Conclusions: The experimentally determined values of the power indices x and γ describing dependence of conductivity $\sigma \sim f^{\chi}$ and permittivity $\varepsilon \sim f^{-\gamma}$ on AC frequency f in polyisoprene-carbon nanocomposite in the vicinity of percolation threshold are consistent with the general scaling principle of the percolation theory $\chi + \gamma = 1$. The obtained values of χ and γ are in agreement with the mechanism of inter-cluster polarisation.

The experimentally observed deviation from the relation $\varepsilon \sim |M - M_C|^{-s}$ of the statistical percolation theory at carbon concentrations above the percolation threshold $M > M_C$ may be a result of particle agglomeration and deviation from statistical distribution. The asymmetric and branching shapes of particle clusters cause strong local electric fields in the matrix between clusters providing additional contribution to the dielectric permittivity.

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Chemical and Thermal Stability of Alkylsilane Based Coatings for Membrane Emulsification

By *Maik J. Geerken, Thomas S. van Zanten, Rob G. H. Lammertink, Zandrie Borneman, Wietze Nijdam, Cees J. M. van Rijn,* and *Matthias Wessling**

Emulsification techniques are widely used in food, pharmacy and cosmetic industry to produce oil-in-water or water-in-oil emulsions. Commonly used emulsification techniques include rotor-stator systems, high-pressure homogenizers and ultrasound.[1] Due to high shear forces, the dispersed phase is divided into small droplets stabilized by surfactants. However, shear stress and thermo sensitive ingredients, like proteins, may loose their bioactivity during this process.[2]

Cross-flow membrane emulsification is a relative new emulsification process. This technique requires less energy, generates less stress to the ingredients, and produces narrower drop size distributions.[3] In this process, the dispersed phase is forced through a porous membrane into the flowing continuous phase (see Fig. 1).

Droplet formation by micro porous membranes requires a surface, which is not wetted by the dispersed phase. In case the dispersed phase wets the membrane, spreading of the dispersed phase over the membrane surface will occur resulting in the production of big strings instead of droplets.

Lately, different types of microporous membranes were employed in research on membrane emulsification. As Table 1 indicates, most of them were exploited for the production of oil in water emulsions requiring hydrophilic membranes.

Until now membrane emulsification technology has not found its way to large-scale manufacturing. This is due to the fact that commercially available membranes possess some disadvantages; they require a high-pressure drop, and consist of a highly porous and irregular morphology on a microscopic scale.[11] To overcome these disadvantages a micro- engineered membrane was adopted from microfiltration.[12] This

[*] M. J. Geerken, T. S. van Zanten, Dr. R. G. H. Lammertink, Z. Borneman, Prof. M. Wessling*
Membrane Technology Group,
Faculty of Science and Technology
University of Twente,
Postbus 217, 7500 AE Enschede, The Netherlands
E-mail: M.Wessling@TMW.utwente.nl

W. Nijdam, Dr. C. J. M. van Rijn
Aquamarijn Micro Filtration bv
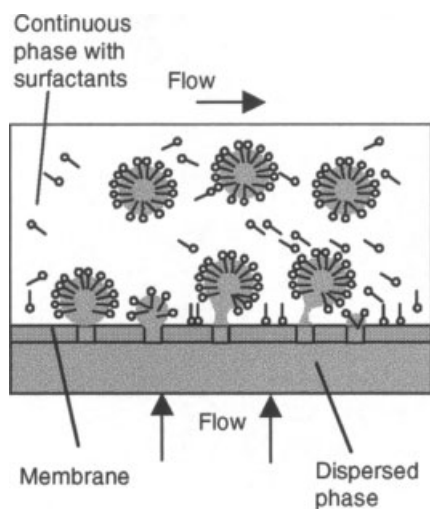Beatrixln 2, 7255 DB Hengelo Gld., The Netherlands

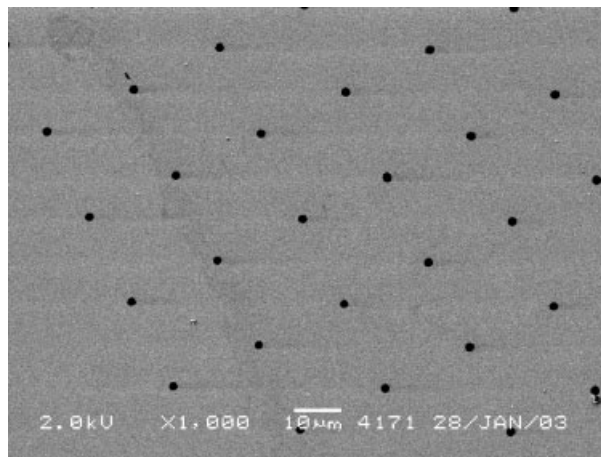Fig. 1. Membrane emulsification process for oil in water emulsions.

Fig. 2. SEM picture of silicon nitride microsieve with defined pore size (2 μm) and pore distribution (pore to pore distance 20 μm) designed for membrane emulsification.

microsieve membrane, fabricated out of silicon nitride with a silicon support, has a precisely defined pore size and narrow pore size distribution as shown in Figure 2, combined with a micron-sized membrane thickness.

As previously mentioned, membrane emulsification needs a surface that is not wetted by the dispersed phase. A hydrophobic surface is required for producing water-in-oil emulsion whereas for oil-in-water emulsions a hydrophilic surface is needed. Due to the silicon nitride processing conditions, groups like silanol (SiOH), primary (SiNH$_2$), and secondary amino groups (Si$_2$NH) are present.[13] Overall this results in a more hydrophilic than hydrophobic surface.

In this paper, we discuss the results of modifying the surface properties to a more hydrophobic state via self-assembled monolayers (SAMs) of organosilanes. We focus in particular on their chemical and thermal stability considering the rigorous cleaning procedures used in food and diary industry.

Self-assembled monolayers based on organosilanes: Self-assembled monolayers are well known as anti-sticking coatings for microelectromechanical systems (MEMS). In these microscaled systems the adsorption of water from humid air onto the surface decreases their performance and lifetime. To prevent this negative effect surface modifications are used to increase the hydrophobicity. The water contact angle can rise from below 30° on SiO$_2$ surfaces to 110° on SAM-coated surfaces.[14]

Table 1. Used membranes for cross-flow membrane emulsification.

Membrane material	Type of emulsions	References
Al$_2$O$_3$	Oil in water	[4]. [5]
Shirasu Porous Glass (SPG)	Oil in water	[6], [7], [8]
Polycarbonat	Oil in water	[9]
Polypropylene	Water in oil	[10]

The formation of silane based SAMs is described in the literature for different silanes on silicon and silica substrates. Applied silanes for hydrophobization include alkylchlorosilanes (R$_n$SiCl$_{4-n}$), perfluoronated alkylchlorosilanes ((CF$_3$(CF$_2$)$_m$(CH$_2$)$_n$)$_p$SiCl$_{3-p}$) and alkylalkoxysilanes ((CH$_3$(CH$_2$)$_m$O)$_4$-Si-R). A variety of silanes, either alkylchloro or alkylalkoxy, with epoxy, amine or thiol terminated alkyl chains are exploited to create hydrophilic surfaces.[15,16]

Due to the fact that chlorosilane coupling agents have a low affinity for the surface[17] it is necessary to convert them into silanol groups. By reacting with water the chlorine atoms split off and hydroxide head groups are formed, which have a higher affinity to the silicon surface. This leads to an adsorption of the hydroxysilanes on the surface (see Fig. 3). The hydrolysis step is followed by the reaction between the hydroxide groups and the silanol groups present on the surface resulting in a covalent Si-O-Si bond. Ideally, the resulting SAM contains molecules that are both covalently linked to the substrate as well as to their neighbors.

Preferably, hydrolysis takes place close to the silicon surface, but the presence of water in the coating solution can result in bulk-polymerization of the silanes before it reacts with the surface. On one hand water is absolutely necessary for SAM formation but on the other hand it is unwanted in the coating solution. To avoid bulk-polymerization, it is recommended to use solvents with a very low water content.[17] If the silicon substrate is exposed to humid air before immersing it into the coating solution the desired water will be present on the surface as a thin adsorbed water layer.[18,19]

Reported values for water contact angles as an indication for the quality of the silane based SAMs and their hydrophobicity range from 90° to 115° depending on the used coating agent (carbon chain length).[18–20] The thermal stability in air, nitrogen and vacuum is well reported. For octadecyltrichlorosilane monolayers (ODTS) constant water contact angles are observed up to 100 to 200 °C in air and up to 500 °C in nitrogen for short annealing durations.[19,21,22]
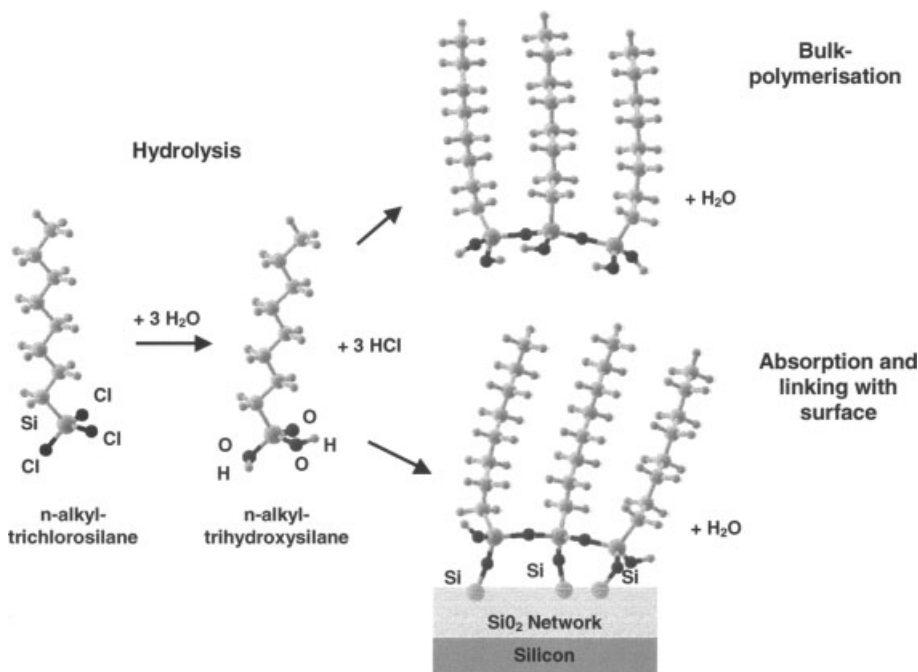
Fig. 3. Schematic illustration of the formation of SAMs on silicon.

Less reported is the chemical stability of the silane based SAMs. Iimura *et al.* studied the chemical resistance of long chain tri-, di- and monochloroalkylsilanes under different conditions.[23] They found that the stability in organic solvents (e.g. benzene, ethanol, chloroform), in acidic (pH 1) and in alkaline solutions (pH 13) decreased from trichloro- to monochloroalkylsilanes. The best results were observed for octadecyltrichlorosilane (ODTS) based SAMs, which show no dramatic changes in the intensity of the observed CH_2 stretching bands after being exposed to the mentioned conditions.

SAM-Formation: Table 2 depicts the results of the static water contact angle measurements in air and hexadecane (Fig. 4). FOTS (perfluoronated octyltrichlorosilane) shows somewhat higher water contact angles in both environments compared to OTS (octyltrichlorosilane), which has the same carbon chain length. Fluorocarbons are known to have lower critical surface tensions compared to hydrocarbons and perfluoronated trichlorosilanes are the most effective chlorosilane reagents to produce hydrophobic coatings.[14] In general, perfluoronated SAMs are known to have a higher hydrophobicity compared to hydrocarbon SAMs.[24]

Stability: Following the surface modification we studied the stability under various conditions. Trichlorosilane coatings are bonded to a silicon surface via silicon-oxygen-silicon bonds as mentioned before. The alkyl chains are, from a chemical point of view, very stable and in case of fluorocarbons even inert. The weak point of these coatings is the substrate bonding part of the molecules. It is known, that the silicon-oxygen bond is susceptible towards hydrolysis in alkaline conditions.[25] To increase the stability under alkaline conditions it is necessary to form a well-ordered and dense monolayer that prevents the penetration of OH^- ions and water through the monolayer to the bonding part.[23]

At first the chemical stability was studied. Coated wafers were exposed to different aqueous solutions with varying pH-values for several days. It was found, that coatings are stable from pH 2 to 11.5 for FOTS and to pH 10 for OTS respectively during the observed time scale (see Fig. 5). When treated with a sodium hydroxide solution of pH 13 the contact angle decreases in both cases very dramatically to values typically for oxidized silicon.

Next, the thermal stability in water was studied. Figure 6 shows the changes of the relative water contact angles for three different temperatures. It can be seen that the thermal stability of FOTS coatings is at all temperatures superior compared to OTS. This corresponds with the higher hydrophobicity of FOTS compared to OTS, which limits the water penetration through the SAM to the substrate.

However, literature only reports on thermal stability in vacuum, nitrogen and air. Sirnivasan *et al.* compared the thermal stability of ODTS and perfluoronated ODTS (FODTS) in air with a humidity not specified and in nitrogen.[18] In air and up to 400 °C, FODTS is more stable compared to ODTS and in nitrogen both are showing the same stability decrease with increasing temperature. In inert environments like vacuum and nitrogen the thermal stability is determined by splitting the Si-C or C-C bonds.[19] In reactive environments like
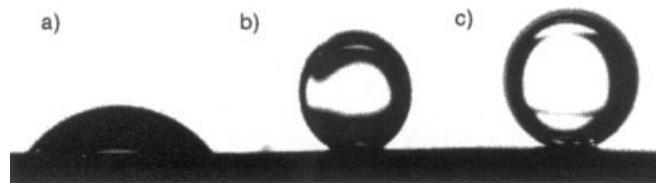
Table 2. Results of contact angle measurements.

	FOTS	OTS
Water/air	112 ± 4.0	104.9 ± 2.0
Water/hexadecane	160.5 ± 8.9	143.8 ± 0.5

Fig. 4. Water drops in hexadecane on a) untreated silicon nitride, b) FOTS coated and c) OTS coated silicon nitride.

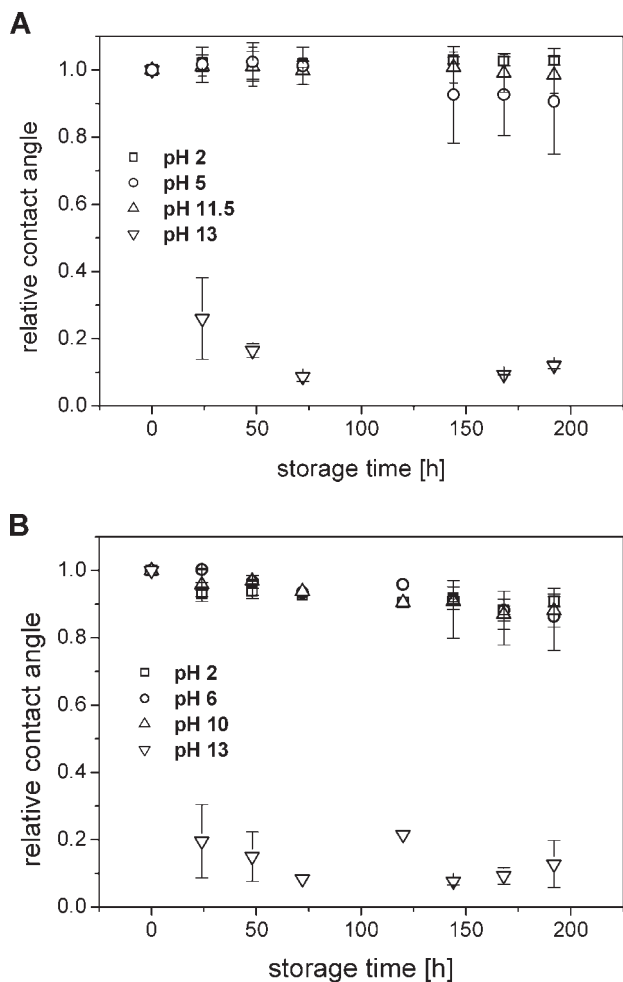Fig. 5. Chemical stability of FOTS (A) and OTS (B) coatings on silicon nitride wafers.

silanes on silicon are described and can be adopted to render Si_xN_y microsieves hydrophobic. A key factor is the stability. In food, diary, and pharmaceutical industry equipment is cleaned by using hot alkaline and acidic solutions. Surface modifications have to withstand these conditions. Most often, the reported stability studies of alkylsilane based surface modifications describe the thermal stability in hot air, nitrogen or vacuum.

This paper discusses and compares the chemical and thermal stability of FOTS and OTS self-assembled monolayers on Si_xN_y. It was found that the perfluoronated coatings are more stable than the corresponding hydrocarbon coatings. It withstands acidic and alkaline conditions in a range from pH 2 to 11.5, it is thermal stable in hot water up to 80 °C and it also withstand hot nitric acid and hot sodium hydroxide solutions in the time scale of the experiment. OTS coatings cannot perform these features in all cases.

The produced FOTS coatings seem to have a well-ordered and denser structure than OTS, which causes a better protection against the cleavage of the Si-O-Si bond by OH⁻ ions and water. Main differences between both coatings are different polarities, different structure and density. From polymer

hot air the C-F bond, which is difficult to polarize, shields the C-C bonds of the backbone leading to increased stability for the perfluoronated compared to the corresponding hydrocarbons. In hot water the hydrolization of the Si-O-Si bond determines the thermal stability.

Cleaning procedures used in food industry combines heat and chemical treatments. Figure 7 depicts the results of FOTS coatings treated with hot nitric acid solutions (pH 5) and with hot sodium hydroxide solutions (pH 10) for nearly 180 h. After this treatment the coating remains hydrophobic. The initial water contact angle decreases less than 5 percent at pH 10 and less than 10 percent at pH 5 for all temperatures studied.

Figure 8 shows the results for OTS. When exposed to pH 5 at 50 and 65 °C the water contact angle only decreased to about 90 percent of the initial value. At 80 °C, however, it decreased to half of its initial value. An even more dramatic loss of hydrophobicity can be observed in case of hot sodium hydroxide solutions.

Conclusions: The preparation of water in oil emulsions with micro-engineered silicon nitride emulsification membranes requires a hydrophobic surface. Several methods using alkyl-
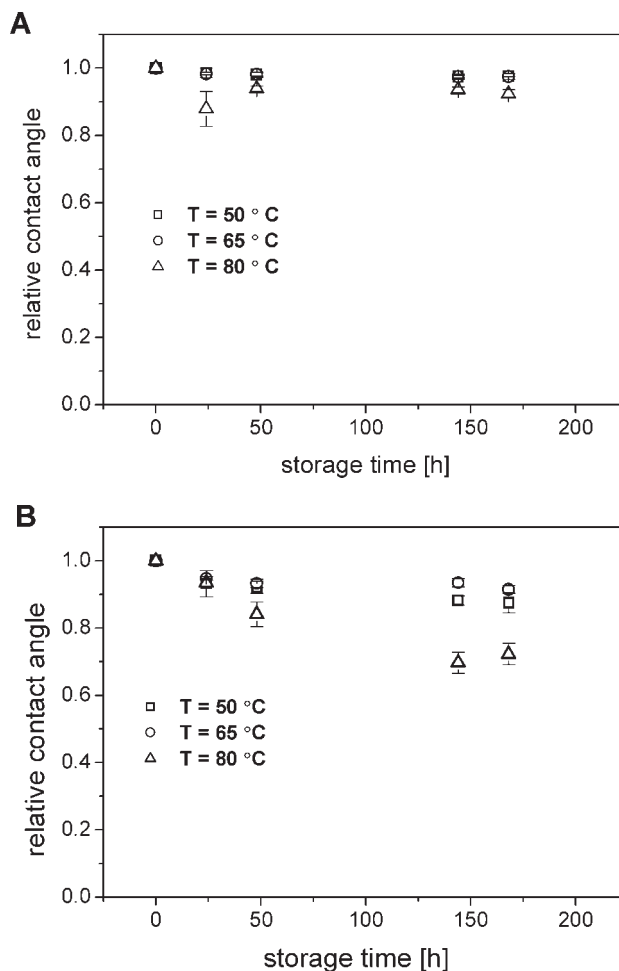

Fig. 6. Thermal stability of FOTS (A) and OTS (B) coatings on silicon nitride wafers.

science it's known that polytetrafluorethylene (PTFE) has a two times denser crystal structure combined with a much higher melting temperature compared to polyethylene (PE).[26] Besides that, PTFE is more resistant towards acidic and alkaline environments compared to PE. These properties are reflected in the stability of the studied SAMs, which clearly favor the perfluoronated one.

Experiments: For the SAM formation two types of alkyltri-chlorosilanes were used. Octyltrichlorosilane (OTS) (Aldrich, 97 %) and a perfluoronated octyltrichlorosilane (FOTS) (Fluka, > 97 %) were used as received. For the preparation of the coating solutions n-hexadecane (Aldrich, > 99 %, < 0.005 % H_2O) and chloroform (Merck, 99 %, < 0,01 % H_2O) were used as solvents and before use dried with molecular sieves to water content below 0.002 %.

A single crystalline silicon wafer (type <100>) is coated with a thin layer (1.2 μm) of lpcvd silicon nitride (low pressure chemical vapor deposition, Tempress Omega junior system). At a temperature of 850 °C, a gas mixture of dichlorosilane (SiH_2Cl_2) and ammonia (NH_3) reacts and will form silicon nitride. Using an excess of dichlorosilane (70sccm:18sccm), silicon rich nitride is formed that has less
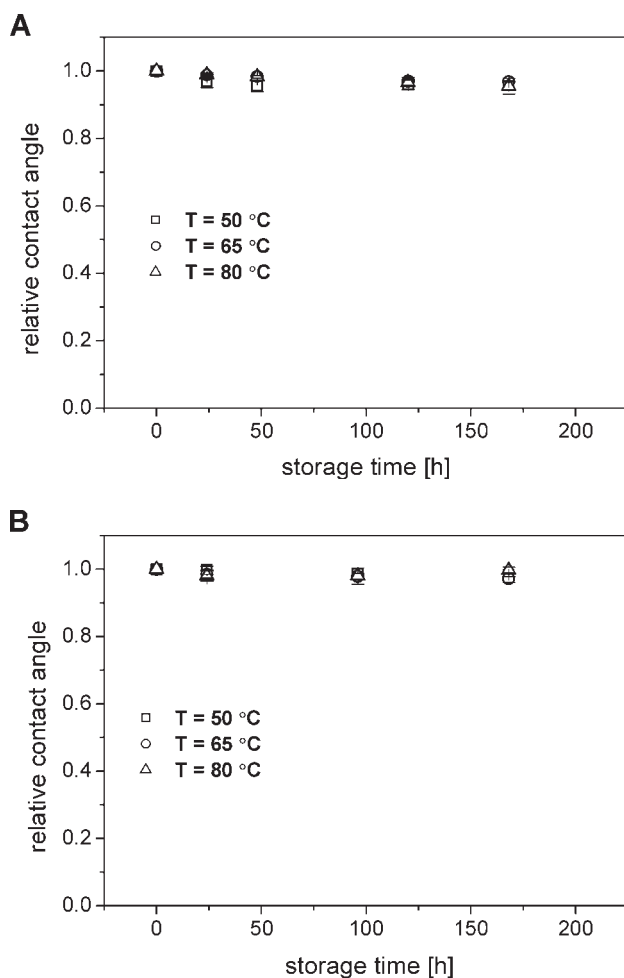

Fig. 7. Stability of FOTS coatings at different temperatures and pH-values (A: pH 5, B: pH 10).
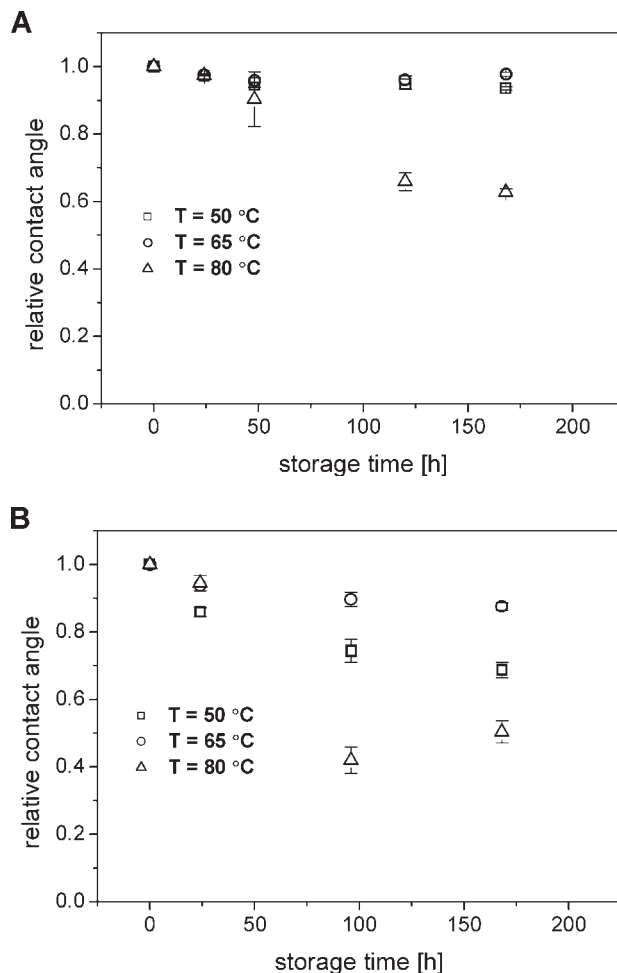

Fig. 8. Stability of OTS coatings at different temperatures and pH-values (A: pH 5, B: pH 10).

internal stress than stochiometric nitride and is as such a good and strong membrane material.[27] Bare silicon wafers coated with a thin silicon nitride (Si_xN_y) layer were cleaned by using a reactive oxygen plasma (10 min, 500 W, pO_2 = 16 mbar) to remove adsorbed impurities. This method is one of the most efficient especially to remove organic contaminants.[28]

The SAM formation took place in solution of 2.5 mmol/l silane in a mixture of dried n-hexadecane and chloroform (4/1 v/v). The wafers were placed in the solution for one hour at room temperature and ambient pressure. Afterwards the wafers were removed from the solution and extensively rinsed first with iso-propanol, then with ultra pure water and dried with nitrogen. After the formation step a stabilization step followed. According to Srinivasan *et al.*[18] the coated wafers were heated at 100 °C for 1h in an oven flushed with nitrogen. It must be pointed out that use of dry equipment is required and that the SAM formation is carried out under a nitrogen atmosphere to prevent an increase of the water content.

The thermal and chemical stability was tested under different temperatures and pH-values adjusted with sodium hy-

droxide and nitric acid. The wafers were stored for several days under these conditions and the changes were observed by measuring the water contact angle in air using a Gonionometer from Dataphysics (OCA 15+).

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Cellulose Fibrils for Polymer Reinforcement**

By *Tanja Zimmermann,* Evelyn Pöhler* and *Thomas Geiger*

Lignocellulosic fibres obtained from renewable resources such as wood become of more and more interest as reinforcing components in composites,[1,2] because they are biodegradable and harmless for the ecological system. Furthermore, they have promising mechanical properties and are less expensive than conventional synthetic fibres.

Within the different cell wall layers of fibres the high tensile-strength cellulose exists as a system of fibrils embedded in the matrix substance lignin. Depending on the break down by disintegration processes the dimensions of the partly crystalline fibrils of wood vary as it is shown in Figure 1. Fibrils have diameters in the nanometer and lengths in the micrometer scale.

[*] T. Zimmermann, E. Pöhler
Swiss Federal Laboratories for Materials Testing and Research
Wood Laboratory
Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland
E-mail: Tanja.Zimmermann@EMPA.CH

Dr. Th. Geiger
Swiss Federal Laboratories for Materials Testing and Research
Laboratory for Functional Polymers
Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland