the tip sample separation D (sum of deflection and position).

$$\frac{\partial U_{\text{interaction}}}{\partial D} = F(D) = -(k \cdot z)_{\text{cant}} \quad \text{with} \quad D = z_{\text{cant}} + z_{\text{piezo}} \quad (3.13)$$

The measured force is a result of different interaction forces. A brief overview is given in Table 3.1. In depth information can be found in literature [14]. A measurement consists of approach, contact and retraction of a probe to/from a surface. The detected PSD current-signal-vs.-piezo-position  $I_{\text{PSD}}(z_{\text{piezo}})$  curves is converted to force-vs.-distance F(D) curves. Figure 3.2 shows a force curve.

Interaction	Based on	Description	Range in nm	
BORN repulsion	indifferent quantum states	repulsive	0.1	
Covalent bond	electron sharing	attractive	0.1	
Ionic bond	electron shift, electrostatics	attractive	1	
VAN DER WAALS	temporary/permanent dipoles	attractive	100	
COULOMB force	charges, electrostatics	attractive/repulsive	> 100	
LORENTZ force	electromagnetics, induction	attractive/repulsive	> 100	
Capillary forces	hydrodynamics, adhesion	attractive	up to 1000	

Table 3.1: Overview of interaction forces. [14]

Adhesion: The probe is often kept in contact with the surface until the cantilever force overcomes the force of adhesion, while the probe is being retracted. This pull-off force is also called adhesion force  $F_{\text{adhesion}}$  and is related to the work of adhesion (see Section 2.2.2). The contact regime mechanic of probe and sample are described in various models. Detailed discussions of their theory and applicability can be found in literature [20]. In brief, two important models are DMT and JKR.

$$F_{\text{adhesion}} = \begin{cases} -2 \cdot \pi \cdot R \cdot W_{\text{adhesion}} & \text{DERJAGUIN, MULLER, TOPOROV} \\ -\frac{3}{2} \cdot \pi \cdot R \cdot W_{\text{adhesion}} & \text{JOHNSON, KENDALL, ROBERTS} \end{cases}$$
(3.14)

The adhesion force is a combination of the electrostatic force  $F_{\rm el}$ , VAN DER WAALS  $F_{\rm VdW}$  capillary force  $F_{\rm cap}$  and chemical bonds  $F_{\rm chem}$ .

$$F_{\rm adhesion} = F_{\rm el} + F_{\rm VdW} + F_{\rm cap} + F_{\rm chem} \tag{3.15}$$

The amount of contribution can be related to the conditions of the measurement. When charge dissipation is ineffective, e.g. insulating materials at low humidity, a significant contribution from electrostatic forces may be present. The VAN DER WAALS forces always contribute in an attractive manner. The surfaces of tip and sample exhibit a thin layer of adsorbed water at ambient conditions. The thickness depends on the hydrophilicity of the surfaces and the relative hydrophilicity. At contact a water neck is formed between tip and substrate due to capillary condensation. The chemical composition, the functional groups present on the tip and surface also influence the adhesion. Attractive forces may occur during contact in the form of specific interactions (receptor-ligand/host-guest/acid-base). Quantification is hindered by the influences of surface roughness and heterogeniety, the adsorption of contaminants and the definition of contact geometry. [20]

**Geometry:** Since the force between two surfaces depends on both the material properties and the geometry of the surfaces an approximated description facilitates the handling of arbitrary geometries. DERJAGUIN's approximation is based on the interaction range being much smaller than the radius of curvature of the probe R. In this case the interaction can be related to the energy per unit area between two planar surfaces  $U_{\text{planar}}$ . [14, 20]

$$U(D) = \int U_{\text{planar}}(x) \, d\mathcal{A} = 2 \cdot \pi \cdot R \cdot \int U_{\text{planar}}(x) \, dx \qquad \text{with} \qquad R = \frac{R_1 \cdot R_2}{R_1 + R_2} \tag{3.16}$$

## 3.5 Drop shape analysis

The evaluation of the contact angle is based on drop shape analysis (DSA). A drop of liquid e.g. DI water, was placed on a planar sample surface with a vertically mounted syringe. From an image, captured by a focused CCD camera, the drop profile was extracted. The vapour-solid horizon was adjusted manually prior to the touchdown of the hanging drop.

**Contact angle:** The contact angle is evaluated from parameters of the drop profile. The evaluation is based on the YOUNG-LAPLACE theory [13]. For the measurement of a static contact angle the drop is expected to maintain its size and shape during the measurement.

This cannot be taken for granted since interfacial interactions may change the contact angle over time. Temporal changes may be based on: evaporation of liquid; migration (diffusion) of dissolved material; contamination of the liquid phase by dissolved solid material; chemical reactions at the liquid-solid interface; swelling of the solid phase by the liquid. One advantage of the static contact angle is that the needle does not stay in contact with the drop during the measurement. Without the distortion of the needle the fit is not limited to the contact regime but the whole drop profile can be evaluated. Usually static contact angles are obtain by placing drops at the same place. To characterise the homogeneity of a surface, drops can be placed ramdomly distributed over the surface. Local irregularities (contaminants, roughness variations, defects, inhomogeneities) are expressed in an increased standard deviation SD of  $\theta$ . The mean contact angle of this semi-dynamic method is not affected as much by surface defects as compared to a standard static measurement. Apart from the evaluation of the static contact angle the data set  $\{\theta_{x,y}\}$  can be used to represent the sample homogeneity, concerning its wettability, by a two-dimensional mapping.

## 3.6 Ellipsometry

Ellipsometry consists of the measurement of the change in the polarisation state of light upon reflection from the sample surface. This reflection experiment utilises polarised light: polarisation distinguishes oscillations perpendicular (s) and parallel (p) to the plane of incidence. An overview of polarisation states and their representation can be found in the Appendix. Upon reflection the intensity of s- and p-polarised light can vary individually. The change in polarisation is determined by the sample's properties (thickness, optical constants, layer build-up).

$$\varrho(\lambda,\phi) = \tan \Psi \cdot \exp(-\imath \cdot \Delta) = \frac{r_{\rm p}}{r_{\rm s}}$$
(3.17)

Eq. 3.17 describes the ratio of transmission  $r_{\rm p}/r_{\rm s}$  by two characteristic angles  $(\Psi, \Delta)$ , which vary with the incidence angle  $\phi$  and the wavelength  $\lambda$  (due to dispersion  $n(\lambda)$ ). This raw data is a fingerprint of the sample of the system at a respective incidence angle. Two ellipsometric techniques to determine (ultra)thin film thicknesses have to be distinguished: spectroscopic ellipsometry and Nullellipsometry. Spectroscopic ellipsometry uses white light. The intensity of respective polariser/analyser settings is metered and Fourier-transformed to calculate  $\Psi, \Delta(\lambda)$ . The setup of the experiment can be found in Figure 3.3. Nullellipsometry uses monochromatic light and relies on the determination of the null settings. Polariser P and analyser A are varied until complete cancellation of the light. The variation of the wavelength in based on dispersion  $n, k(\lambda)$  and different penetration depths  $d(\lambda)$  of light. Measurements at multiple incidence angles are useful to find optimal sensitivity (reflectivity  $R, T(\phi)$  and BREWSTER angle  $R_{\rm p}(\phi_{\rm Brewster}) = 0$ ) of the system. However the thickness is independent of the wavelength and angle of incidence  $th \neq th(\lambda, \phi)$ . In conjunction this technique is referred to as VASE, variable



Figure 3.3: Spectroscopic ellipsometry setup with rotating analyser: a light source L emits light of variable wavelength  $\lambda$ ; it becomes linearly polarised by polariser P; an optional retarder R can introduce a phase shift (e.g.  $\pi/2$  for circular polarisation); incident light is refracted to transmission T and reflection R; the state of polarisation is altered by the sample; since the angles of incidence and reflection are the same( $\phi$ ), the reflected light reaches a rotating analyser A; this second polariser analyses the light beam, letting only linearly polarised light pass; the detector D meters the intensity I of incoming light and refers the ratio of transmission  $\varrho(\lambda, \Phi)$ .

angle spectroscopic ellipsometry. The problems associated with VASE are its sensitivity to misalignments and the non-trivial evaluation procedure. There is also a strong dependance on the aperture sizes, sample alignment and sample reflectivity. An in-depth theory to ellipsometry can be found in the literature [22, 23, 24].

**Thickness determination:** The effective optical properties of a layered sample depend on the individual optical properties and thickness of each layer. Ellipsometry is not suited to determine absolute film thickness to a 1 nm precision, particularly not in a multilayered system on a glass substrate where reflectivity is low. [24]

The evaluation principle is illustrated in Figure 3.4. The most simple model consists of a *volume material* with ambient air. The thickness of the substrate is irrelevant, since it is treated as an infinite half space. The optical properties  $n \pm i \cdot k$  of the substrate are expressed by the CAUCHY relation (Eq. 3.18).

$$n(\lambda) = n_0 + 10^2 \cdot \frac{n_1}{\lambda^2} + 10^7 \cdot \frac{n_2}{\lambda^4}$$
 and  $k(\lambda) = \frac{k_0}{\lambda} + \frac{k_1}{\lambda^3} + \frac{k_2}{\lambda^5}$  (3.18)

CAUCHY describes the dispersion based on a series with coefficients  $n_i$  and  $k_i$ . By introducing a (semi)transparent layer on the substrate another interface is added. To evaluate the properties of this layer the properties of the substrate and ambient have to be known. Depending on the layer's adsorption k the penetration depth d of light has to be considered.

$$d = \frac{\lambda}{2 \cdot \pi \cdot k} \tag{3.19}$$



Figure 3.4: Iterative evaluation principle: there is no way to calculate system properties, like thickness th or optical constants nk directly from the experimental data  $\Psi\Delta$ . Based on predictions and prior knowledge of the system a model  $\{th, n, k\}$  is created. The theoretical ellipsometric angles of this model are compared to the experimental data. The deviation is expressed by a mean squared error MSE. An algorithm (SIMPLEX) alternates the model parameter to iteratively find a model with minimal MSE. Ideally the model should now represent the system.

For transparent layers  $(k \to 0)$  the transmission reaches deep into the material  $(d \to +\infty)$ . If d < th, the transmission is absorped before reaching the second interface. The iterative evaluation is repeated for the  $\{th, n, k\}$  model of the layer system. For more complex systems the multilayer composition has to be evaluated layer by layer. For measurements of thin films on transparent substrates (like glass or PDMS) the frustration of back-surface reflections has to be tackled. The method of VASE on transparent substrates is described in the following.

**VASE on transparent substrates:** The evaluation of a film thickness relies on the knowledge of the optical constants of the layers beneath it. Glass is strongly absorbing below 330 nm and transparent for higher wavelengths. The absorption of PDMS is less than 5% in the visible spectrum. In this work, a strategy has been tested to evaluate the thickness of thin films on transparent substrates.

Typically the film of interest is mounted on a substrate absorbing at the wavelengths of interest. Reflected light, scattered in the film multiple times, is analysed by a polariser and metered. On transparent (non absorbing) substrates, like glass and PDMS, incident light penetrates deep into the material and eventually reaches the back surface (see Eq. 3.19). The light reflected from the back surface and the film system are incoherent with each other. Figure 3.5 illustrates the reflected light from the top and bottom surface. This yields inaccurate data sets (shifts in  $\Psi, \Delta$ ) and inhibits the evaluation. A mathematical correction of the back-surface reflection is possible and implemented in some modern spectroscopic ellipsometers. The mathematical correction does not account for the physical state of the back surface and tweaking the parameters (e. g. number of back-surface reflected beams) for the calculation is cumbersome. It is therefore preferable to eliminate the distracting reflections. Experimental techniques are based on (non-specularer) off-scattering, index-matching or absorption. [25]


Figure 3.5: Light reflected from the top and bottom surface of a transparent substrate: Incidence light is partially reflected  $r_1$  and transmitted  $t_{12}$ . In transparent layers, the transmission can reach the back surface and be refracted once again: continued transmission  $t_{12} \cdot t_{23}$  and backside reflection  $t_{12} \cdot r_{23}$ . The backscatter can be reflected inside the transparent layer multiple times, while the transmitted backscatter  $t_{12} \cdot r_{23} \cdot t_{21}$  can reach the analyser. The reflection of the top  $r_1$  and bottom surface  $t_{12} \cdot r_{23} \cdot t_{21}$  are incoherent from each other. [25]

If the top and bottom surface are spatially separated enough, the back-surface reflected beam will eventually be blocked by the analyser diaphragm and not reach the detector. Therefore, transparent substrates should either be very thick or be shaped like a wedge; similar to the latter, the back surface can be roughened to cause non-spectular backscatter. Index-matching is based on the reduction of the optical contrast at the backside. This can be accomplished by placing the sample in a liquid or gel with optical properties similar to the substrate. Quite contrary, the blackening of the backside reduces the amount of backscatter as well, due to the broad absorption of the black tint. [25]

## 3.7 Raman/Infrared spectroscopy

Raman spectroscopy is based on the RAMAN effect: the incident light is inelastically scattered by the molecular vibrations, crystal lattice vibrations (phonons) or other elementary excitations (plasmons, magnons). Photon energy changes correspond to the energy (frequency) of the vibrations. The shift in energy gives information about the chemical composition in respect to the presence or absence of functional groups in the system. [23]

Infrared spectroscopy yields similar, complementary, information. The energy of photons in the infrared spectrum does not suffice to excite electrons, but may induce vibrational excitation states from covalent bonds and groups. The wavelength and amount of energy absorbed is characteristic. Based on the vibrational motion of bonds in molecules and the transmission or absorption of incident light, spectroscopy enables the identification of such bonds.

Both methods are inherently dependent on the number density, the amount of molecules/bonds present in the volume of excitation. In respect to measurements of thin films on solid substrates the sensitivity may not suffice for their detection. This effect is presented and discussed in Section 5.2. Fundamental theory on vibrational spectroscopy can be found in literature. [26]

## 3.8 Pull-out fibre tensile test

In this work the surface of fibres, pulled out of cured epoxy resin drops by tensile stress, was evaluated. A tensile test is fundamentally a mechanical test of a material by applying tension. The performance of a material can be evaluated from its stress to strain behaviour. The pullout test is performed on the fibre embedded in an epoxy resin drop, as presented in Figure 3.6. Before testing samples were cold cured for 24 h at RT.



Figure 3.6: SEM micrographs of a fibre embedded in a drop of epoxy resin. The epoxy resin wets the fibre surface and forms a miniscus. Image **b** is a magnification of **a**.

The fibre is mounted to the system via a guillotine-like opening. The drop is in contact with the opening. Stress is applied until the fibre-drop system fails and the drop decamps releasing the fibre. The setup, developed and prosecuted at MPI Golm, is shown in Figure 3.7. After mechanical testing, pull-out fibres were provided by J. PANDEY for surface characterisation.



Figure 3.7: Pull-out fibre tensile test apparatus at MPI, Golm. The setup consits of a guillotinelike retainer holding the epoxy resin drop in which the fibre is embedded. The aim is to mechanically characterise the interface properties between fibre and matrix.

# Chapter

## **Experimental section**

## 4.0 Chemicals and materials

## 4.0.1 Substrates

**Fibreglass:** The fibreglass used in this work were 365 S-2 Glass rovings by AGY-EUROPE, France. The thickness of a filament is  $9 \mu m$ . The continous glass strands, gathered without mechanical twist, exhibit a *multi-compatible* sizing. The composition is S-glass.

**Glass slides:** Microscope slides (approx.  $76 \times 26 \text{ mm}^2$ , thickness 1 mm) were purchased from MENZEL-GLÄSER (*Thermo Scientific*) and MARIENFELD (*Laboratory Glassware*). Both are common soda-lime glasses (see Table 2.2), manufactured by norm ISO 8037/1. Glass slides are pre-cleaned/ready-to-use.

**Silicon wafer:** Silicon wafers used are CRYSTEC (625  $\mu$ m thickness) and WACKER SILTRONIC AG, *Poly-Si-RSB* (525 ± 15  $\mu$ m thickness). Both are boron doped, have (100) orientation and exhibit a polished frontside and cauterised back side.

**PDMS:** The PDMS elastomer was prepared by mixing *Sylgard 184* (purchased from Dow CORNING) with a 10:1 ratio by mass of prepolymer to curing agent. The mixture was stirred and dispersed in a carefully cleaned, plain petri dish. Since mixing incorporates air, the system was degassed in a desiccator until the silicone was completely clear. After 24 h at RT and curing at 60 °C for 3 h, the cross-linked PDMS was cut into 30 mm×6 mm stripes.

PDMS elastomer slices exhibit a transparent appearance. Cured PDMS can be elongated to 200% of initial size. Since methyl groups are arranged to the air-interface, the surface is in an hydrophobic state. The surface can be rendered hydrophilic by plasma treatment (oxidation, oxygen incorporation) or immersion into a aqueous solution of HCl (10 % by volume for 24 h).

### 4.0.2 Polymers:

Polybutadiene of predominantly 1,2-addition (1,2-PB) and polyacrylonitrile (PAN) were purchased from SIGMA-ALDRICH. Block copolymers PB-b-Px, synthesised and characterised at MPI Golm, were provided by A. BERTIN. An overview of the polymers used for grafting onto mercaptan-coated substrates can be found in Table 4.1.

Table 4.1: Polymers used for grafting onto mercaptan-coated substrates: polybutadiene (approx. 62 mole%) of predominantly 1,2-addition (1,2-PB), poly(1,2-butadiene-*b*-styrene) (PB-*b*-PS), poly(1,2-butadiene-*b*-ethylene glycol) (PB-*b*-PEO), poly(1,2-butadiene-*b*-4vinylpyridine) (PB-*b*-P4VP) and polyacrylonitrile (PAN). All molecular weights are given in g mol<sup>-1</sup>. The molar-mass dispersity  $\mathcal{D}_{\rm M}$  is given by the ratio  $\overline{M}_{\rm w}/\overline{M}_{\rm n}$ . For blockcopolymers PB-*b*-P*x* the number-average degree of polymerization  $\overline{X}_{\rm n}$  is given, if known.

Polymer	$\overline{M}_{\mathrm{n}}$	$\overline{M}_{\mathrm{w}}$	$\mathcal{D}_{\mathrm{M}}$	$\overline{M}_{n}(\mathbf{P}x)$	$\overline{X}_{n}(\mathbf{P}x)$	$\overline{M}_{n}(PB)$	$\overline{X}_{n}(PB)$
1,2-PB					Aldric	н РN466867	
PB-b-PS	22430	26170	1.167	8670	83	13760	254
PB-b-PEO	53790	5796	1.078	2728	62	2170	40
PB-b-P4VP	12290	15000	1.221		—		—
PAN		150000			Aldric	н РN181315	
				copolyme	er block	polybutad	iene block

## 4.0.3 Chemicals and solvents

**MPTMS:** (3-Mercaptopropyl)trimetoxysilane, also known as 3-(trimethoxysilyl)-1-propanethiol, were purchased from SIGMA-ALDRICH in 95% purity.

**Epoxy resin:** As matrix material two epoxy resins were selected. A cold-curing bisphenol A/F system by R&G COMPOSITE TECHNOLOGY GMBH consisting of *Epoxyharz L* (0.56 g eq<sup>-1</sup> epoxy equivalents) and *Härter S* (71 g eq<sup>-1</sup> H-equivalents aliphatic and cycloaliphatic amines). The mixture was prepared in a 10:4 ratio by mass of epoxy resin to curing agent. The resin was cured for 24 h at RT.

The alternative system *Momentum* 470-300 is a heat curing epoxy vinyl resin by DERAKANE. It consists of a novolac-based epoxy ester with a styrene content of 33 %, designed to provide exceptional mechanical properties at higher temperatures, while having high resistance to solvents and chemicals e.g. acidic oxidisers. The curing agent is *Trignox C*, a *tert*-butyl peroxybenzoate (>98 %), which serves as initiator for (co)polymerisation of styrene (and various unsaturated monomers). Since the decomposition of *tert*-butyl peroxybenzoate at RT is slow, the system only cures at elevated temperatures. With the information provided by DERAKANE, the half-life  $t_{1/2}$  and the decomposition rate constant  $k_{deposition}$  can be calculated by the ARRHENIUS equation (Eq. 4.1). For ambient conditions at RT, the system will not be cured within a reasonable timeframe. At 100 °C, the half-life is 10 h.

$$t_{1/2} = \frac{\ln 2}{k_{\text{deposition}}} \quad \text{with} \quad k_{\text{deposition}} = 2.23 \cdot 10^{16} \,\text{s}^{-1} \cdot \exp\left[-\frac{151.59 \,\text{kJ} \,\text{mol}^{-1}}{\text{R} \cdot T}\right] \quad (4.1)$$

**DI water:** Deionised water was provided by a *Milli-Q Advantage A10* water purification system by MILLIPORE with a pH of approximately 6.

**Additional chemicals and solvents:** Chemicals and solvents used for substrate cleaning and conditioning are presented in Table 4.2 with the respective purity. Table 4.3 shows purchased and distilled solvents.

Table 4.2: Chemicals used for substrate cleaning and conditioning.

Purchased chemicals		Purity	Vendor
Isopropyl alcohol		99.7%	ANALAR
Ammonium hydroxide	$\rm NH_4OH$	25%	Fluka
Hydrogen peroxide	$H_2O_2$	30%	VWR
Sulphuric acid	$\mathrm{H}_2\mathrm{SO}_4$	95%	Fluka
Hydrochloric acid	HCl	32%	Grüssing
	HCl	37%	Riedel-de Haën

Table 4.3: Purchased and distilled solvents.

Purchased solvents	Purity	Vendor	Distilled solvents		
Acetonitrile	MeCN	99.5~%	Merck	Cyclohexane	
Dimethyl sulfoxide	DMSO	99.99%	Aldrich	Dichloromethane	DCM
Ethyl alcohol	EtOH	absolute	J.T. Baker	Dimethyl formamide	DMF
Methyl alcohol	MeOH	absolute	Fluka	Tetrahydrofuran	THF
N-Methyl-2-pyrrolidone	NMP	99.8~%	Roth		
Tetrahydrofuran	THF	99.5~%	VWR		
Toluol		99.8~%	Aldrich		

## 4.1 Procedures

#### 4.1.1 General procedures for the cleaning of silicon oxide substrates

a) Piranha cleaning: The term piranha depicts a mixture of sulfuric acid and hydrogen peroxide (typically in a 3 to 1 ratio by volume), which can be used to remove organic residues off substrates. The addition of  $H_2SO_4$  to  $H_2O_2$  yields peroxomonosulfuric acid ( $H_2SO_5$ ) and water. The formation of the peroxo species is strongly exothermic yielding a seething oxidiser which hydroxylates most surfaces. Therefore not only organic matter can be removed but the surface will be rendered more hydrophilic. In the case of silica of silicon substrates, the number of silanol groups will be increased. Even though, one should mind the aggressive character of this method, which is a corrosive process and can in fact increase surface roughness. [27] Only freshly-prepared piranha solution has been used for the cleaning/activation. After immersion for 5 min the substrates were rinsed with DI water and dryed under nitrogen flow.

**b) RCA cleaning:** Kern et al. proposed a standard set of cleaning solutions (SC) based on hydrogen peroxide for use in silicon semiconductor technology (as part of his work at the RADIO CORPORATION of AMERICA). [28, 27] The original protocol consists of two aqueous hydrogen peroxide solutions with either ammonium hydroxide (SC1) or hydrochloric acid (SC2). SC1 is basically a weak basic piranha solution, capable to remove organic contaminants and cauterise the thin oxide layer on silicon. SC2 is usually applied to remove metallic contaminants. In this work, only SC1 is used for cleaning.

Prior to the RCA cleaning, substrates were immersed in an aqueous solution of isopropanol (75% by volume), sonicated for 15 min and rinsed with DI water. SC1 is performed with a 5:1:1 mixture (by volume) of DI water, hydrogen peroxide and ammonium hydroxide. After immersion at 70 °C for 10 min, substrates were removed from solution, rinsed with DI water and dried under nitrogen flow.

#### 4.1.2 General procedures for the grafting of the silane

a) Wet-chemical silvlation in solution: The substrates were placed in inert flasks. Distilled THF was added to each flask followed by the addition of MPTMS to create solution concentrations of 5% MPTMS by volume, then 0.4% HCl solution (37% by volume). Solutions were held at room temperature for 24 h. The siloxane-treated substrates were then removed from the solutions and subjected to a sequential washing regime: DCM, toluene, cyclohexane, acetone and again DCM. Siloxanes are known to be very soluble in these solvents; therefore, any weakly bound or physisorbed species are be removed by this procedure. Finally the substrates were dried at 70° C for 3 h.

**b)** Wet-chemical silulation of PDMS: The PDMS slices were rendered hydrophilic by immersion in aqueous HCL solution (10% by volume) for 24 h, dried under nitrogen flow and placed in inert flasks. The respective solvent was given to each flask followed by the addition of MPTMS to create solution concentrations of 5% MPTMS by volume, then 0.4% HCl solution (37% by volume). Solutions were held at room temperature for 24 h. The siloxane-treated substrates were then removed from the solutions and subjected to a sequential washing regime (see 4.1.2.a) Siloxanes are known to be very soluble in these solvents; therefore, any weakly bound or physisorbed species are removed by this procedure. Finally the substrates were dried under vacuum in a desiccator.

c) Wet-chemical silvlation by spin-coating: MPTMS was added to distilled THF to create solution concentrations of 50% MPTMS by volume, then HCL 37% was added (0.4% by volume). Solutions were spin-coated on the substrates with a speed of 3500 rpm during 60 s (to obtain thinner layers). To obtain a strongly bonded siloxane network the slides were subjected to drying at 150 °C for 3 h. The siloxane-treated substrates were then removed from the solutions, subjected to a sequential washing regime (see 4.1.2.a) and dried for 3 h at 75 °C.

**d)** Anhydous vapour silylation: The cleaned substrate was placed in a desiccator, together with a dish containing 2 ml of MPTMS. The sealed desiccator was put under vacuum for 24 h. The substrates were washed with THF and dried under nitrogen flow.

e) Hydothermal vapour silvlation of PDMS: The PDMS slices were rendered hydrophilic by immersion in aqueous HCL solution (10% by volume) for 24 h, dried under nitrogen flow and placed in a large dish. Two small dishes were added, containing 400  $\mu$ l DI water or 200  $\mu$ l MPTMS. The large dish was sealed with parafilm and heated to 90 °C for 12 h. The slices were rinsed with THF and dried under nitrogen flow.

#### 4.1.3 General procedure for the grafting of polymer: photoaddition

a) Glass slide/silicon wafer: The silvlated substrates were added to a approximately 4 weight % solution of reagent containing double bonds or nitriles in dry THF (freshly distilled from sodium alloy). The mixture was degassed twice, put under an argon atmosphere and exposed to UV light for 8 to 24 h. The polymer-grafted substrates were subjected to washing with THF and were then dried at  $65 \,^{\circ}$ C for 3 h.

**b) PDMS:** The silvlated PDMS was added to a approximately 4 weight % solution of reagent containing double bonds or nitriles in dry THF (freshly distilled from sodium alloy). The mixture was degassed twice, put under an argon atmosphere and exposed to UV light for 8 h. The polymer-grafted substrates were subjected to washing with THF and were then dried under vacuum in a desiccator (1 h).

## 4.2 Instruments

The following instruments were used for characterisation. Manufacturer and product names are indicated.

**Raman spectroscopy:** Spectra were acquired using a confocal Raman microscope (*CRM300*, WITEC, Germany) equipped with an objective from NIKON ( $100 \times$ , NA = 0.26) and a linear polarised laser (diode pumped green laser,  $\lambda = 532$  nm, CRYSTALASER). The Raman light was detected by a CCD camera (DV401-BV, ANDOR), behind a grating ( $600 \text{ g mm}^{-1}$ ) spectrometer (UHTS300, WITEC).

**Spectroscopic ellipsomety:** Thin films and substrates were characterised with a broad range (UV/VIS/NIR) spectroscopic ellipsometer (*SEresearch 850*, SENTECH INSTRUMENTS GMBH, Germany). The apparatus featured a motorised analyser (32 step scan) and goniometer (incidence angles from 40° to 95°). A super-achromatic compensator (retarder) enabled the determination of the ellipsometric angles in a range of 0° to 90° ( $\Psi$ ) and 0° to 360° ( $\Delta$ ). Incident light by a xenon arc lamp (OSRAM, Germany) with an emission of 350 to 800 nm was detected by a photometer with diode array (UV/VIS) upon reflection from the sample. The accurate sample alignment was accomplished via height and tilt adjustment by an auto collimating telescope. Data acquisition, modeling and fitting was done by the software *PModell* of *SpectraRay I*.

**Scanning force microscopy:** Topographic information were acquired by atomic force microscopy in tapping mode. Two SFM devices were used. The *NanoWizard 1* of JPK INSTRUMENTS AG was utilised using silicon cantilver *NSC15/AlBS* (MIKROMASH, Estonia) with characteristic resonant frequency of 265 to 400 kHz and a force constant of 20 to 75 N m<sup>-1</sup>. The *NanoScope IIIm Metrology* of VEECO METROLOGY GROUP was used for surface characterisation. The applied cantilevers were OLYMPUS micro cantilever *AC160TS* with a characteristic resonant frequency of 301 to 343 kHz and a force constant of 43 to 64 N m<sup>-1</sup>.

**Drop shape analysis:** Contact angles measurements were performed on a DATAPHYSICS *OCA* 20. The evaluation of the drop-profile was software-controlled. The sample table can be moved manually. Drops of liquid were place on the sample via a vertically mounted syringe. The dosage and placement of the liquid was performed manually.

**Infrared spectroscopy:** Spectra were acquired using an infrared microscope (*Tensor 27*, BRUKER) equipped with a transmission/absorption or attenuated total reflection stage. Vibrations were detected in the band of  $4\,000$  to  $400 \,\mathrm{cm}^{-1}$  with a resolution of  $1 \,\mathrm{cm}^{-1}$ .

**Optical microscopy:** For optical imaging a *Axiovert 200* of ZEISS was used.

**Scanning electron microscopy:** Micrographs were imaged using an analytical thermallyassisted field emission scanning electron microscope (*Leo1530*, ZEISS) with a SCHOTTKY-field emmision cathode. IN-LENS, BSE and SE detectors were applied.

**Preparation of glass fibres for SEM:** The fibre samples provided by J. PANDEY were transferred to conducting tape and mounted vertically to a sample holder. Before examination, samples were sputtered with platinum. The thickness of the coating was approximately 1 nm. This change of the surface topography, due to Pt-sputtering, is below the resolving capability of the scanning electron microscope. Platinum has been applied to enhance the conductivity of the sample surface, since non-conducting samples are otherwise easily charged up. Surface charges deny the imaging of precise surface structures.

# Chapter 5

## **Results and discussion**

## 5.0 Chemical approach

The modification is based on a two-step chemical approach developed by A. BERTIN: grafting of mercaptane and photo-addition of polymer. The modification corresponds to a *grafting-onto* mechanism. Grafting-onto denotes a coupling reaction in which a preformed species is covalently connected to a chemically modified surface. In a first step, active sites (initiation species) are introduced on the surface. Secondly a covalent bond is formed utilising the chemical nature of both active site and polymer. In this work olefin-polymers and a nitrile-polymer were grafted-onto surfaces exhibiting sulfhydryl-groups via a thiol-ene and an analogous postulated thiol-nitrile coupling reaction.

## 5.0.1 Model systems

Since the main task of this thesis is to improve the fibre-matrix interaction, the surface of fibreglass had to be modified and analysed. The geometric nature (curved surface, aspect ratio) of fibreglass denies or hinders the application of various methods typically used for surface characterizsation. Appropriate model surfaces can be found on silica (particles or flat substrate), silicon and poly(dimethylsiloxane). With only marginal differences in composition glass slides are most comparable to fibreglass. Silicon wafer exhibit a naturally grown silicon oxide layer. The thickness of SiO<sub>x</sub> typically ranges from 1.5 to 3 nm. Larger natural oxide layers can rarely be found since the growth (at ambient conditions) is diffusion controlled. PDMS is an inorganic polymer  $(Si(CH_3)_2O)_n$ . Upon addition of cross-linking agents and heat, it can be cured to form an elastomeric network. The surface properties depend on the orientation of methyl and silanol groups at the surfaces. The preparation can be found in Section 4.0.1 and 4.1.1. Three model systems have been used: glass slide, silicon wafer and PDMS elastomer slice. The surface modification by a two-step chemical approach is presented in the following.

#### 5.0.2 Silylation

Silane coupling agents are valuable tools to introduce active groups on silicon oxide surfaces. Initially, the silicon oxide surface exhibits silanol groups (in acidic) or silanolate groups (in basic condition), which can be adressed by silane coupling agents. The appropriate coupling agent contains two classes of functionality. A general formula reads as  $Y-(CH_2)_n-Si(R)_xX_{3-x}$ . Y is a nonhydrolysable organo-functionality that imparts desired characteristics (e. g. sulfhydryl). X is a hydrolysable group (alkoxy, acyloxy, halogen, amine), able to form an active silanol species. Monopodial agents have at most three hydrolaysable groups. They can be substituted by alkylgroups, decreasing the reactivity and cross-linkablility. The X-Y distance is set by an alkyl spacer. If the length of the linker is long, the functional group Y has greater mobility and can extend further from the substrate. Deposition can occur by two mechanisms depending on the nature of the agent and the water content, which will be discussed in the following.

**Deposition mechanisms:** Anhydrous deposition of silanes: at ideal water-free conditions the unstable alkoxy groups do only hydrolyse in the vicinity of the substrate surface. The suppressed hydrolysation inhibits the formation of oligomeric species (in the solution). An initial physical adsorption is succeeded by the covalent binding to the surface, initiated by heat. Usually only one bond is formed between each silane silicon atom and substrate. The remaining silanol groups are available for condensation. Thin layers, even monomolecular layers, should be obtainable. Water for hydrolysis can originate from several sources: adsorbed on surfaces (substrate or flask), not completely dry solvents or the atmosphere.[30]

The hydrolytic mechanism of silane deposition is presented in Figure 5.1. Four steps may be distinguished: hydrolysis, condensation, hydrogen bonding and bond formation. Due to the water content, initial hydrolysis not only takes place in the vicinity of the substrate surface



Figure 5.1: Mechanism of hydrolytic silane deposition in sequential order: hydrolysis of the methoxy groups (1); condensation to siloxane oligomers (2); hydrogen bonding of the siloxane to the silanol groups situated at the surface (3); and covalent bond formation with release of water (4). [29]

but in solution as well. Hydrolysed to silanol groups, the silane can undergo condensation forming oligomers. The degree of oligomerisation depends on the amount of water available. Precondensed oligomers non-covalently adsorb to the substrate by hydrogen bonding to hydroxyl groups. Final drying/curing establishes covalent linkage and concomitant loss of water. The hydrolytic deposition is presented as a sequential mechanism but condensation, adsorption and binding may occur simultaneously after hydrolysis. [30] In this work, silicon oxide surfaces have been silylated with (3-mercaptopropyl)trimetoxysilane to introduce sulfhydryl groups.

#### 5.0.3 UV-light induced thiol-ene/thiol-nitrile coupling

The grafting of polymers, done in this work, is based on photo-addition of polymers to sulfhydryl groups. The principle mechanism is a thiol-ene *click* reaction induced by either UV-light or heat. The heat-induced cross-linking reaction is the fundament of natural rubber vulcanisation. Both inductions initiate a radical reaction as presented in Figure 5.2. The result is a *anti-*MARKOWNIKOW-thioether. Thioethers exhibit high resistance to both acids and bases, as well as oxidising and reducing conditions. Since the radical addition is not limited to olefinic species other unsaturated functionalities should react in a similar mechanism. A postulated *thiol-nitrile* mechanism, based on the radical thiol-ene reaction, is presented in Figure 5.2. According to this mechanism nitriles yield S-alkyl-N-alkylenethiohydroxylamines. The thiol-ene coupling is insensitive to water and oxygen. [31]



Figure 5.2: Postulated photo-induced addition of olefin and nitrile to sulfhydryl species: sulfhydryls are transfered to radical species by UV radiation; these radicals add to olefinic groups, followed by a hydrogen-abstraction. A hydrogen-abstraction creates a new radical, continuing the reaction. The radical addition to nitrile groups is postulated in an analogous mechanism. [32]

For polymers with multiple unsaturated groups along the chain the addition is more complex. The UV radiation initiates the free radical reaction. [32] Polymer chains with unsaturated groups are attached to the thiolic-surface. The transferred radial can be passed on along the polymer chain to adjacent groups. In the case of vinyl functions, six-membered (major) or five-membered alkyl rings (minor product) can form. [33] Active surface-bound chains can bind to unsaturated groups of same chain or of chains in solution. As the reaction proceeds the amount of cross-linking increases and the former thiolic surface exhibits a covalently bound insoluble polymer-network.

#### 5.0.4 Polymers

Suitable polymers exhibit unsaturated functional groups. Poly(butadiene) is a polymer of 1,3butadiene monomers. Depending on the polymerisation conditions the monomers are linked via 1,2- or 1,4-addition. 1,2-Addition yields a free vinyl group along the polymer chain. The amount of 1,2-addition for the poly(butadiene) used in this work is approximately 62 mole %. Monomers linked by 1,4-addition yield olefins along the chain in either *cis*- or *trans*-configuration. Even though not all monomers are linked by 1,2-addition poly(butadiene) will be referred to as poly(1,2-butadiene) PB.

Poly(1,2-butadiene) blocks can be used in block-copolymers to attach polymers, which lack unsaturated groups. Block-copolymers used in this work are poly(1,2-butadiene-b-styrene), poly(1,2-butadiene-b-ethylene glycol), poly(1,2-butadiene-b-4-vinyl pyridine), Polystyrene PS blocks exhibit phenyl groups along the chain. Since many epoxy resins contain phenyl groups or are even based on styrene, a coating of PS is desirable. Poly(ethylene glycol) is a polymeric alkyl chain interspersed by ether functions. Due to the high content of oxygen PEO is more hydrophilic and even soluble in water. Poly(4-vinyl pyridine) P4VP resembles poly(styrene) but possesses a nitrogen atom in *para*-position to the phenyl groups. Depending on the protonation of the pyridine groups, P4VP can be tuned from hydrophobic to hydrophilic. P4VP is watersoluble at low pH. By variation of the copolymer block different properties like promoted adhesion can be introduced. In all cases the PB *anchor*-block is essential for the covalent binding to the thiolic surface.

Polyacrylonitrile (PAN) is a polymer with nitrile groups along the chain. Nitrile groups are very polar and are attracted to each other. The interaction of partial charges leads to a pronounced *inter*-chain stabilisation, which increases the density and strengthens the material. PAN is water-soluble.

PB and PAN are commercially available. The block-copolymers of PB were synthesised and provided by A. BERTIN. The characteristics of the polymers, used in this work, can be found in Table 4.1 in Section 4.0.2.

## 5.1 Structural analysis

Polymer-grafted substrates were expected to exhibit a homogeneous polymer layer. Ellipsometry is a commonly used method to characterise thin films and multilayer build-ups. Glass slides were used as a model system for fibreglass, due to their similar chemical composition. Transparent substrates, like glass, hinder the determination of thin film thickness. As preparatory work, a methodology to measure thin films thicknesses on transparent substrates has been elaborated using spectroscopic ellipsometry. This methodology is presented in the following (Section 5.1.0). With the information gathered by spectroscopic ellipsometry, an in-depth structural analysis was done using SFM topography. This analysis of the MPTMS treatment can be found in Section 5.1.1, followed by the presentation of the polymer layer (Section 5.1.2). The structural analysis comprises the presentation of the found structural features and a discussion of the mechanisms involved in the chemical treatments.

#### 5.1.0 Ellipsometry on transparent substrates

Spectroscopic ellipsometry is a fast, non-destructive method to evaluate the thickness of thin films. Fundamentally ellipsometry relies on the assumption of homogeneous isotropic layers with optical contrast. To retrieve accurate information like the top layer of a multi-layered system, many optical properties have to be known up front. For a system of a single layer on top of a substrate, the dispersion of the substrate has to known, or evaluated separately. The dispersion is the wavelength dependent refractive index (and absorption coefficient). Many materials are already characterised and provided by the manufacturer. Most commonly used substrates, like silicon, are implemented in the analysis software in the form of their respective dispersion models. The dispersion is an important physical property for spectroscopic ellipsometry since light of variable wavelengths is applied. Other ellipsometry implementations are restricted to a single wavelength, like *Nullellipsometry*. In this case not the dispersion, but only the optical properties at the respective wavelength have to be known. The result of a null-ellipsometric measurement is a single data point. The spectroscopic ellipsometry is capable of the simultaneous acquisition of ellipsometric data for a broad spectroscopic range. Since the dispersion of the substrate is indispensable but not provided by the manufacturer, it has to be determined discretely.

Dispersion of the substrate: The way of proceeding is based on the determination of the optical properties of the substrate. It is modeled as a *volume* material, independent of the substrate thickness. Ellipsometric angles are acquired by measurements at multiple angles of incidence and at different spots on the material. Fitting the proposed model (single layer with an ambient air phase of n = 1) to the ellipsometric data yields the optical properties (including the dispersion) of the substrate. The determination of the dispersion is not always a straightforward experiment. In the case of transparent materials the determination is hindered by the occurrence of back-side reflections. The phenomenon of back-surface reflections has to be considered if the absorption k of the material is small. For  $k \to 0$  the depth of penetration increases proportionally (see Eq. 3.19). Light reflected at the back-side material surface contributes to the top-side reflection. Since both reflections are not coherent, the analysis yields inaccurate or false values depending on the amount of backscatter. To be able to evaluate the layer thickness of thin films on glass, methods to reduce or eliminate the back-surface reflections were applied and compared. Additionally the use of a retarder in the optical setup of the spectroscopic ellipsometer was studied.



Figure 5.3: The effect of a retarder on ellipsometric angles for a glass substrate: amplitude (left) and phase (right) are distinctly affected by the use of a retarder in the setup. On transparent substrates the main information is retrieved from the amplitude signal  $(\Psi(\lambda))$ . Transparent samples should ideally yield a phase close to or of zero ( $\Delta = 0$ ). A retarder reduces the scatter of the phase signal  $\Delta(\lambda)$ . Both amplitude and phase of the blackened substrate deviate strongly, which is caused by the imbalanced adsorption of the black tint.

**Back-surface reflections:** The ellipsometric data of glass substrates was acquired to evaluate optical properties. An untreated sample was compared to substrates, either roughened by sandpaper, blackened with a marker, or both. The influence of a retarder is presented in Figure 5.3 for an incidence angle of  $65^{\circ}$ . Different angles of incidence (in the range of  $40^{\circ}$  to  $80^{\circ}$ ) were evaluated and show the same effects. Before the comparison of the two methods to reduce back-surface reflections, the effect of a retarder in the ellipsometric setup is presented and discussed.

Linear versus circular polarised light: A retarder is an optional optical component which can be used in the experiment. Since the primary output of the measurement are the ellipsometric angles  $\Psi$  and  $\Delta$ , the effect of the retarder can be seen in their wavelength dependency. The ellipsometric angles describe the ratio of transmission: with  $\Psi$  as amplitude and  $\Delta$  as phase. Figure 5.4 shows the ellipsometric data acquired with and without a retarder in the setup. Both amplitude  $\Psi(\lambda)$  and phase  $\Delta(\lambda)$  are influenced by the presence of the retarder. The most pronounced influence can be found in the phase signal. The data acquired without retarder exhibits more scatter over the whole spectral range. The phase signal measured with retarder is not only less scattered, but also closer to 0°. Since glass is transparent, the phase should ideally be zero. A retarder distinctly improves the quality of the acquired ellipsomeric data set. Inaccuracies captured in the data acquisition impair the results of the data evaluation. The effect of the retarder is the retardation of light: linearly polarised light, leaving the polariser, becomes circular polarised due to a phase shift. This phase shift is induced by the optical element of the retarder. The (ellipsometric) phase of linear polarised light ranges from 0° to 180°. Circular polarised light causes (ellipsometric) phase changes in the range of 0° to



Figure 5.4: Comparison of ellipsometric angles for methods to the elyiminate back-surface reflections: ellipsometric angles are shown for glass substrates, which have either been blackened, roughend or both. Both amplitude and phase of treated glass substrates clearly deviate from untreated ones. By way of comparison, the amplitude of a roughened substrate measured without retarder is indicated to present the effectivity of roughening to reduce back-surface reflections.

360°. In this respect measurements on glass with retarder are more precise. Circular is the preferable polarisation state for ellipsometric measurements on glass. In the following, methods to eliminate back-surface reflections are compared and discussed.

Elimination of back-surface reflections: Figure 5.4 shows ellipsometric data (of Figure 5.3) acquired with a compensating retarder. The effectiveness of the applied methods to reduce back-surface reflections can be compared. Back-surface reflections cause a non-comprehensible shift in the amplitude. The shift is caused by the contribution of incoherent light. It is expected that  $\Psi(\lambda)$  and  $\Delta(\lambda)$  acquired on an untreated glass slide are affected by this shift. Both blackening and roughening change  $\Psi(\lambda)$  and  $\Delta(\lambda)$ . Comparing the data of the treated and untreated glass slides, distinct shifts can be seen in the plots. Amplitude shift and phase shift have to be distinguished: the shift to lower angles is almost equidistant over the whole spectrum. This is comprehensible since the amplitude is dependent on the light intensity. With less light reaching the detector the amplitude signal is set to lower wavelength. This loss of intensity in not compromising the measurement since the light lost originated from the back-surface. The phase shift is indicating an improvement in the acquired data set, similar to the effect of the retarder.

In this respect both blackening and roughening effectively reduce or eliminate back-surface reflections. A combination of both yields similar ellipsometric data ( $\Psi(\lambda)$  and  $\Delta(\lambda)$ ) as the individual treatments. Roughening is an invasive method, which takes a considerable amount of preparation time. In comparison, blackening is not-invasive and the tint can be removed by rinsing with appropriate solvents. The application of black tint is easy and fast: in this work the black tint was sprayed on by nitrogen flow. Spraying is favorable to manual painting, since the result is more even and opaque. Even though blackening is not appropriate if the measurement is performed without retarder. This effect can be seen in Figure 5.3. Both amplitude and phase of the blackened sample measured without retarder exhibit deviations from the expected plot in the range of 500 to 800 nm. Concludingly, both methods are effective for reducing the amount of back-surface reflections. A combination of roughening and blackening is most favourable. For sensitive substrates, blackening itself is a quick modification that can be applied for measurement and removed afterwards.

**Glass substrate:** The dispersion of glass slides was determined of samples both blackened and roughened. A retarder was used for measurement. The ellipsometric data was evaluated for a CAUCHY *volume* material model (see Eq. 3.18). The dispersion of the glass is fitted to

$$n(\lambda) = 1.5425 + 10^2 \cdot \frac{-1.232}{\lambda^2} + 10^7 \cdot \frac{84.43}{\lambda^4} \quad \text{and} \quad k(\lambda) = 0$$
 (5.1)

with MSE below 0.003. The MSE is a figure of merit. If theoretical and experimental values are identical the MSE is 0. The refractive index at 546 nm is  $1.522 \pm 0.003$ . A small deviation is caused by the assumption  $k(\lambda) = 0$ . Therefore the theoretical phase  $\Delta(\lambda)$  is set to zero and cannot be fitted to the experimental phase. The deviation is minimal and does not compromise the evaluation.

**Polymer layer:** With the knowledge of the substrate dispersion and the methodology to eliminate back-surface reflections more complex samples can be evaluated. Polymer-grafted glass substrates, provided by A. BERTIN were evaluated by spectroscopic ellipsometry. The task was to determine the thickness of the grafted polymer layer.

The ellipsometric evaluation yielded unreasonable data with high deviations in the fitting process ( $MSE \gg 1000$ ). The consistency of the substrate model was checked with model samples prepared by layer-by-layer technique. The 80 nm thick polyelectrolyte multilayer on glass yielded reasonable thicknesses compared with silicon based samples.

From the failure of the ellipsometric analysis, it has been concluded that the polymer-grafted glass samples do not exhibit a homogenous isotropic layer system. Therefore the samples were analysed by SFM topography. The analysis of the MPTMS treatment can be found in the following section. The structural features of the polymer layer can be found in Section 5.1.2.

#### 5.1.1 MPTMS treatment

Silicon oxide substrates were treated with MPTMS as described in Section 4.1.2 to introduce sulfhydyls on the surface. The success of the treatment was reviewed by contact angle measurements. The surface state was evaluated using SFM tropography.

A common feature, identified on all samples and independent of the way of deposition and substrate, is a grainy surface structure. Figure 5.5 presents this granular structure. The sur-



Figure 5.5: SFM topography of glass substrates coated with MPTMS by wet-chemical deposition: homogeneous distribution of siloxane islands. Image **b** is a magnification of the area indicated in **a**.



Figure 5.6: SFM topography of substrates spin-coated with MPTMS: homogeneous distribution of the granular siloxane structure. Images **b** refers to the area indicated in **a**.



Figure 5.7: SFM topography of glass substrates coated with MPTMS by wet-chemical deposition. The images show stripes of siloxane-islands on the surface. The border of such a stripe in image **a** is magnified in **b**. Image **c** shows the zoomed area indicated in **b**.

face is covered with grain-like structures in the range of 5 to 20 nm in height. Apart from some larger deposited material, the grains are equally sized and distributed. The surface is condensed with siloxane-structures. Substrates with MPTMS deposited by spin-coating exhibit inhomogeneous areas. Even though, in between, the granular surface described before can be found. Figure 5.6 shows the granular structure. The granular structure can become mechanically damaged. Figure 5.7 presents a stripe-like surface coverage. The defects may either be induced from mechanical force or a result of less activated or even passivated surface domains. Mechanical removal can be caused by handling of the substrates after the treatment or before and during the characterisation. A magnified inspection suggests that only the large grains are removed leaving a residual coating of only few nanometres.

The formation of the granular structure developed under wet-chemical deposition of MPTMS is discussed in the following. Two mechanisms are presented: island growth and self-aggregation.

(3-Mercaptopropyl)trimethoxysilane: MPTMS is a frequently used silane coupling agent for coatings on silicon oxide or gold surfaces. With three hydrolysable methoxy groups, coating result in densely condensed layers. The sulfhydryl group in  $\gamma$ -position of the propyl linker has only little mobility, but may interact with its own silanol groups by hydrogen bonding. Methoxy groups are unstable and rapidly hydrolyse forming a highly reactive intermediate silanol species. Silanols condense with other silanols or with alkoxysilanes to siloxanes upon release of water. This water is catalysing the reaction by promoting hydrolysis. Allara et al. [34] found that proper substrate hydration is a prequisite for deposition, a thin water film of 1 to 1.5 nm serves as a reservoir for the hydrolysis of organosilane molecules. Theoretically, a fully activated (100) orientied silicon wafer exhibit  $5 \times 10^{14}$  silanol groups per cm<sup>2</sup>. [35] In aqueous systems MPTMS is unstable: apolar solutions turn cloudy upon aging due to polymerisation. Alkoxysilanes inherently exhibit a poor solubility in water.

**Island formation and growth:** The treatment was performed in tetrahydrofuran. THF is a polar aprotic solvent which solves MPTMS very well. The formation of a granular surface structure can result from different mechanisms influencing the deposition. One aspect is the patchy growth of the siloxane-domains deposited on the surface. Upon the assumption that no preformed aggregated species are present the grainy structure can be the result of the deposition of MPTMS domains and their growth. Since the solvent is distilled and the amount of water in the solution is minimal hydrolysis of the MPTMS molecule occurs in the vicinity of the physisorbed water layer on the substrate. As described in Section 5.0.2, a reactive silanol species is adsorbed to the surface and eventually bonds covalently. On each surface-bound MPTMS molecule two free silanol groups remain. In ideal conception, these groups only react in a lateral polymerisation with other surface-bound molecules. Loosely associated or even silanol-species from solution can condense with surface-bound MPTMS molecules. Since the polymerisation is not restricted to lateral growth, larger associated siloxane-structures can form and partly condense. The physisorbed water layer has a catalysing effect for the initial hydrolysis.

The spread of the deposited MPTMS is often described as *island growth*. The fundamental deposition of MPTMS from solution is not independent from the already surface-bound or associated molecules. It is possible that MPTMS preferable adsorbs in the vicinity of already existing MPTMS domains. These domains are referred to as *islands* which grow over time. Tight packings and extensive coverage demand long reaction times (e.g. 24 h). This mechanism has been reported by Yang et al. [35] in a comparative study of the growth of octadecyltrichlorosilane and (3-mercaptopropyl)trimethoxysilane self-assembled monolayers on hydrophilic silicon surfaces. The siloxane domains are small round non-dendritic islands, which adsorb in principle sporadically and in isolation. The average island size is expected to increase simultaneously over time, reflecting an OSTWALD ripening mechanism, inculding an exchange of the adsorped islands. [36] It is postulated that the growth and morphology of the islands depend on the alkyl chain length. In fact, since MPTMS has a polar sulfhydryl group, adsorbed molecules have several possibilities to interact with other molecules and surface groups. Sulfhydryls associate to free silanols by hydrogen-bonding. This can be Si-OH groups situated on the surface. In this case, these silanol groups would be inaccessible, thus disturbing the adsorption and hindering uniform growth. Another aspect is that sulfhydryls actively contribute to the association of free silanols from solution and thus promote aggregation. It cannot be expected that sulfhydryl groups condense with silanol groups since oxygen possesses a higher electronegativity than sulfur. Condensation reactions of thiols and hydroxyl groups demand strong acidic conditions, which are not present in the regarded system. Pasternack et al. [37] suggest to perform the wetchemical deposition at elevated temperature (e.g. above 70 °C). The deposition in this work was performed at RT. Increasing the temperature not only reduces the physisorbed water layer but disturbs the association of MPTMS to larger structures apart from the surface. Elevated temperatures strengthen and densify the siloxane layer.

**Self-aggregation in solution:** Apart from the island growth phenomena, a granular structure can result from self-aggregated preformed siloxanes in the solution. Aqueous hydrogen chloride was added to the MPTMS solution to catalyse the deposition. Water and acidic conditions, both, support the hydrolysis of MPTMS in solution. Hydrolysis yields reactive silanols and favours self-aggregation. Since aggregation is associated with the release of water, even small amounts of water available in solution can result in extended siloxane structures. As mentioned before the sulfhydryl group promotes the association of MPTMS molecules. Siloxane polymers eventually adsorb and bind to the surface. As reported before by Luginbühl et al. [38], the residual water adsorbed on the suface is not the reaction speed limiting factor. Self-aggregated species can deposit onto both the free surface and the already silylated domains. There is a tendency to bind to surface defects like scratches. Kumar et al. [39] suggested that there is no influence on the growth of the monolayer by the formation of these *particulates*.

**Granular structure:** A single valid mechanism cannot be discriminated. Most likely the formation of the granular surface state is a combination of both island growth and self-aggregation in solution. The adsorbed MPTMS are interconnected through a loose network. The formation of covalent bonds posses a certain amount of reversability: At curing, by heating (as done in this work for 3 h at 70 °C) or evacuation, bonds may form, brake, and reform to release internal stress. The found structure can be described as grainy structures of deviating heights with an underlying inhomogeneous polylayer of siloxanes. Generally a silylation depends on solvent, reaction temperature, precursor concentration, solution age (time between solution preparation and immersion of the substrate, aging) and water content. In the following different deposition techniques are discussed and compared to the protocol used in this work.

**Deposition techniques:** Various deposition techniques like wet-chemical deposition from aqueous alcohol solution, aqueous solution, anhydrous phase, hydrothermal/anhydrous vapour-phase, spin-coating and spray deposition are known and reported in literature. The least time consuming method is wet-chemical deposition: water or aqueous alcohol enable fast deposition of polylayers. Monolayer deposition can be achieved by aprotic anhydrous conditions. A mono-layer is desirable because it represents a thin homogeneous film, which facilitates and rectifies many characterisation methods like SFM adhesion or contact angle measurements. A lot can be learned from monolayer protocols.

**MPTMS monolayer:** The theoretical thickness of a self-assembled thiol-terminated MPTMS monolayer is approximately 0.7 nm. Literature features various protocols to produce monomolecular thin MPTMS layers on silicon oxide. Fundamentally two techniques can be distinguished: wet-chemical or vapour-phase deposition. A comparative overview of monolayer yielding protocols can be found in Table 5.1. Even though the protocols seem to be quite different from each other, each incorporates distinct features (mostly reducing the content of water) to produce monolayers: Semaltianor et al. predries samples by heat and vacuum before vapour-deposition of pure MPTMS. [40] The method of Ledung et al. is hydrothermal vapourphase deposition. MPTMS and water are placed in individual teffon dishes. Sample and dishes are sealed in a large dish and heated. [41] Park et al. use UV/ozone treatment to activate the surface. The deposition is performed in an alcoholic solution. [42] According to Liu et al. the addition of anhydrous MgSO<sub>4</sub> is effectively reducing the amount of water in the system. There was no need to use distilled solvent (toluene). [43]

In conclusion, one way to reduce the heterogeniety is the deposition technique: vapour-phase deposition is suggested instead of wet-chemical deposition, since in vapour phase the formation of siloxane aggregates is hindered. Even though the substrates are preferably conditioned to exhibit a thinner physisorbed water layer. If wet-chemical deposition is applied, the concentration of MPTMS should be reduced and no additional hydrogen chloride should be added. Both should reduce the amount of self-aggregation in the solution. Hygroscopic additives like

Ί	Table $5.1$ :	Overview	r of vap	pour-phase	(VD) as	nd wet-	chemical	deposition	(WET)	of MPT	MS.
	Protocol	s from lite	erature	, yielding n	nonomol	ecular l	ayers, coi	mpared to a	pplied si	ilylation	pro-
	tocol by	A. Bert	IN.								

Ref.	Cleaning	Deposition	Curing
[40]	Piranha, predried for $1.5 \text{ h}/70^{\circ} \text{ C}/0.1 \text{ mBar}$	VD: $4 h/100^{\circ} C$ , MPTMS	$2\mathrm{h}/100^\circ\mathrm{C}$
[41]	Piranha, $1 \min N_2$ dried	VD: $100 \mu\text{L} \text{ H}_2\text{O}/50 \mu\text{L} \text{ MPTMS}$ in PTFE dish, $1.5 \text{h}/90^\circ \text{C}$	no
[42]	RCA, UV	WET: $1 \text{ mM MPTMS/EtOH}$ + AcOH, $1 \text{ h/RT}$	no
[43]	Piranha, RCA, piranha	WET: $30 \text{ mM MPTMS/toluene}$ + MgSO <sub>4</sub> in PTFE, $1 \text{ h/RT}$ in N <sub>2</sub>	no
[44]	_	WET: $54 \mathrm{mM}$ MPTMS/toluene, $1 \mathrm{h}/60^{\circ}\mathrm{C}$	$10\mathrm{min}/60^{\circ}\mathrm{C}$
MPI	Piranha	WET: $270 \text{ mM}$ MPTMS/distilled THF + $0.4 \text{ vol}\%$ HCl in glass, $24 \text{ h/RT}$	$3\mathrm{h}/70^\circ\mathrm{C}$

magnesium sulfate can be utilised to reduce the amount of water in solution. A substitution of MPTMS by a sulfhydryl silane coupling agent with only one hydrolysable group, would prevent condensation of self-aggregated siloxanes. This will be tested in future work.

#### 5.1.2 Polymer grafting

Polymers were grafted-onto thiolic silicon oxide substrates following the protocol presented in Section 4.1.3.a. The samples were evaluated using contact angle measurement and SFM topography. In the following, PB-based polymers are reviewed first. PAN is presented subsequently.

**PB-based polymer grafting:** Analogous to MPMTS, granular surface structures are present but with increased grain heights. PB-grafted surfaces exhibit grain-like structure with 150 to 300 nm in height. Similar loosely-packed grainy structures can be found on PB-*b*-PEO grafted samples, presented in Figure 5.8. PB- and PB-*b*-P4V-grafted substrates show domains with a tight packing of material resembling a film-like coating. Figure 5.9 illustrates this feature. The coating is dispersed with defects, either hole-like or in from of scratches. These can be a result of mechanical wear. The thickness was determined in reference to the defect depth to be 25 to 50 nm. More precise values cannot be reported due to the heterogeneity of the surface.

The surface of PB-*b*-PS has grains of various heights, ranging from 10 to 80 nm depending on the evaluated surface area. Apart from this high variability PB-*b*-PS coated surfaces possess drop-like structures. Both round (intact) and brim-shaped (damaged and/or partly removed) droplets can be found (see Figure 5.10). The latter can result from mechanical wear acted on the sample by the grafting process, washing, or characterisation, which affects the sample. The sizes range from 100 nm to  $3 \,\mu$ m in diameter. The area inbetween these drop-like structures is governed by the granular surface state described before.



Figure 5.8: SFM topography of silicon oxide substrates grafted with poly(1,2-butadiene) **a** and poly(1,2-butadiene-b-ethylene glycol) **b**. Both images exhibit a granular surface. The grains in image **a** are several hundred nm in height.



Figure 5.9: SFM topography of silicon oxide substrates grafted with poly(1,2-butadiene) **a b** and poly(1,2-butadiene-b-4-vinyl pyridine) **c d**. Images **a** and **c** show an overview of defected film-like structures. Image **b** is a magnification of the area indicated in **a**. Image **d** presents the area marked in **c**. Images **b** and **d** are of the same size and scale for better comparison.



Figure 5.10: SFM topography of silicon oxide substrates grafted with poly(1,2-butadiene-b-styrene): brim-shaped droplet-remains **a** with an in-between granular area magnified in **b**. Images **c** and **d** show round droplet-structures. Image **d** refers to the area indicated in **c**.



Figure 5.11: SFM topography of silicon substrates grafted with poly(1,2-butadiene-b-ethylene glycol): coated domains of wrinkled/crumpled surface states. Image **c** is magnified in **d**.

PB-*b*-PEO exhibits extended domains of elongated drop-like structures. The shapeless domains govern serveral micrometres of surface area. Their surface is either smooth or wrinkled. The folded and crumpled domains feature various *zig-zag* structures, as presented in Figure 5.11. It cannot be said whether the wrinkling is induced by the preparation itself or the post-preparational drying. The evaporation of residual solvent at elevated temperatures can force a stretching of the polymer material. Upon release of stress buckling can yield wrinkled structures. This feature has only been found for PB-*b*-PEO grafted substrates. It is expected that the combination of the polar PEO block with the multiply cross-linked PB yields a flexible film.

**PB-based polymer coating mechnism:** A fundamental surface grafting approach consists of a active sites, confined to the surface, and reactive sites located on the grafting-species. If the grafting-species only exhibits a single reactive group (e.g. terminal), the coupling is a closed reaction step. The respective active site is consumed upon coupling of the grafting-species. Therefore each grafting-step is individual and spatially separated.

The grafting of PB-based polymers is based on the thiol-ene coupling reaction. PB exhibits several olefinic groups along the chain. The vinyl function (reactive group) is suited to undergo a coupling reaction with mercaptan radicals (active site). The active site is not confined to the surface. The radical can be transferred to the chain what enables the cross-linking of chains. Mechanistically, a reactive groups is converted to a new active site after reaction. The coupling is a continuous process involving several vinyl functions. The plurality of reactive groups is enhancing the accessibility of the surface. Each polymer chain can be covalently connected to the thiolic surface via multiple binding sites. In addition, the cross-linking of polymer chains forms a insoluble network. The photoaddition of polymer was performed upon UV radiation for 24 h. The continuous generation of active sites (mercaptan radicals) is a beneficial factor that can cause a identification of the covalently bound network. New radical at the surface can react with already coupled chain and thus be translocated away from the surface. Even if the surface is not accessible for further polymer chains, the translocation of radicals improves their accessibility. Translocated radicals can react with polymers in solution or vinyl groups situated in their vicinity. This process can lead to a densification due to more cross-linking points in the grafted film. Furthermore the modulus of the grafted film is increasing upon densification.

In this respect the PB creates a dense network without functional groups. The combination of functional polymer-blocks with an PB-*anchor*-block enables a high variability of modifications. Upon decreasing the amount of vinyl functions the density of the grafted structure decreases as well.

**PAN grafting:** Poly(acrylonitrile) is reviewed separately, since the grafting-onto mechanism is not a thiol-ene coupling as in the case of PB-based polymers. The reaction of nitriles with sulfhydryls is postulated to be analogous to olefins.

Two main structural features can be found for PAN-grafted surfaces: densely-packed grains (Figure 5.12) and crumpled droplets (Figure 5.13). The granular structures can easily be scratched mechanically. The material can be removed or agglomerated. The drop-like structures found on the surface exhibit a crumpled surface. The structures show a segmentation, which can result from a collapsed hollow shell. In the following the mechanism of PAN-grafting is discussed.



Figure 5.12: SFM topography of silicon substrates grafted with polyacrylonitrile: granular surface state and homogeneous coverage. The structure in **a** exhibits defects, where material has been removed or agglomerated. Image **b** is densely-packed granular structure.



Figure 5.13: SFM topography of glass substrates grafted with polyacrylonitrile: image **a** exhibits structures resembling crumpled drops. Image **b** is a magnification of the area indicated in **a**.

**PAN coating mechanism:** The presented structures demand a review of the postulated grafting-mechanism. The coated structure is either densely packed to a granular film or condensed to a crumpled drop-like structures: the PAN was believed to form a covalent bond to the thiolic surface. Since the deposited layers can be removed from the substrate with ease, PAN may only be adsorbed to the surface. Several aspects favour this assumption.

PAN is synthesised by a radical polymerisation of acrylonitrile. Since the chain growth only proceeds by reaction of vinyl functions, the nitrile groups can be regarded as mostly inert to radical attacks. Apart from a radical-guided mechanism, nitriles are known to react with hydroxyl groups (alcohols) forming an imino ester or an alkyl imidate. This PINNER reaction demands acidic catalysis to activate the nitrile for a nucleophilic attack by the hydroxyl. The conditions of the grafting done in this work are not appropriate for such a reaction of nitrile and thiol. Even if no covalent bond is formed, PAN could adhere to the surface by adsorption. Nitrile groups are polar and preferably interact with each other or through hydrogen-bonding. The MPTMS-treated substrates exhibit sulfhydryl groups with a physisorbed thin-film of water. In the vicinity of the surface PAN molecules can adsorb. Surface-adsorbed chains can interact with PAN molecules from solution forming agglomerated structures.

The formation of crumpled droplet-like structures can be explained by consideration of the solubility. PAN is hydrophilic due to the polar nitrile groups. PAN exhibits a poor solubility in THF. It can be expected that PAN molecules preferably self-agglomerate in solution. Eventually PAN agglomerates adsorb to the surface. A dewetting process, caused by elevated temperatures at curing or increased interaction of nitriles to each other, can yield drop-like structures.

## 5.2 Chemical composition analysis

The chemical composition of the substrate surface can be helpful to understand and judge the success of a surface modification. MPTMS treatment was applied to introduce sulfhydryl groups to the surface. Vibrational spectroscopy offers valuable methods for the detection of functional groups. Sulfhydryls have characteristic signals in the band of 2500 to  $2600 \text{ cm}^{-1}$ . This interval is free of other functional group signals and therefore very indicative for S-H bondings. It has been attempted to proove the presence of free sulfhydryl groups on the MPTMS-treated samples with infrared and RAMAN spectroscopy.

**PDMS**; MPTMS-treated PDMS slices were evaluated by RAMAN spectroscopy. Two weak vibrations were detected in the characteristic band:  $2504 \text{ cm}^{-1}$  and  $2576 \text{ cm}^{-1}$ . Figure 5.14 presents a RAMAN-spectrum of a MPTMS treated PDMS slice. Li et al. identified the  $2576 \text{ cm}^{-1}$  as the free S-H stretch vibration, in a study of thiol additions of silane coupling agents. [32, 45] The  $2504 \text{ cm}^{-1}$  signal can be assigned as a S-H stretch vibration as well. The shift may be caused by the interaction of the sulfhydryl hydrogen with other functional groups e.g. hydrogen



Figure 5.14: RAMAN spectrum of MPTMS treated PDMS: two signals were detected in the band characteristic for sulfhydryls. The following spectral frequencies (cm<sup>-1</sup>) were identified: 186  $\delta/\rho/w(\text{CSiC})$ , 491  $\nu_{s}(\text{SiO})$ , 712  $\nu_{s}(\text{CSiC})$ , 793  $\nu_{a}(\text{CSiC})$ , 863  $\rho(\text{CH}_{3})/T(\text{CH}_{2})$ , 1266  $\delta_{s}(\text{CH}_{3})$ , 1415  $\delta_{a+s}(\text{CH}_{3})$ , 2504  $\nu(\text{SH})$ , 2576  $\nu(\text{SH})$ , 2908  $\nu_{a}(\text{CH}_{3})/\nu_{a}(\text{CH}_{2})$ , 2965  $\nu_{a}(\text{CH}_{3})$  with asymmetric  $\nu_{a}$  and symmetric stretch  $\nu_{s}$ , plane bend  $\delta$ , rocking  $\rho$ , wagging w, twisting T and out of plane bending vibration  $\gamma$ .

bonding to silanol groups. Strong hydrogen bonding reduces the vibrational frequency of the respective group. [46] The presence of two vibrational species of sulfhydryl groups after MPTMS treatment of silicon oxide has been reported by Finocchio et al. [47] in a FT-IR study. They detected a  $2540 \text{ cm}^{-1}$  signal (apart from a  $2581 \text{ cm}^{-1}$  vibration of MPTMS adsorbed on silica in contact with vapour) suggesting that some MPTMS molecules are involved in hydrogen-bonding, possibly with silanol groups situated in their vicinity.

PDMS is an ideal substrate for the evaluation of the MPTMS treatment, since it contains silanol groups at the surface and inside the material. In polar solvents like THF, PDMS swells and increases its surface. Silanol groups in the material can react with MPTMS, yielding a higher concentration of sulfhydryls compared to rigid non-porous materials. Even though, acquired infrared spectra do not show the expected signal in the characteristic band.

**Silicon oxide substrates:** On rigid silicon and glass samples no signals were found in the characteristic vibration band. The detection is hindered by the small concentration of sulfhy-dryls in the excitation volume. Both spectroscopic methods rely on the number density of the

functional group to be detected. Even long integration times (FT-IR: 12 h, FT-Raman 45 min) did not produce adequate results. In literature thiolic substrates were evaluated by infrared and RAMAN spectroscopy under vacuum or inert gas atmosphere. [32, 45, 47] The absence of air facilitates the spectroscopic evaluation.

## 5.3 Wettability analysis

The adhesion of fibre-matrix, or in detail the fibre-polymer-matrix, is essential for the mechanical synergy of the composite. Adhesion is closely related to the wettability of the surface. [13] The wettability of the five polymer-coatings has been investigated by drop shape analysis. The measurement of the macroscopic contact angle grants information about the hydrophilicity and homogeneity of the polymeric and thiolic surface.

**Thiolic substrates:** The MPTMS-treated surfaces have been investigated by drop shape analysis to evaluate the homogeneity after surface modification. Therefore a minimum of 49 sessile drops were placed onto the sample. This has been repeated three times for four MPTMS-treated glass-slides. Figure 5.15 presents the wettability of the evaluated samples mapped with a uniform scale.

The representation of each slide deviates from one another. A small deviation in the wettabitlity maps of a single sample can be expected from the measurement error, e.g. variations of the drop placement or evaluation of the drop profile. More pronounced deviation (larger than 5°) relate from inhomogeneities and different wettabilities. Two substrates (**a**,**c**) exhibit a mean contact angle larger than 85° with a standard deviation of 8°. The other two substrates (**b**,**d**) show a reduced wettability with a mean contact angle of less than 75°, but with a smaller standard deviation of 6°. These values rely on a minimum of 147 evaluated sessile drops. There is a difference of more than  $10^{\circ}$  between the single samples, caused by inhomogeneities. This indicates that the surface treatment with MPTMS has not modified the surfaces in a uniform manner. Each surface exhibits areas of variable wettability. Samples of homogeneous modification should yield standard deviations of less than 5°. Literature features contact angles, determined on MPTMS-monolayers, of  $71^{\circ} \pm 1^{\circ}$  [43] and  $71^{\circ} \pm 3^{\circ}$  [48]. This is in good correspondence with samples **b** and **d**. Samples **a** and **c** exhibit a considerably higher mean contact angle and higher wettability deviations on the surface, up to single contact angles of  $110^{\circ}$ . Increased contact angle can result from contaminants, increased surface roughness and other defects. The effect of surface roughness has to be specified. The roughness can be described as the ratio of the true local surface area to the projected area. WENZEL defined the relation of the apparent to the true contact angle for rough surfaces (see Eq. 5.2).

$$\cos \theta_{\text{apparent}} = r \cdot \cos \theta_{\text{true}} \quad \text{with} \quad r = \frac{\mathcal{A}_{\text{true}}}{\mathcal{A}_{\text{projected}}}$$
(5.2)



Figure 5.15: Mapped contact angles of water on MPTMS-treated glass slides: four substrates were mapped by  $7 \times 7$  (**a**,**b**) or  $8 \times 7$  drops (**c**,**d**). Each substrate has been measured three times, to present the wettability. A homogeneous coated surface should yield minimal deviations of wettability. The mean contact angle is  $89.9^{\circ} \pm 7.5^{\circ}$  **a**,  $74.2^{\circ} \pm 5.5^{\circ}$  **b**,  $85.4^{\circ} \pm 7.7^{\circ}$  **c** and  $68.8^{\circ} \pm 5.5^{\circ}$  for the substrate **d**.

According to this Eq. 5.2, the roughness of the surface further decreases the contact angle for  $\theta_{\rm true} < 90^{\circ}$ , whereas the roughness further increases the contact angle for  $\theta_{\rm true} > 90^{\circ}$ .

**Polymer-grafted substrates:** Concerning the polymer-coating, the wettability introduced by the different polymers is of most interest. A minimum of 30 sessile drops per sample were evaluated to obtain a mean contact angle  $\langle \theta \rangle \pm SD(\theta)$ . An overview of the evaluated contact angles can be found in Table 5.2.

The contact angle of polymer-grafted surface are consistent for glass and silicon substrates. PB-*b*-P4VP exhibits the highest contact angle of  $103 \circ \pm 3 \circ$ . Quite contrary PB-*b*-PEO shows the lowest contact angle. This is comprehensible since the poly(ethylene gylcol) block has a pronounced hydrophilicity. PB-*b*-PS, PAN and PB show moderate wettability of water. Samples with high standard deviations are expected to have more inhomogeneous surfaces than samples with minor deviations. Since these three polymers exhibit contact angles around 90°, the influence of surface roughness can be quite diverse (as predicted by Eq. 5.2). The graduation of wettability is presented in Figure 5.16. The contact angle of water relates to the polarity of the Table 5.2: Contact angles of water on MPTMS silvlated and polymer-grafted substrates: Results for glass GS and silicon SW are consistent with each other. The evaluated contact angles  $\theta$  are given with both standard deviation *SD* and standard error *SE*. Both GS and SW substrates exhibit perfect wettability, directly after RCA and piranha PY cleaning. Aged piranha samples show high hydrophobicity. The cured epoxy resins EP (cold-curing L+S and heat-curing C+T) on GS show comparable wettability. All values of this table are given in degree.

	$\langle \theta \rangle \pm SD$ ( $SE$ )		$\langle \theta \rangle \pm SD (SE)$
GS PB- <i>b</i> -P4VP	$102.9 \pm 2.5 \ (0.42)$	SW PB- <i>b</i> -P4VP	$103.2 \pm 3.0 \ (0.51)$
GS PB12	$94.8 \pm 5.3 \ (0.92)$	SW PB12	$92.4 \pm 7.5 \ (1.30)$
GS $PB-b-PS$	$89.0 \pm 4.2 \ (0.76)$	SW $PB-b-PS$	$92.8 \pm 4.0 \ (0.71)$
GS PAN	$88.5 \pm 3.8 \ (0.65)$	SW PAN	$90.0 \pm 12.3 \ (2.40)$
GS PB- $b$ -PEO	$74.9 \pm 6.3 \ (1.22)$	SW PB- <i>b</i> -PEO	$84.1 \pm 9.5 (1.55)$
GS MPTMS	$79.3 \pm 4.8 \ (0.82)$	SW MPTMS	$101.8 \pm 4.6 \ (0.84)$
GS PY(aged)	$93.0 \pm 4.2 \ (0.73)$	SW PY(aged)	$89.7 \pm 5.8 \ (0.95)$
GS PY	0.0	SW PY	0.0
GS RCA	0.0	SW RCA	0.0
GS EP L+S	$73.9 \pm 2.8 \ (0.48)$	GS EP C+T	$76.8 \pm 0.9 \ (0.16)$



Figure 5.16: Contact angles of water on polymer-grafted substrates. The contact angle values are given in degrees. Substrates with PB-*b*-P4VP exhibit the highest contact angles. PB-*b*-PEO substrates show the most pronounced wettability of the evaluated samples.

surface. Enhanced polarity causes lower contact angles.

Polarity:  $PB-b-PEO \gg PAN \ge PB-b-PS \ge PB \gg PB-b-P4VP$ 

## 5.4 Mechanical analysis

The mechanical analysis is based on a pull-out fibre tensile test developed by J. PANDEY. The effect of the two-step surface modification can be evaluated by comparison of the tensile strength of embedded single fibres with and without modification. The direct result of a pull-out experiment is the stress-strain response. In this work, pull-out fibre were imaged by SEM to evaluate the surface state after testing. This evaluation will be presented and discussed in the following section.

Another approach consists in the evaluation of the mechanical properties of the polymeric film introduced by the chemical modification. SIEBIMM is a technique to evaluate mechanical properties derived from film buckling. This technique is presented in Section 5.4.2 followed by first a preparatory screening of solvents to enable the application of SIEBIMM in future work (see Section 5.4.3).

#### 5.4.1 Pull-out fibre evaluation

Pull-out fibres from the experiment described in Section 3.8 were imaged with scanning electron microscopy. Fibres were imaged as received from J. PANDEY without any further treatment or cleaning. The imaging of the fibre surface helps the understanding of the mechanical failure mechanism of the composite. The fibre embedded in a drop of matrix material (epoxy resin) embodies a micro-systematic attempt to characterise the interfacial adhesion. In a macroscopic composite, various dependencies like fibre orientation, shape, distribution and concentration have to be considered. By reducing the composite to a single fibre in contact with the matrix, the main contributions rely on the fibre surface state, the matrix material and the physicochemical interaction.

The task of this work was to evaluate the influence of an additional polymeric gradient at the fibre-matrix interphase. In the following unmodified and modified fibres of S-glass are compared. The modification is identical to the treatment of the silicon oxide model systems described in Section 4.1.2.a and 4.1.3.a: fibres were activated by acidic treatment, silylated with MPTMS and grafted with PB. Figure 5.17 shows the alteration of the fibre surface by the two step chemical modification. Pull-out fibres were imaged by SEM. Figure 5.18 present typical micrographs of a modified and an unmodified fibre.

One feature, which can be found on all evaluated fibres, is a collar-like residue of epoxy resin around the fibre. The outside (convex side) of this residue is smooth, with the concave inside being rough and fractured. The existence of such a residue originates from the preparation of



Figure 5.17: SEM micrographs of S-fibreglass before and after modification: **a** unmodified fibreglass; **b** after MPTMS silylation; **c**,**d** after PB grafting.



Figure 5.18: SEM micrographs of a modified **a** and unmodified **b** pull-out fibre: each micrograph is composed by superposition of smaller micrographs captured with dynamic focus.



Figure 5.19: SEM micrographs of a modified **a**,**b** and an unmodified **c**,**d** pull-out fibre.

the sample. When the droplet of epoxy resin is placed on the fibreglass a meniscus is formed. The epoxy resin exhibits a lower surface tension  $(30 \text{ to } 40 \text{ N m}^{-1})$  than the fibre surface, which is therefore wetted. Figure 3.6 shows SEM micropgraphs of the miniscus. In the experiment this meniscus of the drop is in contact with the guillotine-like opening of the retainer. When stress is applied, the fibre-drop system eventually fails and the drop decamps releasing the fibre. Since the epoxy resin fragments are sheered off, only a small collar-like residue remains at the initial point of fixation.

Another feature distinguishes modified and unmodified pull-out fibres. The surface of modifed fibres posses a more pronounced surface roughness than unmodified fibres. Figure 5.19 shows SEM micrographs of this feature. The increased roughness can be a result of both the grafted PB-coating and residues of the epoxy resin. The failure mechanism distinguishes several domains where fracture can occur in a fibre-matrix system. The system consists of the fibre surface, the matrix material and the interphase of both. The fracture can occur directly on the fibre surface or inside of the top layer of the fibreglass material. In this case the matrix material would exhibit a higher strength than the fibre. Another point of failure is the matrix material either at the interphase or in the bulk. In both cases fragments of the matrix remain on the fibre after the pull-out.

This can be found on the surface of both modified and unmodified fibres. The surface of unmodified fibres exhibit a clearer, smoother, state. Modified fibres offer, due to the grafted PB, an extended interphase. Monitoring the braking in the interphase region reveals insight to mechanical information. The interaction of the PB-grafted fibre to the matrix is expected to be stronger than the bare fibreglass.

#### 5.4.2 SIEBIMM

The term SIEBIMM references strain induced elastic buckling instability for mechanical measurements. Introduced by Stafford et al. [49], this technique enables the determination of mechanical properties of thin films: a thin film, of higher modulus material, bonded to a lower modulus substrate will buckle when subjected to compressive planar forces. Film buckling is driven by the release of strain energy in the system. The wavelength  $\lambda$  is a characteristic feature from which the elastic modulus of the thin film  $E_{\text{film}}$  can be calculated. Eq. 5.3 describes the film modulus as a result of the elastic modulus of the substrate  $E_{\text{substrate}}$ , the film thickness th and the POISSON ratios  $\nu$  of film and substrate. [50]

$$E_{\rm film} = E_{\rm substrate} \cdot \frac{3 \cdot (1 - \nu_{\rm film}^2)}{(1 - \nu_{\rm substrate}^2)} \cdot \left(\frac{\lambda}{2 \cdot \pi \cdot th}\right)^3 \tag{5.3}$$

The modulus of the substrate can be determined by tensile strength experiments. The wavelength and film thickness have to be known to a high accuracy, since their contribution is on the power of three. Theoretically, SIEBIMM can be adopted to polymeric films prepared by the two-step chemical approach presented in this thesis.

**Adaptation:** PDMS is a commonly used material for SIEBIMM analysis of thin films. This elastomer exhibits silanol groups at the surface. PDMS is an appropriate substrate for the chemical modification with MPTMS and thio-ene polymer grafting. Since buckling is induced by compression forces, the substrate can either be compressed or released from an initial extension. An interesting feature of PDMS is its elatomeric insoluble network, allowing a reversible swelling in appropriate solvents. The deswelling from the extended state can be used to induce film buckling. Therefore the film of interest has to be applied in the extended state, e. g. by polymer-grafting on PDMS in the swelled state. PB exhibits multiple vinyl groups per polymer chain. The thio-ene reaction causes cross-linking and yields an insoluble polymeric network of PB. This network is covalently bound to the PDMS return to its initial unstrained state. From the wavelength of the buckled film and the film thickness the elastic modulus can be calculated. The film thickness can be determined by ellipsometry or SFM topography. Since PDMS is transparent the methodology elaborated for glass substrates can be used.


Figure 5.20: SFM topography of PDMS swollen in THF after dying: welled surface state.

Since the application of the film (grafting of PB) is performed in solution, the swelling behaviour of PDMS in the respective solvent has to be evaluated. To allow the application of film buckling experiments, the solvent compatibility of PDMS was investigated.

#### 5.4.3 PDMS solvent screening

PDMS substrates were treated with HCl solution to increase hydrophilicity. The hydrophilic PDMS was immersed in MPTMS solution, following protocol in Section 4.1.2.b. The initial protocol involves THF as solvent. PDMS swells in THF and extends its size to approximately 138%. After drying the surface was evaluated using SFM topography revealing a welled uneven surface state, as presented in Figure 5.20. The PDMS substrate possessed an opaque surface.

Two approaches were selected to avoid the formation of such uneven surfaces: substitution of the solvent and vapour phase deposition.

Low solubility solvents of PDMS: Cured PDMS has a very low resistance to most nonpolar solvents. Since PDMS exhibits a cross-linked network, it will not be dissolved but swell. The elastomeric structure will in general not be destroyed by the solvents, rather deformed by swelling and will regain its original shape once the solvent has evaporated. PDMS does not swell in contact with water. In a polar solvent like THF a pronounced swelling of 138 % can be found. Solvents with low solubility are water, most alcohols (MeOH, EtOH), nitriles (acetonitrile), disubstituated amides (NMP, DMP), sulfoxides (DMSO) and pyridines. These solvents have a moderate to high polar character. The swelling ratio has been investigated by Lee et al. for PDMS-based microfluidic devices. [51] Table 5.3 presents the swelling ratios of selected low-solubility solvents and THF.

The PDMS was immersed in MPTMS solution, following protocol in Section 4.1.2.b, but with substitution of THF by selected solvents of low solubility: DMF, DMP, DMSO, acetone, EtOH, MeOH and MeCN. After drying, the success of the MPTMS treatment was evaluated using RAMAN spectroscopy. All samples expressed signals in the characteristic band for sulfhydryls



Figure 5.21: SFM topography of PDMS silvlated with MPTMS via hydrothermal vapour-phase deposition: image **a** and **b** show granular siloxane structures. Image **b** presents a welled surface state, that may have been caused by rinsing the substrate with THF. The siloxane grains oft both images are approximately 60 nm high.

Table 5.3: Swelling ratios of PDMS in selected solvents: the swelling ratio is given as the size of a PDMS slice in its swollen state to its initial non-swollen size. [51]

Solvent	Swelling ratio	Solvent	Swelling ratio
Tetrahydrofurane (THF) Acetone Ethyl alcohol (EtOH)	$1.38 \\ 1.06 \\ 1.04$	Methyl alcohol (MeOH) Acetonitrile (MeCN) Dimethyl sulfoxide (DMSO)	$1.02 \\ 1.01 \\ 1.00$
N-Methyl-2-pyrrolidone (NMP) Dimethyl formamide (DMF)	1.03 1.02	Water	1.00

(see chemical composition analysis in Section 5.2). All seven selected solvents are compatible with the MPTMS treatment. Therefore, depending on the selected solvent an extention of 0 to 6% can be yielded. Drying by evaporation in preferable to drying by heat. At elevated temperatures the (above  $70 \,^{\circ}$ C) to evaporation proceeds too fast and can result in bursting of the PDMS.

Vapour-phase deposition: As presented before, substrates can be silvlated with MPTMS via vapour-phase deposition. By omitting the solvent, no extension of the PDMS substrate should occur. Hydrophilic PDMS was silvlated by vapour phase, as described in Section 4.1.2.e. Samples were evaluated by SFM topography. Figure 5.21 presents the surface topography of a PDMS substrate silvlated by vapour-phase deposition. The surface shows the typical granular surface structure. Some small areas on the surface are welled. This can be a result of the samples being rinsed with THF after deposition. Concluding, both vapour-phase deposition and substitution of the solvent are applicable to reduce surface deformation.

# Chapter 6

### Retrospective and outlook

### 6.1 Conclusion

The aim of this thesis was to evaluate a surface modification inspired by the primary cell wall assembly of plants. Model substrates modified with the two-step chemical treatment were partly prepared at MPI Golm and Bayreuth University and partly provided by A. BERTIN.

**MPTMS deposition:** The initial step of the modification, a deposition of MPTMS, was analysed using SFM topography. The formation of the granular surface state of siloxanes covalently bound to the surface was attributed to two mechanisms: island formation/growth and self-aggregation. Both mechanisms antagonise the formation of a homogeneous siloxane-sulfhydryl layer. Wet-chemical deposition of MPTMS yields grain-like structures in the range of 5 to 20 nm. Both deposition by immersion and spin-coating result in similar structures. Methods described in the literature to increase the homogeneity were presented and discussed.

The heterogeneity of MPTMS deposition was evaluated by contact angle mapping of MPTMStreated glass slides. Pronounced deviations from the mean contact angle indicated domains of different surface roughness or/and deposition coverage. FT-IR and RAMAN spectroscopy were tested as methods to analyse the chemical composition of the surface, but failed for glass and silicon samples. The aim was to proove the presence of free sulfhydryl groups covalently bound to the surface. The concentration of sulfhydryl groups in the excitation volume is expected to be to little to be detected. In contrast, MPTMS-treated PDMS was successfully analysed by RAMAN spectroscopy exhibiting two relevant signals. Both vibrations are located in the frequency band typical for sulfhydryls. The presence of a signal at 2504 cm<sup>-1</sup>, which shifted to lower wavenumbers, is expected to be caused by strong hydrogen-bonding of the sulfhydyl group. Different solvents were checked for applicability for wet-chemical deposition of MPTMS on PDMS to enable techniques like SIEBIMM in future work. Vapour-phase deposition was tested to omit the effect of swelling of PDMS by solvent. The structural analysis exhibited granular surfaces similar to wet-chemical deposition. In conclusion, both deposition techniques (wetchemcial and vapour-phase) successfully introduce sulfhydryl groups on silicon oxide surfaces. The amount of water available in the system (solution or atmosphere) is the main factor of the formation of self-aggregated polysiloxanes (grains). The hydrolysation of MPTMS is inhibited in anhydrous conditions. An anhydrous deposition of MPTMS is expected to yield surface structures less granular and of higher homogeneity.

**Polymer grafting:** Four PB-based polymers and PAN were used for surface modification PB-based polymers were grafted-onto MPTMS treated silicon oxide substrates via a thio-ene *click* reaction. The grafting of PAN was identified to follow a different mechanism. The evaluated surface layer of PAN is expected to be adsorbed and not covalently bound to the surface. For PB-based polymers different surface features were found: PB and PB-*b*-PEO both show granular surface states with grains in the range of 50 to 500 nm in height. PB and PB-*b*-P4VP exhibit film-like structures with line or hole defects. For PB-*b*-PS, round or brim-shaped droplets can be found. Interesting structures in the form of *zig-zag* folded or crumpled domains are present of PB-*b*-PEO grafted samples. PAN exhibits densely-packed granular structures, which can be easily scratched and removed, or structures resembling crumpled droplets.

The wettability of the surface coatings was evaluated by contact angle measurements with water. The heterogeneity of the surface structure is expressed in the contact angle deviations. PB-*b*-PEO showed the highest polarity (pronounced wettability of water) and PB-*b*-P4VP the lowest polarity (reduced wettability of water). Concluding, PAN is not appropriate for thio-"ene" grafting. PB-based polymers are well suited. The combination of different polymers (with the desired functional groups) with an *anchor*-block of PB enables the tuning of the surface polarity/wettability. Therefore both adhesion promotion and the introduction of functional groups on the surface (or the fibre-matrix interphase) are possible.

The mechanical synergy effect of PB-grafting was evaluated by SEM of fibreglass subjected to a pull-out tensile test. A typical collar-like residue of epoxy resin was assigned to the preparation method. Modified fibres present a pronounced surface roughness compared to unmodified fibreglass. The fracture is identified to appear at the interphase, not in the bulk phases of epoxy resin or fibreglass. The interaction of PB-grafted fibre and matrix is expected to be stronger than for the bare fibreglass.

**Methodology of VASE on glass:** A methodology to measure thin film thickness on transparent substrates like glass has been elaborated and tested for the regarded system. Back-surface reflections can effectively be reduced by back-surface roughening or blackening. The determination of the dispersion of glass demands the use of a retarder in the ellipsometric setup. Ellipsometry is appropriate for homogeneous isotropic layer build-ups. VASE fails for the samples prepared by the two-step chemical modification, since both layer composition and thickness spatially deviate.

#### 6.2 Outlook

Closely related to wettability, adhesion arises from the balance of attractive and repulsive forces acting between contacting surfaces. It is planned to quantify the interaction of matrix and fibre by colloidal probe adhesion measurements. SFM is suited to measure the adhesion energy between an epoxy resin colloidal probe and polymer-grafted surfaces. On the basis of their attractive binding (adhesive) energy during separation, the dominant interaction could be determined. Epoxy probe cantilevers can be prepared by dipping. By addition of a fluorescent label to the uncured epoxy resin, the three-dimensional shape of the epoxy probe can be determined by CLSM.

Polymer-grafted samples of higher homogeneity can be prepared by optimisation of the initial MPTMS deposition. This can be achieved by either reducing the amount of water available in the system (predrying of samples, hygroscopic additives, vapour-phase deposition) or substitution of MPTMS by a silvlation coupling agent with only one hydrolysable group. Deposition layers of higher homogeneity may enable the application of SIEBIMM and VASE.

The aim is a better comprehension of adhesion principles and thus optimising fibreglassbased synthetic composites inspired by plant gradient-material, which may benefit from the hierarchical principle found in plant cell wall assembly.

#### 6.3 Zusammenfassung

Das Ziel dieser Arbeit war die Beurteilung einer ächenmodifikation, die von dem Aufbau der primären Pflanzenzellwand inspiriert war. Die Modifikation der Modellsubstrate , nach einem zweistufigen chemischen Verfahren, wurde teilweise am MPI Golm und der Universität Bayreuth vorgenommen. Präparierte Modellsubstrate wurden zudem von A. BERTIN zur Verfühung gestellt.

**MPTMS Behandlung:** Der erste Schritt der Modifikation, das Aufbringen von MPTMS, wurde mit Hilfe von SFM Topographie untersucht. Die Ausbildung einer gekörnten Oberflächenstruktur aus kovalent an die Oberfläche gebundenen Siloxanen, wurde zwei Mechanismen zugeschrieben: Inselbildungwachstum und Selbst-Aggregation. Beide Mechanismen wirken der Ausbildung einer gleichmäßigen Siloxan-Thiol-Lage entgegen. Das nass-chemische Aufbringen von MPTMS erzeugt kornartige Strukturen in der Größe von 5 bis 20 nm. Das Eintauchen in eine Lösung sowie das Auftragen mittels Spin-coater ergeben gleichartige Strukturen. In der Literatur beschriebene Methoden zur Verbesserung der Homogenität der Siloxane-Schicht wurden päsentiert und diskutiert.

Die Ungleichmäßigkeit der MPTMS-Auftragung wurde durch Kontaktwinkelmessungen auf MPTMS behandelten Objektträgern untersucht. Deutliche Abweichungen von dem mittleren Kontaktwinkel zeigten Bereiche verstäkter Oberflächenrauhigkeit oder ungleichmäßiger Oberflächenbelegung an. Es wurde versucht, mit Hilfe der Methoden FT-IR und RAMAN Spektroskopie, die chemische Zuammensetzung der Oberfläche zu ermitteln. Beide Methoden sind zur Charakterisierung behandelter Glass- oder Siliziumsubstrate nicht geeignet. Das Ziel war der Nachweis freier, kovalent an die Oberfläche gebundener, Thiol-Gruppen. Die Konzentration der Thiol-Gruppen im Anregungsvolumen scheint für eine Detektion zu gering zu sein. Mit MPTMS behandeltes PDMS wurde erfolgreich mit RAMAN Spektroskopie untersucht. Die Charakterisierung weist zwei Signale in dem für Thiole relevanten Frequenzbereich auf. Es wird vermutet, dass die Verschiebung des einen Signals  $(2504 \,\mathrm{cm}^{-1})$ , zu geringeren Wellenzahlen, von starken Wasserstoffbrückenbindungen der Thiolgruppe herrührt. Verschiedene Lösungsmittel wurden auf ihre Anwendbarkeit in dem nass-chemischen Auftragen von MPTMS auf PDMS untersucht, um zukünftige Untersuchungen mit Methoden wie SIEBIMM zu ermöglichen. Silylierung per Gasphase wurde getestet um auf Lösungsmittel zu verzichten und das Anschwellen von PDMS zu vermeiden. Die struktuelle Untersuchung zeigte ähnliche gekörnte Oberfläche wie das nass-chemische Verfahren. Zusammenfassend kann gesagt werden, dass beide Verfahren (nass-chemisch und per Gasphase) erfolgreich Thiolgruppen auf der Siliziumoxidoberfläche einführen. Der Wassergehalt im System, ob Lösung oder in der Atmosphäre, ist der Hauptgrund für die Ausbildung von Polysiloxanen (Körnern) durch Selbst-Aggregation. Im Wasserfreien ist die Hydrolyse von MPTMS gehemmt. Deshalb wird erwartet, dass ein wasserfreies Aufbringen von MPTMS weniger gekörte und gleichmäßigere Oberflächen erzeugt.

**Polymer-Aufpfropfen:** Für die Oberflächenmodifikation wurden vier auf PB-basierende Polymere und PAN verwendet. Auf PB-basierende Polymere wurden, durch eine Thiol-En *Klick*-Reaktion, auf MPTMS behandelte Siliziumoxidsubstrate, nach einem *graftig-onto* Mechanismus, aufgebracht. Dem Aufbringen von PAN wurde ein anderer Mechanismus zugeordnet. Es wird vermutet, dass die untersuchte Oberflächenlage von PAN nicht kovalent an die Oberfläche gebunden, sondern lediglich adsorbiert wird. Für auf PB-basierenden Polymeren wurden verschiedene Merkmale gefunden: PB und PB-*b*-PEO zeigen beide eine gekörnte Oberflächenstruktur mit Korngrößen von 50 bis 500 nm. PB und PB-*b*-P4VP zeigen filmartige Strukturen, teilweise mit Linien- oder Lochdefekten. Merkmale von PB-*b*-PS haben die Form von Tropfen oder Tropfenrückständen. Sehr interessante Strukturen zeigten sich auf PB-*b*-PEO Oberflächen mit welligen Zickzackfaltungen. PAN zeigt entweder dichtgepackte gekörnte Strukturen, welche leicht mechanisch angekratzt und entfernt werden können, oder verknitterte Tropfenstrukturen.

Die Benetzbarkeit der Oberflächenbeschichtungen wurde durch Kontaktwinkelmessungen mit Wasser untersucht. Ungleichmäßigkeiten der Oberflächenstruktur zeigten sich in der Streuung der Kontaktwinkelwerte. PB-*b*-PEO wies die höchste Polarität auf (verstärkte Benetzbarkeit), PB-*b*-P4VP die Geringste (verringerte Benetzbarkeit mit Wasser). Zusammenfassend wurde festgestellt, dass PAN für ein *grafting* nach dem Thiol-En-Mechanismus nicht geeignet ist. Polymere, die auf PB basireren, eignen sich hingegen gut. Unter Verwendung verschiedener Kombinationen an Polymer-Blöcken (mit gewünschter Funktionalität) mit PB, als *Verankerungs*-Block, ermöglicht das Einstellen verschiederer Polaritäten/Benetzbarkeiten der Oberfläche. Demnach können zugleich die Adhesion verbessert und funktionelle Gruppen eingeführt werden.

Die Synergie der mechanichen Eigenschaften, durch das Aufbringen von PB, wurde durch SEM Messungen an Glasfasern, welche einem Faserauszugstest unterzogen wurden, durchgeführt. Der an allen Faser gefundene kragenartige Epoxidharzrückstand konnte der Präparationsmethode zugeschrieben werden. Modifizierte Fasern weisen, im Vergleich zu unbehandelten Glasfasern, eine erhöhte Oberflächenrauhigkeit auf. Der Bruch entstand an der Matrix-Faser Grenzfläche, nicht in dem Faser- oder Epoxidmaterial. Es wird erwartet, dass durch die Modifizierung mit PB die Wechselwirkung von Faser und Matrix verstärkt wird.

Die Methodik von VASE auf Glas: Eine Vorgehensweise die Schichtdicke dünner Filme auf transparenten Substraten wie Glas zu bestimmen, wurde erarbeitet und für das vorliegende System getestet. Störende Rückseitenreflektionen können durch Aufrauhen oder Schwärzen der Rückseite effektiv reduziert werden. Für die ellipsometrische Bestimmung des wellenlängenabhängigen Brechungsindex von Glas sollte ein Retarder im Aufbau verwendet werden. Ellipsometrie eignet sich um gleichmäßige isotrope Schichtsysteme zu untersuchen. VASE versagt bei den zweistufig chemisch modifizierten Proben, da Zusammensetzung und Schichtdicken sich örtlich stark unterscheiden.

#### 6.4 Ausblick

Die Adhäsion, welche eng mit der Benetzbarkeit verbunden ist, stellt ein Gleichgewicht von, an der Kontaktfläche auftretenden, anziehenden und abstoßenden Kräften dar. Es ist geplant, die Wechselwirkung von Matrix und Faser durch SFM Adhäsionsmessungen mit Sonden kolloidaler Größe, zu quantifizieren. Rastersondenkraftspektroskopie ist eine geeignete Methode um Adhäsionsenergien zwischen einer kolloidalen Sonde aus Epoxidmaterial und einer Polymerbeschichteten Oberfläche zu messen. Auf Basis der, bei der Trennung (von Sonde und Oberfläche) auftretenden attraktiven (adhäsiven), Bindnungsenergien könnte die dominante Wechselwirkung bestimmt werden. Kolloidale Epoxidsonden können durch Eintauchen des *Cantilevers* in Epoxidharz hergestellt werden. Durch Zugabe eines Fluoreszenzfarbstoffes ist es möglich die dreidimensionale Form der Epoxid(tropfen)sonde mit Hilfe der CLSM zu bestimmen.

Eine höhere Homogenität der Polymer-beschichteten Probenoberflächen sollte durch eine Optimierung des ersten Modifikationsschrittes (MPTMS Behandlung) möglich sein. Dies kann entweder durch eine Verringerung des, für die Hydrolyse zur Verfügung stehenden, Wassergehalts oder durch Verwenden eines Silanisierungsmittels mit nur einer hydrolysierbaren Gruppe erreicht werden. Gleichmäßige Polymerschichten könnten Methoden wie SIEBIMM oder VASE ermöglichen.

Das Ziel ist ein besseres Verständnis der (Faser-Matrix) Adhäsion um synthetische (Glas)Faserverbundstoffe, welche von pflanzlichen Gradientenmaterialien inspiriert sind, zu optimieren. Diese Materialen könnten Vorteile des hierarchischen Bauprinzips der Pflanzenzellwand nutzen.

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### Appendix

**Statistics:** In probability theory and statistics the standard deviation SD(x) is a measure of the variability or dispersion of a data set  $\{x_i\}$ . A low standard deviation indicates a small spread of the *n* data points from the mean value  $\langle x \rangle$ .

$$\langle x \rangle = \frac{1}{n} \cdot \sum_{i=1}^{n} x_i$$
 and  $SD(x) = \sqrt{\frac{1}{n-1} \cdot \sum_{i=1}^{n} (x_i - \langle x \rangle)^2}$  (1)

Furthermore the standard error of the mean is designated as SE(x). It is the standard deviation of the sampling distribution of the mean.

$$SE(x) = \frac{1}{\sqrt{n}} \cdot SD(x)$$
 (2)

This formula does not assume a normal distribution: the larger the sample size, the smaller the standard error of the mean. It is not suitable to describe the deviation of a experimental value like a contact angle but is introduced herein to be able to compare data referred in literature. The standard deviation of calculated values can be approximated by the *Gaussian fault propagation* and the respective standard deviations SD(y). For a value  $y(x_i)$  it yields

$$SD(y) = \sqrt{\sum_{i} \left\{ \left( \frac{\partial y}{\partial x_i} \right)^2 \cdot SD(x_i)^2 \right\}}.$$
(3)

**States of polarisation:** Several states of polarisation can be distinguished. The following table presents linear, elliptical and circular polarisation with the respective phase difference of p- and s-polarised light  $(\delta_p - \delta_s)$ .

Phase shift	Polarization		
	$E_{0p} \neq E_{0s}$	$E_{0p} = E_{0s}$	
$\delta_{\rm p} - \delta_{\rm s} = 0^{\circ}$	linear		
$0^{\circ} < \delta_{\rm p} - \delta_{\rm s} < 90^{\circ}$	elliptical		
$\delta_{\rm p} - \delta_{\rm s} = 90^{\circ}$	elliptical	circular	
$90^\circ < \delta_{\rm p} - \delta_{\rm s} < 180^\circ$	elliptical		
$\delta_{\rm p}-\delta_{\rm s}=180^{\circ}$	linear		
$180^\circ < \delta_{\rm p} - \delta_{\rm s} < 270^\circ$	elliptical		
$\delta_{\rm p} - \delta_{\rm s} = 270^{\circ}$	elliptical	circular	
$270^{\circ} < \delta_{\rm p} - \delta_{\rm s} < 360^{\circ}$	elliptical		

Table: States of polarisation based on the phase shift

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