BIOFILMS ON SILICONE RUBBER MATERIALS FOR OUTDOOR HIGH VOLTAGE INSULATION

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ABSTRACT

Silicone rubber high voltage insulators are sometimes colonised by microorganisms which form a biofilm on the surface of the infected unit. In this work insulators exposed to the outdoor environment in Sweden, Sri Lanka and Tanzania respectively have been studied. The biofilms colonising the insulators were shown to be of roughly the same composition regardless of their origin. Algae in association with bacteria dominated the biofilms and provided nutrition to mold growth. The isolated microorganisms were further used to study the effect of a biofilm on different silicone rubber materials. New tools for diagnosing biological growth on polymeric materials were developed and used to analyse the silicone rubber samples.

No evidence of biodegradation of the polydimethylsiloxane (PDMS) molecule has been found in this work. However, this does not mean that PDMS rubbers used in high voltage insulators can be called bioreistant. Silicone insulating materials always contain additives and these may promote or hinder growth. For this reason, an extensive test program was developed, in order to evaluate the effect of different additives on the degree of biological growth. The program spanned from fast and easy methods, useful for screening large amount of samples, to the construction of specially designed microenvironment chambers in which mixed biofilms, similar to those formed on the surface of silicone rubber insulators in the field, were successfully grown.

The test program showed that the flame retardant zinc borate protected the materials, whereas alumina trihydrate (ATH) did not hinder biological growth. On the contrary, environmental scanning microscopy (ESEM) in combination with X-ray energy dispersive spectroscopy (EDS) showed that the surface roughening caused by the addition of ATH to the silicone rubber matrix made the materials more difficult to clean.

Furthermore when the hydrophobic surface of a silicone rubber insulator is covered by a hydrophilic biofilm this leads to a reduction of the surface hydrophobicity of the material. This may alter the electrical properties of the insulator. It is therefore important to develop methods to identify biofouled units. In this work, laser-induced fluorescence (LIF) spectroscopy was explored as a tool for the detection of biofilms on silicone rubbers. The experiments revealed that weak traces of algae or fungal growth, even those not visible to the naked eye, could be detected by this technique. In addition, it was shown that photography and subsequent digital image analysis could be utilised to estimate the area covered by biofilm growth. The results obtained indicate that LIF spectroscopy in combination with image analysis could be used for field diagnostics of biological growth on insulators in service.
LIST OF PAPERS

This Thesis is a summary of the following papers


THE AUTHOR’S CONTRIBUTION
The author was responsible for and carried out the major part of the work in paper I-V

In paper VI the author was responsible for sample preparation and assisted in the measurement of fluorescence, the analysis of the data and the writing of the paper.

In paper VII the author was responsible for sample preparation and microscopy and assisted in the analysis of the data.

Mathematical processing of data from fluorescence measurements and image analysis were performed by Magnus Bengtsson and Andreas Dernfalk respectively in all studies performed.
# Table of Contents

1 PURPOSE OF THE STUDY .................................................................................................................. 1

2 INTRODUCTION ................................................................................................................................. 3
   2.1 HIGH VOLTAGE INSULATORS ................................................................................................. 3
   2.2 PROPERTIES OF SILICONE RUBBER .................................................................................. 4
   2.3 DEGRADATION MECHANISMS ............................................................................................... 5
   2.4 DIAGNOSTIC METHODS ........................................................................................................... 6
      2.4.1 Accelerated ageing ........................................................................................................... 6
      2.4.2 Analytical tools ............................................................................................................... 6
      2.4.3 On-line measurements .................................................................................................. 7
   2.5 COMPOSITION OF BIOFILMS ............................................................................................... 8
   2.6 DAMAGES CAUSED BY BIOFILMS ...................................................................................... 9
      2.6.1 Fouling ............................................................................................................................ 9
      2.6.2 Degradation of leaching components .......................................................................... 9
      2.6.3 Biotic degradation ......................................................................................................... 10
      2.6.4 Hydration and penetration .......................................................................................... 11
      2.6.5 Color and odor .............................................................................................................. 11
   2.7 PREVENTION OF MICROBIOLOGICAL GROWTH ............................................................... 11
      2.7.1 Biocides .......................................................................................................................... 11
      2.7.2 Cleaning ........................................................................................................................ 12
      2.7.3 Surface modification ...................................................................................................... 12

3 EXPERIMENTAL ................................................................................................................................ 13
   3.1 MATERIALS ............................................................................................................................... 13
      3.1.1 Silicones .......................................................................................................................... 13
      3.1.2 Insulators ........................................................................................................................ 14
      3.1.3 Microorganisms ............................................................................................................. 14
   3.2 GROWTH TESTS ..................................................................................................................... 15
      3.2.1 Powder test, mold ........................................................................................................... 16
      3.2.2 Powder test, algae ......................................................................................................... 16
      3.2.3 IEC 68-2-10, mold .......................................................................................................... 16
      3.2.4 ASTM G21-90, mold ...................................................................................................... 16
1 PURPOSE OF THE STUDY

Silicone rubber high voltage outdoor insulators are sometimes colonised by microorganisms which form a biofilm on the surface of the infected units. This problem was first noted in tropical climates [1-8], but it has now also been observed in temperate environments [9-11]. Since silicone rubbers are considered to be bioresistant materials, the biofouling problem was not expected and little reported research could be found in relevant areas [12-14]. This project was initiated to develop knowledge of the effects of a biofilm on silicone rubbers used as high voltage insulating materials.

Areas of interest for this study included the identification of the microorganisms causing the observed fouling problem, the examination of their effect on the chemical and mechanical properties of infected materials, and the evaluation of different silicone rubber formulations with respect to their ability to hinder biological growth. In addition, potential test methods for the identification of infected silicone rubber insulators in use were explored.
2 INTRODUCTION

2.1 HIGH VOLTAGE INSULATORS

An electrical insulator in a high voltage system is designed to support a charged conductor and electrically isolate it. Insulators made from glass or porcelain have been used for this purpose in power transmission lines for over 120 years. Over the last 40 years new designs have been developed and used for the construction of high voltage insulators. A modern composite insulator, as shown in Fig 2.1, consists of a mechanically supporting structure covered by a housing. The main functions of the housing are to protect the core from environmental stresses and to minimise leakage currents between the energised end and ground [14, 15]. The core often consists of a glass-fibre reinforced resin-bonded rod onto which two metal end-fittings are attached. The housing is made from polymeric materials such as EPDM or silicone rubber. Today it is widely agreed that regarding service performance and ageing, silicone rubber is the best housing material available [16].

Figure 2.1 a) Schematic drawing of a composite insulator. b) Picture of two silicone rubber insulators.
2.2 PROPERTIES OF SILICONE RUBBER

Silicone elastomers made from crosslinked polydimethylsiloxane (PDMS) (Fig. 2.2) mixed with suitable fillers and additives are used in many applications such as medical devices, textile coatings, foams, seals and electrical insulation. The silicone elastomers used as high voltage insulation materials generally contain at least two kinds of fillers, reinforcing fillers to improve the mechanical properties and a flame retardant filler to dissipate heat from energetic events in the high voltage system. Silica is the most common reinforcing filler and the most commonly used flame retardant is alumina trihydrate (ATH) [17]. Furthermore, additives such as antioxidants, colorants, crosslinking agents, processing aids and stabilisers are often used. The types and amounts of fillers are of major importance for the properties of the rubber.

![Fig 2.2 The repeating unit of PDMS](image)

PDMS molecules display low intermolecular forces, high intramolecular siloxane bond energy, high backbone flexibility, and a partially polar backbone. These characteristics give PDMS-rubber a number of properties that make the material suitable for the production of high-voltage insulators [18]:

- Good dielectric properties
- High surface mobility
- Excellent resistance to weathering
- Low surface free energy
- Hydrophobic surface properties
- Non-adhering surface
- Insolubility in water
- Low glass transition temperature
- High thermal and oxidative stability
- Low reactivity, toxicity and combustibility

The low surface free energy of a silicone rubber means that the material has excellent surface hydrophobicity. In addition, silicone rubber has the potential to recover this feature after exposure to ageing factors in the environment. Several plausible mechanisms for the hydrophobic recovery are suggested in the literature. However, most researchers believe that the migration of low molar mass PDMS is the dominant mechanism for the hydrophobic recovery [19].
Other advantages of silicone rubber insulators over conventional porcelain insulators are that they are less attractive targets to vandals, and their lightweight and minor vulnerability make them easy to store, transport and install [20]. The possibility of producing insulators with a smaller surface area and a long leakage path is also advantageous, and this improves the function of the insulator under wet and contaminated conditions [15, 21].

2.3 DEGRADATION MECHANISMS

Even though silicone rubbers (SIR) have a number of characteristics that make the materials suitable for high voltage applications, rubbers are more sensitive than inorganic materials to degradation under exposure to discharges and arcing [22, 23]. Surface-eroding climatic factors such as wind, rain, temperature, and UV radiation, also contribute to the degradation of the rubber, despite the fact that silicones are known to exhibit excellent resistant to weathering. [19, 22, 24, 25].

Electric fields at the edges of high voltage insulators or around water droplets on a hydrophobic silicone rubber surface can give rise to corona discharges [26]. These discharges produce a temporary loss of hydrophobicity [27, 28]. When hydrophobicity is lost, dry-band arcing capable of decomposing the polymeric material may occur [29]. Dry-band arcing causes tracking and erosion and the heat generated can seriously damage the insulating material [30, 31]. Low molecular weight (LMW) silicones, which contribute to the hydrophobic recovery, have relatively low boiling temperatures (<400C), which means that LMW silicones evaporate from the rubber at the elevated temperatures reached [32]. However, the generated heat also form new LMW-chains by inducing chain scission reactions in the material [25, 33].

In addition to electrical ageing factors, silicone rubbers used in high voltage insulators are exposed to severe environmental stresses such as UV-radiation. Even though PDMS-rubber is known to be very stable towards UV-radiation from sunlight, prolonged exposure can lead to crosslinking reactions in the surface of the material [34, 35]. It is also known that exposure of fouled SIR surfaces to UV increases the rate of hydrophobic recovery; indicating that chain scission reactions producing LMW-silicones are induced [36].

All PDMS-materials are highly insoluble in water, but this does not mean that organosilicones do not interact with humid surroundings. For example, water on the surface of silicone rubber gives a temporary loss of hydrophobicity by reorientation of methyl groups and by solubilisation of LMW chains [37]. Acid rain may also affect silicone rubbers. Artificial acid rain with pH 1.5-2.5 has been shown to cause chemical changes in the rubber matrix [38]. Even though natural rainfall never reaches such a low pH, acid rain may still harm an insulator. Fillers such as ATH are more sensitive to acidic pH and can be eroded by acid rain with a pH of about 5 [39]. However, diffusion of LMW-silicones helps silicone rubber materials to recover their original surface properties even after severe exposure to acid rain [40].
Degradation of PDMS through clay-catalysed hydrolysis is a well studied phenomenon [41, 42]. Clay minerals in soil are able to catalyse the hydrolysis of PDMS to dimethylsilanediol, a substance that is accessible to microorganisms and can be biodegraded to CO₂, SiO₂ and H₂O [43-45]. However, organosilicones of higher molecular weight do not provide an easily accessible carbon source for microorganisms. Silicones are artificial materials, and no biological process is known that produces or degrades the covalent bonds of a PDMS-molecule [46]. Therefore, PDMS-materials always respond as bioresistant in biodegradability tests [42]. Nevertheless microorganisms can affect silicone rubber by several different mechanisms, as will be discussed further.

2.4 DIAGNOSTIC METHODS

2.4.1 Accelerated ageing

The diverse interactions of a silicon rubber insulator with its surrounding environment mean that it is complicated to create relevant procedures to simulate the ageing of insulating materials. Even the most ambitious test programs often fail to represent true service conditions [10, 47]. In spite of this, several methods have been designed to test the performance of an insulator or a silicone rubber under the influence of accelerated ageing.

Insulators or test rods can be placed in a fog chamber, were they are energized and exposed to artificial fog, often contaminated with salts or other eroding substances [48, 49]. Tracking wheel tests where samples are dipped in a water-bath and subsequently exposed to a high voltage are also common. [50]. Weatherometer ageing is another method often used to simulate the combined effects of several climatic ageing factors such as UV-radiation, elevated temperature, temperature cycling, thermal shock, high humidity and gaseous contamination. The electrical performance of the insulators or materials is recorded during the tests in order to determine the resistance of the samples to the applied stresses [51].

To reduce the risk of artefacts, insulators can be aged under field conditions. This is time-consuming, but the results obtained are adequate and useful [52, 53]. An unforeseen ageing factor discovered during field ageing was the biofouling of silicone rubber. Insulators aged outdoors in a tropical climate were found to be covered with a greenish-black film of biological origin [2]. None of the techniques for accelerated ageing address the problem of biological growth on the surface of an insulating material.

2.4.2 Analytical tools

Numerous analytical techniques are suitable for studying the changes in the chemical and morphological characteristics of silicone rubber. One often used tool is scanning electron microscopy (SEM), with which it is possible to monitor the surface microstructure of a rubber and thus study morphological changes. After corona exposure, small cracks can be observed at the sample surface. Thermal stress also causes cracks, and UV-radiation makes ATH filler particles appear on the surface of the material [25, 54]. If chemical changes in the silicone
material are to be observed, techniques such as Fourier transform infrared spectroscopy (FTIR) or Electron spectroscopy for chemical analysis (ESCA) are needed. FTIR is commonly used to verify scission or recombination of chemical bonds in the surface layer of silicone rubber, such as the silanol groups formed by oxidation reactions induced by UV-exposure, corona or dry-band arcing [25]. ESCA can be used to study the proportions of different elements at the surface of a silicone rubber insulator. The of C/Si and Si/Al ratios indicate the magnitude of ageing in PDMS and the amount of ATH filler respectively [25, 55].

Another feature that is often affected by ageing is the surface hydrophobicity of the silicone rubber [25, 54]. The most common method used to study the loss and recovery of hydrophobicity is water contact angle measurement. By measuring the angle between the silicone rubber surface and a drop of water, the hydrophobicity of the material can be assessed [22]. Low molecular weight silicones, important for the hydrophobic recovery of a silicone rubber, can be detected by gas chromatography (GC) [56, 57]. If PDMS-oils of higher molecular weights are to be studied, size exclusion chromatography (SEC) is a reliable and often used method [33, 56, 58].

2.4.3 **On-line measurements**

Today there is no standardised or widely used technique for the inspection of composite insulators in service [21]. Nevertheless a majority of utilities examine the condition of their insulators on the line [59]. The most common inspection technique used is visual examination. An experienced inspector can detect surface damage as well as evidence of internal faults just by looking at an insulator. Night vision equipment also enables discharge activity on the surface of the insulator to be distinguished [21, 59, 60].

Manual inspection is however operator-dependent and more objective techniques would be preferred. Infra-red thermography exploits the fact that the degradation caused by electrical events in the high voltage system is associated with heat. The infra-red radiation produced can be used to locate defects in composite insulators from the ground. Electrical field measurement is another promising method for the detection of faulty insulators. At the location of a defect, the electrical field is changed and this change can be recorded. However it is necessary to climb the tower to perform the measurement [59-61].

One disadvantage with the described techniques is that they only detect large defects like puncture and cracks, not fouling or other changes in surface properties of the insulator. New diagnostic methods are needed to detect smaller defects. Digital image analysis is one potentially useful technique. Information extracted from digital images of aged insulators enables features such as loss of hydrophobicity or extent of biofouling to be assessed. [62-65]. Laser-induced fluorescence offers another solution to the problem. By measuring the spontaneous emission of radiation by which electrons in atoms or molecules relaxes from an upper energy level to ground state level, changes in material properties of an insulator can be observed and biological growth detected [66-69].
2.5 COMPOSITION OF BIOFILMS

Microorganisms colonising a bioresistant substrate tend to form a film on the surface of the material. Such a biofilm consists of microorganisms embedded in a highly hydrated matrix of extracellular polymeric substances (EPS), mainly polysaccharides and proteins. Mixed populations of bacteria, fungi, protozoa and algae often coexist in the film [70]. However, in a mature biofilm, the fraction of living cells is often small. Water is the most abundant element in most biofilms and the organic portion of the film is often dominated by EPS. In addition, particulate matter such as clay, humic substances, corrosion products etc. can be included in the mature biofilm. When the cause of a biofouling problem is being sought, it is easy to overlook the small content of microorganisms in the biofilm; thus neglecting the cause of the fouling [71].

Biofilm formation is an interfacial process, and surface features of the microorganisms and the substrate material are important for biofilm adhesion and growth. Interaction forces between adhering cells and substrate, such as van der Waals forces, electrostatic forces and acid base interactions, are of great importance for the initial microbial adhesion [73]. These forces, together with several other factors, some of them summarised in Tab. 2.1, also influence the growth rate and strength of adhesion of a biofilm [72].

Table 2.1

<table>
<thead>
<tr>
<th>Factors affecting the adhesion and growth of a biofilm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Genotypic factors</td>
</tr>
<tr>
<td>Physio-chemical factors</td>
</tr>
<tr>
<td>Stochastic processes</td>
</tr>
<tr>
<td>Deterministic phenomena</td>
</tr>
<tr>
<td>Mechanical Processes</td>
</tr>
</tbody>
</table>

The structure of the biofilm formed varies, depending on the interactions of the microorganisms with the surrounding environment. However, most biofilms have a sponge-like structure containing a system of pores and channels in which a liquid phase is free to move and transport oxygen and nutrients between different parts of the biofilm [72, 74].

From an ecological point of view, life in a biofilm offers many advantages to a cell; such as protection against desiccation, accumulation of nutrients from the bulk water phase, protection against toxic substances, facilitated exchange of genetic material and opportunities for co-metabolism [70, 72]. The incitement for biofilm formation is therefore strong and biofilms are abundant in nature.
2.6 DAMAGES CAUSED BY BIOFILMS

A biofilm can affect the properties of a polymeric material by several different mechanisms. Undesired effects range from discoloration to complete degradation of the polymeric material. Some of the major damaging mechanisms are summarised in figure 2.3 [70].

<table>
<thead>
<tr>
<th>Process</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fouling</td>
<td>Change in surface properties</td>
</tr>
<tr>
<td>Degradation of leaching components</td>
<td>Loss of stability</td>
</tr>
<tr>
<td>Biotic degradation</td>
<td>Loss of stability</td>
</tr>
<tr>
<td>Hydration Penetration</td>
<td>Conductivity Swelling</td>
</tr>
<tr>
<td>Colour</td>
<td>Change in appearance</td>
</tr>
</tbody>
</table>

*Figure 2.3 Undesired effects caused by a biofilm*

2.6.1 Fouling

Many polymeric materials are considered to be inert to microbial attack. However, these materials may still function as a support for a biofilm. The unwanted deposition of biological matter is referred to as fouling [75]. If the colonised material resists degradation, microorganisms can use pollutants from the surroundings to gain nutrition [76-78]. This was the case at a Florida-based transmission station where silicone bushings were trapping airborne pine pollen that served as a feedstock for a severe mould growth [8]. This ability of a biofilm to use an external carbon source makes laboratory testing difficult. Materials that seem to be inert in degradation studies may nevertheless encourage growth when exposed to outdoor conditions [79].

A fouling problem does not change the bulk properties of the infected material; it can however disturb the surface properties of the colonised object. When a silicone rubber insulator is covered by a hydrophilic biofilm, the hydrophobic surface properties are reduced. This has been shown to cause an increase in leakage current under wet conditions, compared to clean insulators [8].

2.6.2 Degradation of leaching components

Plastics and rubbers often contain additives and impurities that may leak from the matrix to the surroundings and interact with a biofilm. Impurities such as unreacted low molecular weight material and residual processing aids can provide nutrients for an attached biofilm [77]. Fillers such as adiapates, epoxidised fatty acids, oleates, stearates and polyesters are also known to serve as nutrients for biological growth [80]. The same is true of carbon-based plasticizers and many other additives [70, 77, 80]. There are indications that some silicone
rubber materials used in high voltage insulators contain additives susceptible to microbiological attack [7, 10].

In contrast, accelerators such as dithiocarbamates and sulphur-based components may inhibit growth, as may residual heavy metal catalysts and many other additives [77, 80]. Field studies have shown that not all insulators are affected by biological growth. This may be due to the protective effect of additives used in the production of the silicone rubber.

2.6.3 Biotic degradation

If a polymer is to be used as a source of nutrition for biological growth, it has to be degraded to segments small enough to be transported across the cell membrane [81]. This degradation can be mediated by degrading factors in the surrounding environment, such as wind, rain, oxygen, UV-radiation etc [82]. However, degradation can also be directly initiated by the living cell through the production of degrading substances such as enzymes, radicals or organic acids [82-86].

Surface degradation is an interfacial process depending on parameters such as pH, redox potential and the concentration of oxygen and salts. Biofilms can strongly influence these parameters [70]. Microorganisms sometimes excrete organic acids as by-products of metabolism. The excretion of organic compounds is usually the result of an unbalanced growth, a surplus or a limited supply of some compound essential for the metabolism of the microorganism. Anions, that are final products of microbial metabolism, react with cationic components and form salts. An increase in the salt concentration or a drop in the pH may facilitate the breakdown of the polymer [85].

Microorganisms can also incite the breakdown of an insoluble polymeric material by the production of exoenzymes, capable of mediating degradation outside the cell. It has been suggested that siloxane oils degrade under the influence of enzymes produced by bacteria [87], and there are indications that silicone rubber voice prostheses degrade under the influence of a mixed biofilm [88, 89]. The three most probable processes by which enzymes influence polymer degradation are [84]:

1. Hydrolysis by lysosomal enzymes of susceptible polymers
2. The oxidation of polymers by oxidase enzymes
3. The breakdown of natural biopolymer structures by enzymes such as collagenase

Many molds develop powerful enzyme systems with the ability to degrade highly stable polymeric structures. Among these, the white rot fungi hold a unique position. This class of molds has developed non-specific mechanisms for degrading the complex polymeric structure of lignin. The enzyme system responsible for the degradation includes peroxidases that promote the reduction of peroxides to free radicals [90-93]. It has been suggested that the white rot fungus *Phanerochaete chrysosporium* is able to degrade PDMS as well as lignin [94].
2.6.4 Hydration and penetration

Fungal hyphae can penetrate their support and thereby cause cracks and pores in the material. The mechanism of the penetration is unclear, but it is known that hyphae are able to create great turgor pressures that force the cells through the material. This leads to a decrease in mechanical stability and offers a way for water to enter the polymeric material [70, 95]. The latter may increase the electrical conductivity of an insulating material.

2.6.5 Color and odor

Many microorganisms produce pigments. These pigments are often lipophilic and therefore tend to diffuse into the matrix of a polymeric material. The stains produced are impossible to remove by simple cleaning [70, 78]. In addition, metabolites from biodegradation are sometimes sources of odour. A small concentration of a substance can be enough to cause problems [80]. However, this problem is of an aesthetic nature and does not affect the insulating properties of the silicone rubber.

2.7 PREVENTION OF MICROBIOLOGICAL GROWTH

2.7.1 Biocides

Active substances that eliminate microorganisms or inhibit their reproduction are denoted biocides. Numerous additives of this kind exist on the market, and it is a demanding task to choose a biocide able to protect a high voltage insulator from biological growth. It is important that the substance is compatible with the rubber and does not affect its properties. It is also necessary that the biocide effectively kills unwanted microorganisms, while leaving people and the environment unharmed. In addition, to be effective in an outdoor environment, inhabited by an enormous variety of microorganisms, a biocide has to have a broad effectiveness spectrum and offer small probability for microorganisms to develop resistance to the active substance [78, 80].

High voltage insulators are meant to function in an outdoor environment for many years with no need for service or replacement. This put demands on biocides that often have to be present on the surface of the silicone rubber in a certain minimum concentration to be effective. The active substance consequently has to be effective in low concentrations and have a low washout if it is required to be active over a long period of time [78]. It is important to take the washout effect into account when testing the effectiveness of a biocide. It has been shown that a biocide with a high initial activity can become inactivated after a period of outdoor storage. This may be due, for example, to washout or inadequate light stability [80].

It is quite common to use a biocide not as an additive to prevent growth but as a surface treatment to kill a mature biofilm. This is not to be recommended since the biocide kills the microorganisms, but it does not remove the dead biomass from the system. The accumulation of biodegradable organic material often give rise to a rapid microbial regrowth [71, 96].
2.7.2 Cleaning
Cleaning an infected material removes dead biomass from the system and thus makes the surface less attractive for microorganisms. A rational cleaning often includes two steps, one where the physical stability of the biofilm is weakened and a second in which the biofilm is removed from the system. Oxidisers or detergents are useful for the first step, while flushing, brushing or similar physical techniques are useful for the second step. [71]. Tests performed on silicon rubber insulators shows that water repellent properties and other properties disturbed by the biofilm were partially restored after cleaning with alcohol and high pressure water [8].

2.7.3 Surface modification
The hydrophobic nature of a silicone rubber contributes to its resistance to utilisation by microorganisms. Water and nutrients are essential for all kinds of biological growth and both are limited on a hydrophobic surface where water forms droplets that run off the material washing nutrients away [77]. In addition, the hydrophobicity substantially decreases the rate of hydrolysis and microbial attack of the polymer [82].

The low surface free energy of silicone rubber makes it useful in the production of non-stick coatings [97]. Silicone rubber is used in applications were biofouling cannot be avoided, such as in the coating of fishing nets. The weak adhesion between the adhering biofilm and the silicone-coated net facilitates cleaning [98]. Changing the microstructure of the rubber surface can further strengthen the non-stick characteristics of the silicone rubber. Micro-scale riblets or pyramids printed on to the surface of a silicone rubber sample may protect the material from biofouling [99, 100].
3 Experimental

3.1 Materials

3.1.1 Silicones

PDMS rubber base with 20% SiO₂ filler and 0.52% di(4-methyl benzoyl)peroxide added as crosslinker was mixed with Martinal OL-104 S vinylsilane surface treated aluminium trihydrate (ATH) and Firebrake 290 zinc borate delivered by Wacker Silicone as shown in table 3.1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Material</th>
<th>Flame retardant (pph)</th>
<th>Flame retardant %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Base</td>
<td>No flame retardant added</td>
<td>No flame retardant added</td>
</tr>
<tr>
<td>2</td>
<td>Base + ATH</td>
<td>100 pph ATH</td>
<td>50% ATH</td>
</tr>
<tr>
<td>3</td>
<td>Base + ATH + zinc borate</td>
<td>90 pph ATH + 10 pph zinc borate</td>
<td>45% ATH + 5% zinc borate</td>
</tr>
<tr>
<td>4</td>
<td>Base + zinc borate</td>
<td>10 pph zinc borate</td>
<td>9% zinc borate</td>
</tr>
<tr>
<td>5</td>
<td>Commercial mix</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
</tbody>
</table>

Table 3.1

Type and amount of flame retardant added to the silicone rubber materials

Materials were kneaded at 12 rpm in a Brabender internal mixer for 15 min prior to curing. The curing was performed in a Schwabentan Polystat press for 10 min at a temperature of 180°C and a pressure of 10 MPa. The resulting discs had a diameter of 200 mm and a thickness of 2 mm. Samples were post-cured for 4 h in a hot air oven at 200°C before use. The commercial material was pressed and cured in accordance with instructions from the supplier.

To study the degradation of PDMS mediated by enzymes or radicals more defined materials were needed. Silicone oil with a viscosity of 100 cSt and decamethyltetrasiloxane from Sigma Aldrich were used together with a platinum catalysed PDMS rubber. The rubber was prepared by mixing vinyl terminated PDMS oil with crosslinker (6% of methylhydrodimethylsiloxane) and catalyst (35 ppm of a platinum divinyltetramethyldisiloxane complex).
The curing was performed in a Pasadena Hydraulics Inc. 0230 press for 15 min at 135°C under a pressure of 2 MPa [101].

3.1.2 Insulators

Insulators infected by biological growth were collected from the Bagamoyo test station, Tanzania (tropical climate), the University of Peradeiya, Sri Lanka (tropical climate) and the Anneberg test station, Sweden (temperate climate). The insulators had been in service for several years and no information about the composition of the materials used for production of the housings was available.

The worst infected parts of the insulators were analysed with ESEM/EDX before and after gentle cleaning with a soft cloth dampened with distilled water. Small pieces of rubber cut from the centre of the insulators were used as reference.

3.1.3 Microorganisms

Isolates

Microorganisms were isolated from the studied insulators by inoculating different growth media with finely grained biofilm suspended in water. Algae were grown on BG 11, a medium designed for the isolation of green and blue-green algae, and Jaworski’s medium with added NaSiO₃ for the isolation of green algae and diatoms [102]. Fungal growth was observed on potato dextrose agar and malt extract agar; i.e. two commonly used undefined media designed for the growth and isolation of fungi [103]. Isolation was than made from malt extract agar diluted to one tenth of the recommended concentration. This medium is poor in nutrients and thus resembles the natural habitat of the isolated fungi better than the nutrient-rich medium used for observation.

Hyphal tips, colonies or spores were selected for isolation. 50 fungal cultures and 20 algae cultures from each biofilm were isolated. Each fungal culture was subcultured three times on malt extract agar and algae were subcultured three times on BG 11 (as agar and in liquid dilution series). All isolates were visually examined and studied under a light microscope to roughly determine their class. The three most common fungal species isolated from each biofilm were sent to Centraalbureau voor Schimmelcultures, the Netherlands, for identification, while algae cultures were submitted to the Department of Agricultural Microbiology, Agricultural University of Wroclaw, Poland.

Standard test organisms

The molds prescribed in standard tests and the molds used in the degradation studies performed are listed in Tab. 3.2. All microorganisms were grown and kept in accordance with instructions given by the supplier.
Table 3.2
Fungal strains used in standard tests and degradation studies

<table>
<thead>
<tr>
<th>Fungal specie</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspergillus niger</td>
<td>DSMZ – Strain DSM 1957</td>
</tr>
<tr>
<td>Aspergillus terreus</td>
<td>DSMZ – Strain DSM 1958</td>
</tr>
<tr>
<td>Aureobasidium pullulans</td>
<td>DSMZ – Strain DSM 2404</td>
</tr>
<tr>
<td>Chaetomium globosum</td>
<td>DSMZ – Strain DSM 1962</td>
</tr>
<tr>
<td>Paecilomyces varioti</td>
<td>DSMZ – Strain DSM 1961</td>
</tr>
<tr>
<td>Penicillium funiculosum</td>
<td>DSMZ – Strain DSM 1944</td>
</tr>
<tr>
<td>Scopulariopsis brevicaulis</td>
<td>DSMZ – Strain DSM 9122</td>
</tr>
<tr>
<td>Trichoderma virids</td>
<td>DSMZ – Strain DSM 1963</td>
</tr>
<tr>
<td>Phanerochaete chrysosporium</td>
<td>DSMZ – Strain DSM 1556</td>
</tr>
<tr>
<td>Phanerochaete chrysosporium</td>
<td>CBS – Strain CBS 481.73</td>
</tr>
<tr>
<td>Phanerochaete chrysosporium</td>
<td>ATCC – Strain 34541</td>
</tr>
</tbody>
</table>

3.2 GROWTH TESTS

The resistance of silicone rubber to biological growth was tested using standard test procedures in combination with new methods developed for this study. All the samples used were washed with 70% ethanol and dried in a sterile air-flow overnight before inoculation with microorganisms. Inoculation was mediated by spraying the surface of the samples with suspensions of microorganisms, at the same time controls were inoculated with sterile medium. Unless otherwise stated, tests were performed in triplicate on circular samples with a diameter of 30 mm and a thickness of 2 mm. In most cases, the extent of biological growth was judged according to the scale in Tab. 3.3.

Table 3.3
Scale for determining the extent of growth on the specimens.

<table>
<thead>
<tr>
<th>No.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>No growth apparent under a nominal magnification of 60×</td>
</tr>
<tr>
<td>1</td>
<td>Growth not, or hardly visible to the naked eye, but clearly visible under the microscope</td>
</tr>
<tr>
<td>2</td>
<td>Growth plainly visible to the naked eye, but covering less than 25% of the test surface</td>
</tr>
<tr>
<td>3</td>
<td>Growth plainly visible to the naked eye and covering more than 25% of the test surface</td>
</tr>
<tr>
<td>4</td>
<td>Growth plainly visible to the naked eye and covering more than 50% of the test surface</td>
</tr>
</tbody>
</table>

A stereomicroscope with 20x ocular and 3x objective was used to evaluate the samples. In cases where the contrast between biological growth and sample surface was low, SEM was used for the evaluation.
3.2.1 Powder test, mold
Zinc borate and ATH were mixed into malt extract agar in concentrations from 20 pph to 100 pph. The resulting agar was sprayed with suspensions of fungal spores in distilled water. Three different suspensions were prepared, one for each country studied, by pouring 15 ml of distilled water onto the surface of the fungal isolates. The wetted surface of each culture was scraped with a sterile platinum wire and the suspended spores were filtered through a thin layer of glass wool to an Erlenmeyer flask containing glass beads. Suspensions were shaken to break clusters of spores and mix the suspension. The resulting liquid was used for inoculation of samples. Samples were incubated in room temperature for 28 days prior to evaluation.

3.2.2 Powder test, algae
Zinc borate and ATH were mixed into BG11 agar [102] in concentrations from 20 pph to 100 pph. The resulting agar was sprayed with suspensions of algae cells in BG11 liquid growth medium. Suspensions were prepared by pouring 15 ml of BG11 onto the surface of the algae isolates. The wetted surfaces were scraped with a sterile platinum wire and the resulting liquid was used for inoculation of the samples. Samples were incubated at room temperature in a window for 28 days prior to evaluation.

3.2.3 IEC 68-2-10, mold
The silicone rubber materials described in Tab. 3.1 were tested in accordance with the basic environmental testing procedure IEC 68-2-10, part 2, test J, mold growth. However, in some of the experiments, the microorganisms stipulated in the standard test were replaced by the fungal isolates. Two variations of the test were carried out; the first one specified inoculation of the specimen with a suspension of mold spores in distilled water, while the second variation specified inoculation with mold spores suspended in a nutrient solution. Samples were incubated for 84-days in 98% humidity at 28°C prior to evaluation.

3.2.4 ASTM G21-90, mold
The silicone rubber materials described in Tab. 3.1 were tested in accordance with the ASTM G21-90 standard practice for determining the resistance of synthetic polymeric materials to fungi. However, in some of the experiments, the microorganisms stipulated in the standard test were replaced by the fungal isolates. Samples of virgin materials and materials aged with oxygen plasma were incubated for 84-days in 98% humidity at 28°C prior to evaluation.

3.2.5 ASTM D 5589-97, algae
The silicone rubber materials described in Tab. 3.1 were tested in accordance with the ASTM D 5589-97 standard test method for determining the resistance of paint film and related coatings to algal defacement. The algal isolates were used as test organisms. Samples were incubated in room temperature under a fluorescent lamp with a cycle of 14 h light and 10 h darkness for 21-days at a relative humidity of ≥ 85% prior to evaluation.
3.2.6 Quick test, mold

10 ml of water was added to each of the following mold cultures: *Aspergillus niger*, *Trichoderma virens*, *Chaetomium globosum*, *Penicillium funiculosum* and *Aureobasidium pullulans*. The surfaces of the wetted cultures were scraped gently with a flame-sterilised platinum wire. The suspended spores were filtered through a thin layer of glass wool to an Erlenmeyer flask prepared with 20 solid glass beads. The mixture was then diluted with distilled water to a volume of 100 ml and the flask was shaken to mix the spores. Samples of the silicone rubber materials described in Tab. 3.1 were put on malt extract agar. Virgin materials as well as materials aged with oxygen plasma were tested. The mounted samples were sprayed with the mixed spore suspension and the containers were sealed to maintain a moist atmosphere. The sealed Petri discs were stored in room temperature for 28 days prior to evaluation.

3.2.7 Microenvironment chambers

Discs of the materials described in Tab. 3.1 were cut into plates shaped as a quarter of a circle with a radius of 10 cm. Three plates of each material were hung in inclined positions using nylon thread. The lowest plate of each material was divided into two sections. One was mechanically aged with sandpaper; the other was aged with oxygen plasma just before inoculation with microorganisms.

The assemblies of the five studied materials were placed in four closed microenvironment chambers as shown in Fig 3.1. Three chambers represented the studied countries respectively. The fourth was used as a reference chamber with negative control specimens. All chambers were maintained at a temperature of approximately 25°C and a relative humidity of ≥85%. A daylight lamp with a cycle of 12 h light and 12 h darkness was used to provide the UV radiation necessary for algae growth.

![Figure 3.1 Schematic drawing of a microenvironment chamber.](image)

30 day old mixed cultures, containing algae bacteria and fungi from the different biofilms, were harvested from BG11 agar by pouring 10 ml of BG11 liquid broth onto the agar surface and gently scraping the microorganisms with a sterile platinum wire. Plates were inoculated...
with a solution of microorganisms from the specific country by spraying. All specimens were reinoculated with microorganisms suspended in BG 11 once a week during the first five months of the experiment, to create a self-sustaining biofilm; thereafter samples were reinoculated once every month to support the growing biofilm. Reference samples were sprayed with sterile BG11 liquid broth.

Samples were photographed and evaluated by image analysis and laser-induced fluorescence after 6 months of incubation. After one year, the effects of the biofilms on the materials tested were studied using ESEM/EDS and IR. At the same time, the hydrophobicity of the second sample in each assembly of materials were evaluated in accordance with instructions given in STRI Guide 8, were the drop pattern formed after wetting of a surface is studied in order to assess surface hydrophobicity [104, 105]. Hydrophobicity was recorded before and after gentle cleaning of the tested surface with a cloth damped with distilled water.

3.3 LASER-INDUCED FLUORESCENCE

In order to study the effect of mold growth on the laser-induced fluorescence of different silicone rubber materials a series of samples, listed in Tab. 3.4, was prepared by spraying the materials described in Tab. 3.1 with suspensions of mold spores. Fungal spore suspensions were prepared by pouring 20 ml of IEC 68-2-10 fungal nutrient medium on the agar surface of each of the fungal isolates. The surfaces of the wetted cultures were scraped gently with a flame-sterilised platinum wire. The resulting suspensions were filtered through thin layers of glass wool to Erlenmeyer flasks prepared with 30 ml of IEC 68-2-10 nutrient medium and 10 solid glass beads. The flasks were shaken and the suspensions were sprayed onto the silicone rubber samples. All samples were incubated for 45 days at 27°C and 95% relative humidity before measurements were conducted.

<table>
<thead>
<tr>
<th>Fungal strain used</th>
<th>Materials tested</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Epicoccum nigrum</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>Microsphaeriopsis</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Cladosporium cladosporioides</strong></td>
<td>x</td>
</tr>
<tr>
<td><strong>Fusarium semitectum</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Polyscytalum fecundissimum</strong></td>
<td>x</td>
</tr>
<tr>
<td><strong>Stagonospora</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Curvularia lunata</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Cladosporium tenuissimum</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Clean materials</strong></td>
<td></td>
</tr>
</tbody>
</table>

A laser generating radiation in pulses (3 ns, ~15 Hz, ~1 µJ) at a wavelength of 337 nm was used to study samples from the microenvironment chamber as well as the samples listed in
Tab. 3.4. Each spectrum was accumulated from 100 laser pulses and 20 spectra were collected from each sample. The laser light was guided via a telescope through a fused silica optical fibre, 600 µm in diameter, to the sample under investigation. The tip of the fibre was placed about 1 mm above the sample. The laser-induced fluorescence was spatially emitted in all directions and a fraction of it was collected by the same fibre and guided back to an optical multi-channel analyser system. The resolution of the system, set by the 100 µm slit width, was 2.2 nm, and the spectrum could be recorded up to 805 nm. A detailed description of the system can be found in Ref. [106].

Data obtained from the analysis were pre-processed by mean normalisation and mean centring in order to produce a fluorescence spectrum representing the sample. In some cases, this spectrum was simplified using principal component analysis (PCA) that projects the large data set of the spectra analysed into a smaller set of data that is easier to overview. The first principal component (PC1) is the combination of variables that explains the greatest amount of variation between spectra. The second PC (PC2) describes the second greatest amount of variation orthogonal to the first PC and so on. Higher order PCs correspond to small variances and can be seen as noise [107].

### 3.4 IMAGE ANALYSIS

Samples were laid flat on a blue background and photographed using a standard Canon IXUS V3 digital colour camera. The image analysis was then performed in six steps using Matlab.

1. In the first step, the background was separated from the sample. This was done by determining differences in colour between sample and background. First, each image was represented as a set of three matrices, containing intensity values of the red, green and blue components, respectively. The blue component was then divided by the sum of the three colour components. The quotient of this operation differs between sample and background; hence the sample can be separated from the background through intensity thresholding [108]. The result of this operation is a black and white image of the sample alone.

2. In the second step, the possible influence of shading at the sample edge was removed by erosion of the image by a circular element, removing object pixels at its boundaries.

3. The third step produced a colour image of the sample from the black and white image obtained in the two first steps by multiplication of this image by the original colour image.

4. The fourth step compensated for illumination variations by dividing the sample into a set of sub-images in which the maximum values are identified and used to calibrate the remaining operations.

5. The fifth step separated biological growth from silicone rubber. Again, the blue component of the image was used for segmentation of the sample into covered and non-covered areas by means of intensity thresholding [109]. Blue was selected since
the contrast between the rubber and the biofilm was highest in this component. The resulting black and white image separates regions of growth from clean regions. Finally, the covered area was calculated by counting the numbers of pixels classified as growth. To avoid the need for calibration, the covered area was always related to the area classified as sample surface.

3.5 DEGRADATION STUDIES

In order to decide whether the chemical bonds of the PDMS molecule can be affected by biologically mediated processes, an unfilled PDMS rubber, PDMS oil and a DMS oligomer were treated with lignin-degrading enzymes or radicals produced through the Fenton mechanism. In each case 0.020 g of the sample was weighed into a 100 ml Erlenmeyer flask where the reaction was performed. Samples and reference samples were set in triplicates.

After treatment, PDMS rubber was removed from the reaction vessel and studied with SEM and IR. Oils and oligomers were extracted to chloroform according to the following procedure.

1. The content of the Erlenmeyer flask was filtered through a finely meshed strainer into a separation funnel, and solid matter caught by the mesh was returned to the Erlenmeyer flask.
2. 10 ml of chloroform was then added to the separation funnel and the funnel was manually agitated for 5 min.
3. After 5 min equilibration the chloroform phase was emptied into the Erlenmeyer flask.
4. Steps two and three were then repeated with fresh chloroform.
5. Finally, the Erlenmeyer flask was treated in an ultrasonic bath for 10 min.

After extraction PDMS oil was analysed using SEC and GC/FID, while PDMS oligomers were analysed with GC/FID only.

3.5.1 Enzymatic degradation

According to United States Patent No 6,020,148, the lignin-degrading fungus Phanerochaete chrysosporium is capable of degrading the siloxane bond of PDMS [94]. The growth medium prescribed in the patent is known to promote the formation of peroxidases [110]. The test described was repeated twice, using fungal strains from DSMZ and CBS respectively, in order to study the degradation process. In addition, the trial was repeated a third time using an optimised growth medium and an ATCC strain of Phanerochaete chrysosporium [111, 112].

Optimised growth medium was prepared by dissolving 0.1 g (NH₄)₂SO₄, 20 g glucose, 1.0 g KH₂PO₄, 0.2 g NaHPO₄, 0.5 g MgSO₄·7H₂O, 0.017 g MnSO₄·H₂O, 10 µg ZnSO₄·7H₂O, 20 µg CuSO₄·5H₂O, 100 µg CaCl₂, 100 µg FeSO₄·7H₂O and 5 µg thiamine in 50 mM Malonate
buffer spiked with 0.1% Tween 80. The pH was adjusted to 4.5 before the addition of fungal spores.

Samples were incubated as stationary cultures in 20 ml liquid growth medium at 30°C for a period of 60 days before extraction and analysis.

3.5.2 Degradation by Fenton mechanism
When hydrogen peroxide and Fe$^{2+}$ react, OH• radicals are formed through Fenton mechanism. These radicals may be able to degrade the chemical bonds of PDMS [113]. A simple Fenton reaction was performed as follows: 10 ml of a 10 mmol/L solution of FeSO$_4$*7H$_2$O was added to each sample. Reaction was then initiated by drop wise addition of 10 ml of a 1 mol/L solution of H$_2$O$_2$. The reaction was completed at room temperature overnight before extraction and analysis.

3.6 INSTRUMENTATION

3.6.1 Oxygen plasma ageing
Oxygen plasma aging was performed in a V15-G microwave frequency reactor from Plasma-Finish GmbH, operated at 2.45 GHz and 100 W for 180 s at an oxygen pressure of 28 Pa and a gas flow of 50 ml/min.

3.6.2 Light microscopy
A Leitz Ortholux II POL-BK optical microscope was used to study the biofilms and the isolated microorganisms.

3.6.3 SEM
A Jeol JSM-5400 Scanning Electron Microscope was used at an acceleration-voltage of 10 kV. Samples were dried in vacuum at room temperature overnight and sputtered with palladium/gold before analysis.

3.6.4 ESEM/EDS
An XL TMP (W) Environmental Scanning Electron Microscope from FEI/Philips was used in the low vacuum mode at an acceleration voltage of 10 kV. Microanalysis for determination of atomic composition in the surface layer was carried out with an EDS-system from EDAX.

3.6.5 IR
Infrared spectra were recorded on a Perkin Elmer Spectrum 2000 FTIR equipped with a golden gate normal single reflection ATR accessory. Infrared absorption was recorded from 600 to 4000 cm$^{-1}$.  

21
3.6.6 **GC/FID**

A Varian 3400 Gas Chromatograph equipped with a flame ionisation detector and a CP8752 column, 30 m x 0,32 mm, film thickness 0,25 μm, from Varian was used. The column temperature was raised from 40°C to 250°C at a rate of 10°C/min. The injector was used in split mode at 250°C, while the detector was operated at 275°C.

3.6.7 **SEC**

A 510 Size Exclusion Chromatograph from Waters equipped with three PLgel 10μm mixed-B columns, 300x7,5 mm, from Polymer Labs was used at room temperature and a flow rate of 1 ml/min. Spectra were recorded with a PL-ELS 1000 evaporative light scattering detector.
4 RESULTS AND DISCUSSION

4.1 COMPOSITION OF BIOFILMS

Biofilms are complex structures in which a multitude of microorganisms from different biological classes may coexist, compete or co-operate. The composition of the biofilm affects its interaction with the support material [70]. Therefore it is important to know the composition of the biofilm colonising the surface of interest, in this case silicone rubber insulators.

In this work, three different biofilms, collected from silicone rubber insulators exposed to the outdoor environment in Sweden, Sri Lanka and Tanzania, have been analysed. Filamentous fungi and micro algae in association with bacteria were isolated from the biofilms under study. Even though the insulators were collected from three different continents, the compositions of the biofilms studied were remarkably similar. Small unicellular green algae of the *Chlorella* family, living in symbiosis with bacteria, dominated the biofilms and traces of filamentous fungi were spread through the algae matrix. The similarity between the different biofilms indicates that the mechanism of biofouling of silicone rubber insulators is the same all over the world. The identified species, listed in Tab. 4.1, were therefore used to test the resistance of several silicone rubber formulations to biological growth.

Table 4.1
Microorganisms used for inoculation of silicone rubber samples.

<table>
<thead>
<tr>
<th>Country</th>
<th>Fungi</th>
<th>Algae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweden</td>
<td><em>Epicoccum nigrum</em></td>
<td><em>Chlorella saccharophila</em></td>
</tr>
<tr>
<td></td>
<td><em>Microsphaeriopsis</em>(^1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Cladosporium cladosporioides</em></td>
<td></td>
</tr>
<tr>
<td>Sri Lanka</td>
<td><em>Fusarium semitectum</em></td>
<td><em>Chlorella vulgaris var. Autotrophica</em></td>
</tr>
<tr>
<td></td>
<td><em>Polyscytalum fecundissimum</em></td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Stagonospora</em>(^2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Curvularia lunata</em></td>
<td><em>Chlorella vulgaris var. Autotrophica</em></td>
</tr>
<tr>
<td></td>
<td><em>Cladosporium tenuissimum</em></td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) Not possible to identify on species level. \(^2\) This anamorph has not been given a formal name.
4.2 EFFECT OF ADDITIVES

Not all insulators in the field are affected by biological growth, indicating that some formulations are protected. In an attempt to identify the source of the observed differences in sensitivity, it was decided to analyse some of the materials used. The investigation was soon focused on the effect of the flame-retardants. A series of tests, designed to determine the sensitivity of a polymeric material and its additives to microbiological growth, was developed and used to evaluate the effect of zinc borate and alumina trihydrate (ATH) on biological growth. Results of the tests were evaluated according to the scale given in Tab. 3.3, in which 0 denotes a clean surface and 4 a surface covered to more than 50 % by biological growth.

4.2.1 Powder tests

Tests with flame-retardants, zinc borate and ATH, as powder mixed in growth medium were performed in order to study the immediate influence of these chemicals on microbiological growth. As can be seen in Tab. 4.2, mold growth was not hindered on any of the samples containing ATH. Zinc borate on the other hand seems to have a preventive effect on the growth of mold, as can be seen in Tab. 4.3. The extent of growth on samples with added zinc borate is dependent on the concentration of additive as well as on the types of microorganisms tested. It seems that while molds from Tanzania is very sensitive to the toxic effects of zinc borate, molds from Sri Lanka and Sweden are able to tolerate higher concentrations of the substance.

Table 4.2
Extent of mold growth on 3 samples for each concentration of ATH.

<table>
<thead>
<tr>
<th>Concentration of ATH (pph)</th>
<th>Sweden</th>
<th>Sri Lanka</th>
<th>Tanzania</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>40</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>60</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>80</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>100</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 4.3
Extent of mold growth on 3 samples for each concentration of zinc borate.

<table>
<thead>
<tr>
<th>Concentration of zinc borate (pph)</th>
<th>Sweden</th>
<th>Sri Lanka</th>
<th>Tanzania</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>40</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>60</td>
<td>3</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>80</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>
Further testing showed that zinc borate powder could prevent algal growth as well as mold growth. As can be seen in Tab. 4.4, the addition of ATH to the algae culture medium did not affect the growth of algae. On the other hand, addition of zinc borate inhibited algal growth as shown in Tab. 4.5. The living algae cells sprayed on the surface of the agar could not reproduce when zinc borate was added to the medium. When the concentration of zinc borate was high, all the algae cells died and lost their green colour.

**Table 4.4**  
Extent of algae growth on 3 samples for each concentration of ATH.

<table>
<thead>
<tr>
<th>Concentration of ATH (pph)</th>
<th>Sweden</th>
<th>Sri Lanka</th>
<th>Tanzania</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 2 3</td>
<td>1 2 3</td>
<td>1 2 3</td>
</tr>
<tr>
<td>20</td>
<td>4 4 4</td>
<td>4 4 4</td>
<td>4 4 4</td>
</tr>
<tr>
<td>60</td>
<td>4 4 4</td>
<td>4 4 4</td>
<td>4 4 4</td>
</tr>
<tr>
<td>100</td>
<td>4 4 4</td>
<td>4 4 4</td>
<td>4 4 4</td>
</tr>
</tbody>
</table>

**Table 4.5**  
Extent of algae growth on 3 samples for each concentration of zinc borate.

<table>
<thead>
<tr>
<th>Concentration of zinc borate (pph)</th>
<th>Sweden</th>
<th>Sri Lanka</th>
<th>Tanzania</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 2 3</td>
<td>1 2 3</td>
<td>1 2 3</td>
</tr>
<tr>
<td>20</td>
<td>2 2 2</td>
<td>0 0 0</td>
<td>2 2 2</td>
</tr>
<tr>
<td>60</td>
<td>0 0 0</td>
<td>0 0 0</td>
<td>0 0 0</td>
</tr>
<tr>
<td>100</td>
<td>0 0 0</td>
<td>0 0 0</td>
<td>0 0 0</td>
</tr>
</tbody>
</table>

The powder tests developed for this study are fast and easy to use. A clear trend was observed already one week after incubation, and after 28 days it could definitely be concluded that zinc borate is toxic to the microorganisms tested, while ATH is not. However, for some of the species, a very high concentration of zinc borate was needed to effectively hinder growth. This should not be interpreted as meaning that zinc borate is not effective as a growth suppressor in silicone rubber materials. Growth conditions are very poor on the surface of a silicone rubber material compared to those in the agar used in the powder tests, where nutrients are abundant.

**4.2.2 Tests of silicone rubbers**

The difference in growth conditions between powder tests and tests performed on polymeric materials was clearly shown when silicone rubber materials containing ATH or zinc borate were evaluated. The silicone rubber formulations described in Tab. 3.1 were subjected to a series of tests to determine their resistance to biological growth.

Two variations of the standard procedure IEC 68-2-10, designed for the determination of the resistance of a material to mold growth, were used in the present work; one in which nutrients that support mold growth were added to the silicone rubbers together with the spores and one in which the specimens were inoculated with nothing but mold spores and water. In the latter case, the fungi must use the supporting rubber as the single source of nutrient for growth.
Tests were carried out with standard test organisms and with organisms isolated from the insulators studied in this work. Results of the tests are shown in Tab. 4.6 and Tab. 4.7.

Table 4.6
IEC 68-2-10 Extent of mold growth on silicone rubber treated with spores and nutrients.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sweden</th>
<th>Sri Lanka</th>
<th>Tanzania</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 2 1</td>
<td>2 3 3</td>
<td>1 2 3 1</td>
<td>2 2 2 3</td>
</tr>
<tr>
<td>Base</td>
<td>3 3 3</td>
<td>3 1 1</td>
<td>2 2 2</td>
<td>3 3 3</td>
</tr>
<tr>
<td>Base + ATH</td>
<td>3 3 3</td>
<td>1 1 1</td>
<td>3 3 3</td>
<td>3 3 3</td>
</tr>
<tr>
<td>Base + ATH + ZnBO3</td>
<td>3 3 3</td>
<td>0 0 0</td>
<td>2 2 2</td>
<td>3 3 3</td>
</tr>
<tr>
<td>Base + ZnBO3</td>
<td>2 2 2</td>
<td>0 0 0</td>
<td>2 2 2</td>
<td>3 3 3</td>
</tr>
<tr>
<td>Commercial mix</td>
<td>3 3 3</td>
<td>2 2 2</td>
<td>3 3 3</td>
<td>3 3 3</td>
</tr>
</tbody>
</table>

Table 4.7
IEC 68-2-10 Extent of mold growth on silicone rubber treated with spores and water.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sweden</th>
<th>Sri Lanka</th>
<th>Tanzania</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 2 1</td>
<td>2 3 3</td>
<td>1 2 3 1</td>
<td>2 2 2 3</td>
</tr>
<tr>
<td>Base</td>
<td>1 0 0</td>
<td>0 0 0</td>
<td>0 0 0</td>
<td>0 0 0</td>
</tr>
<tr>
<td>Base + ATH</td>
<td>0 0 0</td>
<td>0 0 0</td>
<td>1 1 1</td>
<td>0 1 0</td>
</tr>
<tr>
<td>Base + ATH + ZnBO3</td>
<td>0 0 0</td>
<td>0 0 0</td>
<td>0 0 0</td>
<td>0 0 0</td>
</tr>
<tr>
<td>Base + ZnBO3</td>
<td>0 0 0</td>
<td>0 0 0</td>
<td>0 0 0</td>
<td>0 0 0</td>
</tr>
<tr>
<td>Commercial mix</td>
<td>2 1 1</td>
<td>1 1 1</td>
<td>2 2 2</td>
<td>2 2 2</td>
</tr>
</tbody>
</table>

The results of these standard tests show clearly that, if no nutrients are added to the samples, none of the silicone rubber materials mixed in the laboratory support growth. However, the commercial silicone rubber mix supports mold growth. These results strongly suggest that some component or combination of components in the commercial mix promotes the ability of the material to support mold growth.

When nutrients were added to the silicone rubbers, most of the samples supported mold growth. In an outdoor environment, nutrients from the surroundings may adhere to the surface of a silicone rubber insulator and provide nutrients for growth of a biofilm. However, growth is less severe on samples with zinc borate added. The low concentration of flame retardant used in the materials is sufficient to partially protect the silicone rubber from mold growth. This could not be predicted from the powder tests.

The sensitivity of the fungal species to the addition of zinc borate also differs between the standard tests and the powder tests. The fungal cultures from Tanzania seemed very sensitive when powders were tested, but standard tests show that, when these molds are grown on silicone rubber materials, they can tolerate higher concentrations of zinc borate. Instead, fungal cultures from Sri Lanka, that were easy to grow on the agar used in the powder test, were very hard to grow on silicone rubber and impossible to grow when zinc borate was added to the rubber. Nevertheless, both types of tests show clearly that the sensitivity to zinc borate differs between different fungal species. This emphasises that care is needed in the
selection of test organisms. If possible, species likely to infect the material under normal service conditions should be chosen.

On the other hand, valuable information can also be gained from standard tests performed as recommended. Microorganisms recommended in standard test procedures are chosen for their ability to negatively affect the tested materials, and they can therefore be said to represent a worst-case scenario. In this work, the advantages of using standard test organisms was shown when samples were subjected to the ASTM G21-90 standard for determining the resistance of synthetic polymeric materials to fungi. Samples were treated with mold spores and nutrient salts, but no source of carbon was added to the solution. If the spores were to germinate, they would thus have to use the test material as the source of carbon. The results of the test, when performed with organisms isolated from the insulators studied, are shown in Tab. 4.8 and they resemble the results of the IEC 68-2-10 standard tests.

Table 4.8
ASTM G 21-90 Extent of mold growth on silicone rubber treated with spores and salt.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sweden</th>
<th>Sri Lanka</th>
<th>Tanzania</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Base + ATH</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Base + ATH + zinc borate</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Base + zinc borate</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Commercial mix</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

However, when the test was carried out with the organisms stipulated in the standard, more information was gained. In Fig. 4.1, results from the unmodified ASTM standard test are shown together with results from a new test method called the Quick Test. In this method, growth was initiated and well established on highly nutritive agar before it started to colonise the sample. The fact that a material is easily colonised may be important, not for the initiation but for the advance of biological growth. Both tests were performed on virgin material as well as on materials aged with oxygen plasma prior to inoculation with microorganisms.

Figure 4.1
Results from the Quick Test and the ASTM G21-90 standard test when performed using the microorganisms stipulated in the standard. Tests were performed in triplicates and results were evaluated according to the scale described in Tab 3.3. The average of this evaluation is plotted.
The results obtained again indicate that the commercial silicone rubber is the most sensitive material, while the silicone rubber formulations with added zinc borate seem to be more protected. However, when the very potent fungal species stipulated in the standard test were used, the extent of growth varied among the materials tested. Apart from the fact that zinc borate protects the samples; the results indicate that ATH promotes growth to some extent. This could be due to the surface treatment of the ATH particles, the vinylsilanes used contain carbon that may provide a source of nutrients for microorganisms. However, for the degree of colonisation measured in the Quick Test, the surface roughening caused by the addition of ATH-filler is probably more significant. A rough surface offers better support for an advancing growth than a smooth material. Results from the Quick test also indicate a difference between virgin materials and materials aged with oxygen plasma. Growth advanced faster and further on the aged samples when compared to unaged rubber of the same type. This is probably due to the partially hydrophilic nature of the plasma treated rubbers. The wetted surface formed by the treatment provided water and support to the advancing mold-growth.

The sensitivity to algae growth of the silicone materials under investigation was tested according to the procedure described in the ASTM D 5589-97 standard practice. Algae use CO₂ as source of carbon through photosynthesis, therefore no source of carbon was added to the growth medium used in these experiments. The results shown in Tab. 4.9 indicate that zinc borate is toxic to the studied algae. Growth was not affected on pure silicone, the mix with ATH or the commercial mix, but algal growth was hindered or inhibited on materials with added zinc borate. This can be very important for the performance of the materials when they are used outdoors. Algae growth is not expected to degrade its support material directly; but in an outdoor environment mixed biofilms are formed. Algae growth may attract other kinds of microorganisms that can use the colonised material as a carbon source.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sweden</th>
<th>Sri Lanka</th>
<th>Tanzania</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>2</td>
<td>2</td>
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</tr>
<tr>
<td>Base +ATH</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Base +ATH + zinc borate</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Base + zinc borate</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Commercial mix</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

### 4.3 DETERMINATION OF BIOFOULING

In order to simulate biofilm growth on high voltage insulators in an outdoor environment, microenvironment chambers were prepared. In these chambers, mixed biofilms resembling those formed on insulators in field use were grown on the silicone rubber materials. Algae cells immediately started to grow on materials not containing zinc borate. After several
weeks, fungal growth started to develop on the materials infected by algae growth, and biofilms similar to those formed on insulators in the field were formed. The zinc borate-filled materials where algae refused to grow seemed protected from fungal growth as well. Microorganisms in a biofilm tend to live in symbiosis. It is known that the algae used in this study often grow in association with bacteria, and it seems probable that the fungal species isolated from the studied biofilms need algae as a source of nutrients for growth [114-116]. This means that the protective effect of zinc borate against algal growth also strengthens the protection against mold growth.

Materials incubated in the microenvironment chambers were not used only to study the resistance of the silicone rubbers to the formation of a biofilm. ESEM/EDX and IR analysis were performed on the materials in order to detect changes in chemical composition of the sample surfaces, while image analysis and laser-induced fluorescence spectroscopy were used to study the development of the biological growth.

4.3.1 Image analysis

Manual inspection is the most commonly used way to estimate the area covered by biological growth. However, the method is operator-dependent and therefore suffers from a lack of precision. Samples from the microenvironment chambers were therefore subjected to image analysis in an attempt to determine the covered area more precisely. Six months after inoculation, samples were photographed and the resulting digital images were subjected to image analysis in order to determine the extent of growth on the different materials. This was done by segmentation of the photographs into regions of similar chromatic appearance. A typical result obtained through the application of this segmentation technique is shown in Fig 4.2, where regions classified as growth have been marked in red. As can be seen, the highlighted regions correspond well to the areas covered by growth.

Figure 4.2 A typical result obtained through image analysis. a) Photograph of an ATH-filled silicone rubber sample infected by a biofilm from Tanzania. b) Regions identified as growth by using image analysis are marked in red.
As can be seen in Fig. 4.3, the image analysis results clearly show that the flame-retardant zinc borate hinders the development of the biofilm, and that ATH has no hindering effect on the growth. In fact, results again indicate that ATH might even support the biofilm. Another effect observed was that the biofilm originating from Sri Lanka developed faster on the commercial material tested, than on the other two biofilms under study. This might be due to the composition of the biofilm. Microscopic studies showed that the biofilm from Sri Lanka contained a larger proportion of fungi than the biofilms isolated from either Tanzania or Sweden. The commercial rubber was, as the previous discussion shows, sensitive to fungal growth.

Another observation was that direct UV exposure from a daylight lamp effectively hindered the growth of the biofilm. Fig. 4.4 shows that the samples that were nearest to the daylight lamp in the microenvironment chambers were almost completely free from growth. On the middle plates that were partly shaded growth developed much better. This effect can also be seen at high voltage insulators in service, where growth develop quicker on the shaded parts of the insulators [1, 5, 13].

The plates that were close to the bottom of the environmental chambers should, according to theory, be the worst infected samples, since they were partly shaded and hydrophilic [72]. However, this was not supported by results. This discrepancy is probably due to the method of inoculation. In an outdoor environment, microorganisms are deposited on the silicone rubber by wind and rain, whereas in the microenvironment chambers, microorganisms are sprayed onto the silicone rubber samples, and droplets form on the surface of the material. On the hydrophilic samples, these droplets pool together, form wetted traces, and run off the plate.

4.3.2 Laser-induced fluorescence

Recent studies indicate that image analysis can be used to estimate the area and distribution of growth on both material samples and complete insulators [65]. Nevertheless, the technique
has its drawbacks. For instance, the method does not discriminate between biological growth and other coloured pollutants on the insulator surface. To overcome this problem, and possibly increase the sensitivity compared to photography, laser-induced fluorescence (LIF) spectroscopy was explored as a tool for the detection of growth.

In LIF surface spectroscopy, the material under study is irradiated with monochromatic light from a laser source. Molecules in the sample surface absorb photons and electrons become excited. Fluorescent light is emitted and detected when the electrons spontaneously return to their ground state. The intensity of the fluorescent light is often substantially higher from a clean surface than from a surface covered by biological growth [66]. However, the absolute intensity is dependent on several factors, such as laser pulse energy, area of excited region, and the angle between the surface under study and the laser beam. Thus, the absolute intensity does not provide unambiguous information about the samples. A more promising approach is to use the spectral shape of the normalised fluorescence spectrum. The fluorescence spectrum from a fungi-covered silicone rubber is often wider than the spectrum from a clean sample and, if algae are present on the surface, an additional peak at about 685 nm indicates chlorophyll fluorescence [69]. These effects were clearly seen when samples from the microenvironment chambers were studied. The broadening effect and the algae peak were more pronounced on silicone rubbers with a severe biofilm growth than on cleaner samples. The algae peak disappeared completely on samples with zinc borate added, as can be seen in Fig. 4.5.

![Figure 4.5 Results from LIF-surface spectroscopy.](image)

A) Spectra collected from the ATH-filled silicone rubber. The red spectrum obtained from a sample infected by a dense biofilm is wider than the corresponding blue reference spectrum and the algae peak at 685 nm is clearly visible. B) Spectra from the zinc borate-filled rubber. The sample looked clean to the naked eye, since no mature biofilm had formed. The red spectrum obtained from the sample infected with microorganisms is only slightly broader than the blue reference spectra and there is no peak corresponding to chlorophyll fluorescence.

In addition, LIF surface spectroscopy was found to be a very sensitive method for the detection of microorganisms; areas that looked clean to the naked eye sometimes gave a response as if they were contaminated. When these areas were studied under the microscope it...
was found that traces of biological growth were in fact present. This indicates that LIF surface spectroscopy may be used to detect microbiological attack on silicone rubber insulators before a mature biofilm visible to the naked eye has formed.

However, the method has its drawbacks. While it is easy to detect algae defacement of a silicone rubber surface, detection of fungal growth is more problematic. The observed broadening of the LIF-spectra is not always easy to detect from the full spectrum obtained. A simplified score plot based on the variations between spectra is easier to handle and it can, if there are significant differences between samples, separate clean samples and samples infected by fungal growth into distinctly different classes.

Fig 4.6 a) shows typical fluorescence spectra of eight different fungal cultures grown on silicone rubber filled with ATH. Spectra obtained from the fungus-covered samples are wider than the spectrum of the clean ATH-filled silicone rubber material used as reference. However, for some samples these effects were small and difficult to detect in the spectra obtained. Results are easier to interpret from a simplified score plot of the sample set. In Fig. 4.6 b) spectra obtained from the infected materials are showed and compared to spectra from clean material in a simplified score plot. Each spectrum is reduced to a single dot in the score plot. Dots originating from spectra of samples infected by fungal growth are spread out to the left in the score plot, when compared with the encircled dots from the clean material. The spread is due to the combination of fluorescence from the fungal growth and the material. A heavily contaminated sample ends up further to the left in the score plot compared to a cleaner sample. When results are displayed as a simplified score plot it is easy to differentiate between a samples infected by fungal growth and a clean material. The different fungal cultures studied all followed the same trend in the simplified score plot. In addition, further studies showed that the method gave the same general response when other silicone rubber materials were tested. This is desirable for the development of a general inspection technique for composite insulators.

Fig. 4.6. Fluorescence spectra of eight fungal cultures grown on silicone rubber with added ATH a) Full fluorescence spectra of the sample set. b) Simplified score plot of the studied samples. Results from the clean ATH-filled silicone rubber material are located within the circle, while spectra from materials infected with fungal growth are spread out to the left in the plot.
When a silicone rubber sample infected by biological growth is subjected to a combination of LIF surface spectroscopy and image analysis, this gives a more complete picture of the situation than either method can give on its own. While LIF surface spectroscopy can be used to decide the type of contaminant and reveal information of contaminants invisible to the naked eye, image analysis can be used to estimate the severity of the growth. Both methods have a potential for use as in-service diagnostic techniques. However, by utilizing LIF for creating images depicting certain spectral properties, so-called imaging measurements, a combination of LIF and digital image analysis can be obtained, which is probably even more interesting for future applications. A mobile and self-contained light detection and ranging systems that could be used for field measurements of this kind already exists [117].

### 4.3.3 Hydrophobicity

One of the reasons why silicone rubber materials are preferred to ceramics in high voltage insulators is the hydrophobicity of the silicone rubber surface, but when a biofilm covers the insulator surface, the hydrophobicity of the rubber is disturbed [3, 6, 7] The most common way to measure surface hydrophobicity is by water contact angle measurements. However, this is not practical when the effect of a biofilm on surface hydrophobicity is to be recorded. In most cases, the biofilm is unevenly distributed over the sample surface, making it difficult to choose representative spots for the measurement. A biofilm may also function as a sponge withdrawing the water drop used for the contact angle measurement.

To avoid these problems, the hydrophobicity of the silicone materials incubated in the microenvironment chambers were tested in accordance with the STRI hydrophobicity classification guide [104]. In this method the pattern formed by the drops when a large surface area is sprayed with water is studied and compared to a series of seven reference images with different hydrophobicity classes (HC). HC 1 denotes a very hydrophobic sample on which only discrete droplets are formed, while HC 7 describes a hydrophilic sample on which a continuous water film is formed over the whole tested area. The method has a potential for use on insulators in the field; and the results can be evaluated either by visual inspection or by use of image analysis [62].

The worst infected samples from the microenvironment chambers were classified according to the STRI-hydrophobicity classification guide. The results, displayed in Tab. 4.10, clearly show that samples covered with microorganisms were more hydrophilic than virgin materials and reference materials treated with nutrient salt solution. However, after cleaning the surface of the infected materials with a soft cloth damped with distilled water, the hydrophobicity of the materials were somewhat restored. However, materials containing large amounts of filler particles were not as easy to restore as were less filled materials. Filler particles cause surface roughening and it seemed that the gentle cleaning procedure applied was not effective enough to completely remove the biofilm from the rough surface of the filled materials.
Table 4.10

HC of silicone rubber infected by biofilms and reference materials

<table>
<thead>
<tr>
<th>Samples from microenvironment chambers</th>
<th>Contaminated</th>
<th>Cleaned</th>
<th>Virgin materials</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sri</td>
<td>Tz</td>
<td>Sw</td>
</tr>
<tr>
<td>Base</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Base + ATH</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Base + ATH + zinc borate</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Base + zinc borate</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Commercial mix</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

4.3.4 ESEM/EDX

If a severe growth has developed on an active silicone rubber insulator, it may be necessary to remove the biofilm. Spraying with a biocide is not a good alternative; this may kill the microorganisms but it does not remove them from the insulators. Dead biomass is left in the system and this opens the way for a rapid microbiological re-growth [71]. If insulators are to be treated in some way, cleaning is a better alternative. However, cleaning is only effective if the adhesion between the biofilm and the silicone rubber is not too strong.

To examine the possibility of cleaning an infected silicone rubber insulator, samples from real insulators as well as samples from microenvironment chambers were analysed by using an environmental scanning electron microscope (ESEM) with X-ray energy dispersive spectroscopy (EDS). ESEM/EDS not only give a microscopic picture of the infected surface but also combine this information with an overview of the elemental composition of the surface of the tested material. Since the molecules in the biofilm differ in chemical composition from those of the supporting silicone rubber, the atomic composition of the surface layer can be used to monitor the amount of contaminants before and after a washing procedure. If traces of the biofilm remain after cleaning the surface, it can be assumed that the adhesion between the biofilm and its support is too strong to allow the applied washing procedure to be effective.

Silicone rubber samples cut from insulators situated in Tanzania, Sri Lanka and Sweden were analysed with ESEM/EDS. The results shown in Fig 4.7 and Fig 4.8 indicate that it was possible to clean the African insulator efficiently by gently wiping the surface with a soft clot wetted with distilled water, but that the Asian rubber was not that easy to clean from biofouling. Traces of Mg, Na and Fe originating from the biofilm were detected after the cleaning. ESEM pictures supported the results of the elemental analysis; the silicone rubber from Sri Lanka showed a rough surface after cleaning, while the rubber surface from Tanzania looked clean and smooth. The results of ESEM/EDS analysis of the Swedish insulator resembled those of the insulator from Sri Lanka.
Fig 4.7
ESEM/EDS of insulator from Tanzania

It was possible to restore the surface of the silicone rubber by the gentle cleaning procedure applied. After cleaning, ESEM images show a smooth surface and EDX does not show traces of molecules originating from the biofilm.

a) EDS of virgin SIR

b) EDS of SIR covered by growth

c) ESEM of SIR covered by growth

d) EDS of SIR after cleaning

e) ESEM of SIR after cleaning
Results and discussion

Fig 4.8
ESEM/EDS of insulator from Sri Lanka

It was not possible to restore the surface of the silicone rubber by the gentle cleaning procedure applied. After cleaning, traces of Mg, Na, and Fe originating from the biofilm were detected by EDS and ESEM showed a rough surface.
Unlike the Tanzanian insulator, EDS analysis showed that the insulators from Sri Lanka and Sweden contained large amounts of the flame retardant ATH. It seems that an ATH-filled silicone rubber is more difficult to clean, than a rubber containing less filler. In order to verify this hypothesis, samples from the microenvironment chambers were analysed with ESEM/EDS. After one year of incubation in the microenvironment chamber representing Sri Lanka, small samples covered with a dense biofilm were cut from ATH-filled silicone rubber and Base rubber. These samples were analysed before and after cleaning. Results verified that it was easy to remove the biofilm from the Base rubber, but the ATH-filled material was more difficult to clean. This is probably due to the fact that the ATH-filled rubber had a rougher surface structure than the Base material. A rough surface is more accessible for microbiological growth [72].

4.4 BIODEGRADATION OF THE PDMS MOLECULE

Despite the fact that an ATH-filled silicone rubber is difficult to clean from biological growth, no evidence was found that the biofilms examined in this study are able to degrade the silicone rubber matrix. When samples from the microenvironment chambers were cleaned from biological growth and analysed with infrared (IR) spectroscopy, no difference in spectra could be observed between samples treated with microorganisms and virgin materials. This indicates that no chemical bonds had been disrupted by the influence of the biofilm.

The PDMS molecule is known to be very stable and no biological process is known that produces or degrades covalent bonds in organosilicones [46]. Nevertheless, silicone rubber could still be degraded by biological processes through secondary mechanisms. Many microorganisms secrete powerful enzymes with the ability to degrade very stable polymeric structures. Among these, the white rot fungi hold a unique position. This class of molds has evolved non-specific mechanisms for degrading the complex polymeric structure of lignin. The enzyme system responsible for the degradation includes peroxidases that promote the reduction of peroxides to free radicals [90, 93]. These radicals have been shown to attack stable polymeric materials such as polyvinyl chloride, nylon and polyethylene [118-120]. Claims have been made that these molds could also degrade PDMS oils [94].

According to United States patent No: 6,020,184, silicone oils of high molecular weight could be degraded by the lignin-degrading fungus *Phanerochaete chrysosporium*. The fungus is grown for 60 days in a liquid medium spiked with a small amount of silicone oil. According to the results reported this procedure degrades 17-50% of the added silicone oil. However, we have repeated the experiment, as described in the patent, and after modifications recommended by experts in the field of lignin degradation. Still, no reliable proof of PDMS degradation has been observed in any of the tests performed.

In order to study the biologically mediated degradation of the silicone molecule in detail, tests were performed on a PDMS rubber, on a PDMS oil of high molecular weight, and on a DMS oligomer. After treatment with the lignin-degrading fungus *Phanerochaete chrysosporium*,

37
oils were analysed by SEC in order to detect main-chain scissoring reactions, oils and oligomers were analysed with GC/FID in order to observe degradation mediated by chain end or side chain mechanisms, and rubbers were analysed for chemical changes in the surface layer by use of IR.

No significant difference in surface composition of the rubber or the molecular weight of the oil was observed and no low molecular weight degradation products were found in the GC analysis performed after treatment of the siloxane materials with the lignin-degrading fungus. It was therefore decided that experiments with radicals generated by chemical mechanisms should be performed as a compliment to the biodegradation study. The materials mentioned above were exposed to hydroxyl radicals generated by the Fenton mechanism. However, subsequent analysis showed no significant influence of the hydroxyl radicals on the silicone materials analysed. Some results from the performed tests can be seen in fig. 4.9-4.11.
The results obtained from the degradation study indicate that the PDMS molecule is very stable against biodegradation. However, it cannot be concluded, based on these results only, that PDMS is a biologically inert material. It is possible that degradation could occur if a more effective experimental design were developed. If, for example, the silicone oil could be dispersed or dissolved in the reaction medium, the PDMS molecules would be more accessible to degrading enzymes and radicals. Even so, the probability that the silicone rubber matrix of a high voltage insulator could be degraded by the direct influence of microorganisms is very small.
Conclusions

5 Conclusions

Subsequent effects ranging from fouling to degradation of the polymer matrix occurs when a polymeric material is colonised by a biofilm. For silicone rubbers in high voltage insulators this study showed that fouling is the most severe problem. The polydimethylsiloxane (PDMS) molecule is highly stable and no evidence of biodegradation has been found. Neither microorganisms isolated from insulators in service nor aggressive ligninolytic fungal species seemed to be able to break the chemical bonds of PDMS.

Biofouling can, however, seriously influence the function of an insulator. This study showed that the hydrophobicity of a silicone rubber is reduced when the material is colonised by a biofilm. This can alter the electrical properties of a fouled insulator. It is therefore important to develop methods for the identification of infected units. In this work, laser-induced fluorescence (LIF) spectroscopy was successfully used to identify biological contamination on silicone rubber surfaces. Photography followed by image analysis was then used to estimate the extent of growth.

The surface hydrophobicity of the silicone rubber can be restored by removing the attached biofilm. The effectiveness of a cleaning procedure depends, however, on the composition of the rubber. A silicone rubber containing large amounts of alumina trihydrate (ATH) has a rougher surface structure, compared to an unmodified silicone. This makes it difficult to remove an attached biofilm in an effective way.

In addition, surface treated ATH makes a material more accessible to microorganisms. This was shown when different silicone rubber formulations were subjected to a series of microbiological growth tests developed for this study. Methods useful for fast evaluation of samples were used together with standard test methods and microenvironment chambers constructed for long-term studies in a simulated outdoor environment. These tests showed that while the commercial silicone rubber tested supported growth, addition of the flame-retardant zinc borate to a material made it able to suppress the growth of mold, algae and mixed biofilms.
6 FUTURE WORK

It has been shown in a series of growth tests that addition of zinc borate to silicone rubber protects the material from severe biofouling. However it would be advantageous if materials could be tested outdoors under true service conditions.

The methods developed to study the biodegradation of PDMS should be perfected in order to definitely confirm or exclude the degradation of PDMS under the influence of enzymes or radicals.

In this work laser-induced fluorescence (LIF) spectroscopy has been successfully used to identify silicone rubbers infected by biological growth. However the causes of the observed differences between clean and fouled materials are not yet fully understood. It would be beneficial for the future development of the technique if the biological structures responsible for the observed differences in fluorescence could be identified.

Finally, methods combining LIF-spectroscopy and image analysis should be developed further and used to identify contaminated insulators in the field. One promising attempt in this direction is the mobile light detection and ranging (LIDAR) system used by Dernfalk et al for detection of biological growth on silicone rubber insulators. This method has the potential to be used to diagnose energised insulators from a safe distance [66].
Future work
ACKNOWLEDGEMENTS

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To my colleagues, you were always the best part of the job. Thanks to all of you, especially former and present members of the SK-research group, Nadja, Walker, Guillaume, Ana, Fran, Jonas, Emma, Åsa and Sara

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Love to all my friends not kept in institution, especially to Jocke (breakfast soon?), Anna (the wedding planner) and Jenz, Tobias and Lina, (cats!), Maja, Fredrik and Maria (Stayokay) Micke (Byrådirektör Toll). Love also to Josefin (with family!), Elin and Josefin, your friendship means a lot to me, as does “kvinnokampssemestera”.

Still, my warmest gratitude goes to my family. You have never pushed me, always helped me and never stopped loving me. I feel safe knowing that you will always be there for me.

To Anders, for the rest of our days.
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