LOSS AND RECOVERY OF HYDROPHOBICITY OF POLYDIMETHYLSILOXANE AFTER EXPOSURE TO ELECTRICAL DISCHARGES

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To my family
Loss and Recovery of Hydrophobicity of Polydimethylsiloxane After Exposure to Electrical Discharges

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Silicone rubber based on polydimethylsiloxane is used as high voltage outdoor insulation, due to its ability to preserve the hydrophobic surface properties during service and even regain hydrophobicity after exposure to electrical discharges. The underlying processes for the hydrophobic recovery are diffusion of low molar mass siloxanes from the bulk to the surface and reorientation by conformational changes of molecules in the surface region. Only little is known of which factors are responsible for the long-term stability of this hydrophobic recovery. It is therefore important to increase the knowledge about the fundamental mechanisms for the loss and recovery of hydrophobicity of silicone rubbers, exposed to electrical discharges. Addition-cured polydimethylsiloxane networks, with known crosslink densities, were exposed to corona discharges and air/oxygen-plasma and the loss and recovery of hydrophobicity was characterised by contact angle measurements. The degree of surface oxidation increased with increasing exposure time with a limiting depth of 100-150 nm, as assessed by neutron reflectivity measurements. The oxidation rate increased with increasing crosslink density of the polymer network, according to X-ray photoelectron spectroscopy. Within the oxidised layer, a brittle, silica-like layer was gradually developed with increasing exposure time. The hydrophobic recovery following the corona or air/oxygen-plasma exposures occurred at a slow pace by diffusion of cyclic oligomeric dimethylsiloxanes through the micro-porous but uncracked silica-like surface layer or at a much higher pace by transport of the oligomers through cracks in the silica-like layer. The oligomers were present in the bulk, but additional amounts were formed during exposure to corona discharges. High-temperature vulcanised silicone rubber specimens were aged in a coastal environment under high electrical stress levels (100 V/mm). The changes in surface structure and properties were compared to the data obtained from specimens exposed to corona discharges/plasma. The dominating degradation mechanism was thermal depolymerisation, initiated by hot discharges. This resulted in the formation of mobile siloxanes, of which the low molar mass fraction consisted of cyclic oligomeric dimethylsiloxanes. Oxidative crosslinking resulting in silica-like surface layers was not observed during these conditions.

Keywords: silicone rubber, polydimethylsiloxane, hydrophobicity, corona, air-plasma, oxygen-plasma, surface characterisation, degradation products, crosslink density.
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1. INTRODUCTION

1.1 Purpose of this study

This thesis deals with the loss and recovery of hydrophobicity of silicone rubber surfaces after exposure to electrical discharges. The project was directed to form a link between electrical engineering and polymer science, focusing on the understanding of the mechanisms of deterioration of silicone rubber used as high voltage outdoor insulation.

Silicone rubber is currently replacing glass or porcelain as outdoor insulation. One of the benefits is the hydrophobic surface properties of polydimethylsiloxane (PDMS); the polymer used in these silicone rubber formulations. On glass and porcelain insulation, water readily forms a continuous film on the hydrophilic surface. In the presence of contamination, leakage currents develop, which may result in a flashover of the insulator. The hydrophobic surface of PDMS prevents the formation of such continuous water films. If the polymer is exposed to electrical discharges this can cause a loss of hydrophobicity due to surface oxidation. PDMS, however, has the unique ability to recover hydrophobicity after the exposure. When the project was initiated, a hypothesis of the lifetime of the hydrophobic recovery of PDMS was formulated: the intrinsic surface properties of PDMS are essentially preserved during Period 1 (Fig. 1.1). After a certain incubation time (or dose of energetic species) a glassy, amorphous skin is formed which severely retards the rate of hydrophobic recovery. The 'end of the life of hydrophobicity' is then reached (Period 2).

The goal of the project was to test the hypothesis that the lifetime of hydrophobic recovery of PDMS could be divided into two different periods.

![Figure 1.1](image.png)  
Figure 1.1 Schematic representation of the time-dependence of hydrophobic recovery rate of two different silicone rubber formulations.
In order to answer the question, the main mechanisms for the deterioration of PDMS used for outdoor insulation must be established. This would allow the development of proper evaluation techniques of silicone rubber outdoor insulation. It was decided to use electric discharges (corona, air-plasma) as accelerated testing of both commercial silicone rubbers as well as ‘exact’ PDMS networks.

The thesis is organised as follows:
Chapter 2 starts with a general description of PDMS. This is followed by a description of silicone rubbers in outdoor insulation applications. Furthermore, the mechanisms for the loss and recovery of the hydrophobicity of PDMS is reviewed.
In Chapter 3 the experimental methods are described.
Chapter 4 describes the surface properties of PDMS after exposure to electrical discharges. The rate of hydrophobic recovery is correlated to the properties of oxidised, ‘silica-like’, surface layers. The hypothesis of lifetime of hydrophobic recovery is tested. Finally the nature of the diffusing low molar mass siloxanes is analysed and their role in the hydrophobic recovery is discussed.
In Chapter 5 chemical analysis of field-tested silicone rubbers, aged under alternating current (AC) or direct current (DC) voltage, is presented and related to the results obtained from the laboratory tests (Ch. 4).
Chapter 6 summarises the results, including the properties of the ‘silica-like’ surface layer on the hydrophobic recovery rate. The difference in deterioration mechanism between corona/air-plasma exposed and field-aged PDMS is discussed.
Chapter 7 discusses the practical implications of the results on the long-term properties of hydrophobicity; a revised lifetime model of hydrophobicity upon exposure to corona is suggested.

Most of the experimental details are not included in Chapters 4 and 5, but can be found in the appended papers.

1.2 The author’s contribution

The author was responsible for and carried out the major part of the work on papers I and III-VI.
In paper II the author performed contact angle measurements, SEM and analysis of XPS data, summarised the results and wrote the paper.
Tomas Gustavsson was responsible for paper VII. The author performed the major part of the chemical analysis of the field-aged samples and assisted in the analysis of the data and the writing of the paper.

The entire work was supervised by Ulf W. Gedde.
2. BACKGROUND

In this chapter a general description of silicone rubber, based on Polydimethylsiloxane, and its use as high voltage outdoor insulation is presented. The mechanisms responsible for the loss and recovery of hydrophobicity of silicone rubbers are summarised. The presentation is not intended to be extensive, but rather wishes to illustrate the width of the subject. The aim is to familiarise the reader with some of the chemical and physical aspects of hydrophobicity loss and recovery of silicone rubbers and its relevance to high voltage outdoor insulation applications.

2.1 Properties of polydimethylsiloxane

2.1.1 General description
Polydimethylsiloxane (PDMS) is the polymer commonly used in silicone rubber formulations for high voltage outdoor insulation applications. PDMS consists of an inorganic backbone of alternating silicon and oxygen atoms. Methyl groups are attached to the silicon atoms forming the repeating unit in the polymer (Fig. 2.1).

\[
\text{CH}_3 \text{SiO} \text{CH}_3 \quad \text{SiO} \text{CH}_3 \quad \text{SiO} \text{CH}_3 \quad \text{SiO} \text{CH}_3 \quad \text{SiO} \text{CH}_3
\]

**Figure 2.1** Repeating unit of PDMS.

The low surface free energy - 16-21 mN m\(^{-1}\); the precise value depends on the molar mass,\(^1,2\) is due to closely packed methyl groups in the surface. Four structural characteristics of PDMS account for its surface properties: (1) the low intermolecular force between methyl groups, (2) the unique flexibility of the siloxane backbone (Si-O-Si: 143\(^\circ\)), (3) the high strength of the siloxane bond and (4) the partial ionic nature of the siloxane bond\(^3\). The Pauling electronegativity difference of 1.7 between silicon and oxygen results in a 40-50\% polar character of the siloxane bond.\(^3\) The polar nature of the siloxane bond makes, however, PDMS susceptible to hydrolysis, especially during acidic or basic conditions. The positively polarised silicon atom is electron withdrawing, thus polarising the methyl group and makes it less susceptible to radical attack. Thus the methyl groups in PDMS have higher thermal and oxidative stability compared with a methyl group within a hydrocarbon polymer (e.g. polypropylene).\(^1\) Another reason for the excellent thermal stability of PDMS is the high dissociation energy of the siloxane bond (445 kJ mol\(^{-1}\))\(^4\). The energy barriers for torsion around the main chain bonds are very low compared to that of other polymers: < 4 kJ
mol\(^{-1}\) for PDMS\(^5\), compared to 15 kJ mol\(^{-1}\) for polyethylene\(^6\). The segmental mobility and the high free volume of PDMS are reflected in its low glass transition temperature, - 127\(^\circ\)C\(^7\) and very high permeability and diffusivity to gases. The oxygen permeability at room temperature is 21 times greater for PDMS than for natural rubber and 170 times greater than for low-density polyethylene\(^8\). The regular chain structure makes PDMS a crystallisable polymer. The equilibrium melting point is - 54\(^\circ\)C and the enthalpy of fusion is very low, 2.75 kJ/(mole repeating unit)\(^9\). The entropy of fusion is 6.28 J/(mole of flexible main chain bonds) which is lower than for polyethylene (9.9 J/(mole of flexible main chain bonds)\(^10\). Hence, the low melting point of PDMS is due to its very low enthalpy of fusion.

2.1.2 Production of the polymer
Silicon dioxide (SiO\(_2\)) is reduced to silicon by reaction of a carbon electrode. A SiO intermediate is formed, followed by the production of a chemical grade of powdered silicon. Linear PDMS is usually manufactured from dimethyldichlorosilane, which is produced by the reaction of powdered silicon with methyl chloride. A mixture of cyclic (c) and linear (l) PDMS oligomers is obtained by hydrolysis of the dichlorosilane followed by condensation reactions (Reaction 1):

\[
(CH_3)_2SiCl_2 \xrightarrow{H_2O} (CH_3)_2SiO]_c + HO[(CH_3)_2SiO]_lH
\]  

(R1)

High molar mass polymers are then produced by anionic or cationic ring-opening polymerisation of the cyclic oligomers or by polycondensation of the silanol end-blocked linear oligomers\(^11\).

2.1.3 Production of a crosslinked network
High temperature vulcanisation
In high temperature vulcanising (HTV) silicone rubbers crosslinking of the polymer chains takes place through decomposition of peroxides at temperatures above 100\(^\circ\)C. The peroxides decompose into free radicals which react with unsaturated bonds and/or by abstraction of hydrogen atoms, depending on type of peroxide used. The free radicals then recombine and form crosslinks between the siloxane chains. Residual volatile decomposition products within the HTV silicone rubbers are generally removed by a post-curing step (storage at elevated temperatures).

Room temperature vulcanisation
Two different crosslinking methods are generally used for room temperature vulcanising (RTV) silicone rubbers for outdoor insulation applications. One uses a condensation reaction of silanol groups to form siloxane bonds with the liberation of water (Reaction 2). The reaction involves water and is an equilibrium process, catalysed by acid or base.

\[
≡SiOH + ≡SiOH \xrightarrow{H_2O} ≡SiOSi ≡ + H_2O
\]  

(R2)
The hydrosilylation reaction involves the addition of a silicon hydrogen (Si-H) to an unsaturated carbon bond, usually a vinyl group (-CH=CH₂), catalysed by a noble metal, e.g. a platinum complex (Reaction 3).

\[ \equiv \text{SiH} + \text{H}_2\text{C} = \text{CHSi} \equiv \xrightarrow{\text{Pt}} \equiv \text{SiCH}_2\text{CH}_2\text{Si} \equiv \]  

(R3)

This second reaction is very specific and the crosslink density can be controlled very accurately by this method.

2.1.4 Rubber formulations for high voltage outdoor insulation

To the uncrosslinked PDMS, reinforcing silane-treated fillers are added, e.g. 10-20% of amorphous silica. Silica can also be used for rheological control of the compound. Typically ~50% aluminum trihydrate (ATH) is added as a flame-retardant because unfilled PDMS is too flammable for these applications. ATH decomposes to aluminium oxide and water when heated to temperatures above 200°C. The liberation of water is endothermic and the surface is cooled, which may extinguish an electric arc (Reaction 4). Furthermore, the resistance against tracking (‘electrical erosion’) is improved.

\[ 2\text{Al(OH)}_3 \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \]  

(R4)

Typical formulations also contain smaller proportions of silicone oil for process control, pigments, and chemicals used for vulcanisation (cross-linking) reactions.

2.2 Silicone rubber as outdoor high voltage insulation

2.2.1 General applications

Silicone rubbers have, since their introduction in the 1960’s, steadily gained market share from porcelain and glass as outdoor high voltage insulation (e.g. transmission line insulators, bushings, surge arresters and cable terminations). The silicone rubbers are used in composite insulators as housing material on a load-bearing core, e.g. glass-fibre-reinforced plastics. An example of a composite insulator (line insulator type) is shown in Fig. 2.2a. The main functions of the silicone rubber housing are to protect the core from the outdoor environment and to provide a suitable profile for the insulator, i.e. minimise leakage currents between the energised end and ground. An example of installed line insulators is shown in Fig. 2.2b.

Silicone rubbers have a property profile – hydrophobic surface properties (water repellence), low surface and bulk conductivity, fracture toughness over a wide temperature range – which gives them distinct advantages compared to ceramic materials. Low weight, vandalism resistance and contamination resistance are other important characteristics of composite insulators with silicone rubber housings\textsuperscript{12,13}. An alternative rubber material used for housings is EPDM (Ethylene-Propylene-Diene Monomer).
However, silicone rubber insulators have been reported to perform better compared to porcelain, glass and EPDM both in heavily polluted areas and in severe marine sites\textsuperscript{14-18} and also during laboratory tests\textsuperscript{19-21}. Using porcelain or glass high voltage insulators, water readily forms a continuous film on the hydrophilic surface. In the presence of severe contamination, leakage currents develop, which may result in a flashover of the insulator. The initially hydrophobic surface properties of EPDM are permanently lost when exposed to electrical discharges or pollution\textsuperscript{22}. The hydrophobic surface properties of silicone rubber prevents the formation of continuous water films, instead water droplets are formed which simply bead off the surface. This hydrophobicity can, however, be temporarily lost during exposure to electrical discharges (corona, dry band arcing)\textsuperscript{22-24}, or by rapid build-up of a continuous layer of pollution, i.e. salt or dust\textsuperscript{25-28}. After a subsequent period of rest, hydrophobicity is, however, regained. Silicone rubbers thus have the ability to recover hydrophobicity. This will be further discussed in Section 2.3-2.4.

2.2.2 Long-term performance
A central question to assess is the long-term performance of composite insulators. Currently there are no well-defined specifications for accelerated ageing of composite polymer insulators or polymeric insulating materials\textsuperscript{29}. Several national and international organisations attempt to develop such standards. These include IEEE, IEC, CIGRE, American National Standards Institute (ANSI) and National Electric Manufacturers Association (NEMA)\textsuperscript{29}. However, most of the existing tests for accelerated ageing are primarily useful for ranking of materials, thus only tests in field stations and actual performance on power lines and outdoor substations can yield realistic results on outdoor service performance\textsuperscript{29}. Different electric tests of composite insulators and materials under both field and laboratory conditions have recently been reviewed by Fernando and Gubanski\textsuperscript{30}, Bärch et al.\textsuperscript{31} and Sebo and Zhao\textsuperscript{32}.

A central concern of polymeric composite insulators is the surface degradation of the housing, which may decrease its ability to prevent
water ingress to the glass-fibre reinforced core. In the case of silicone rubber this question is closely correlated to the surface hydrophobicity. In 1974 Niemi and Orbeck suggested that a failure of polymeric insulators was a result of progressive tracking or by direct flashovers, initiated by large leakage currents and dry band arcing\textsuperscript{33}. This mechanism was further developed by Gorur et al. who suggested that ageing of silicone rubber housings in an outdoor environment started with the loss of hydrophobicity due to dry band arcing\textsuperscript{34}. The arcing erodes the surface, by depolymerisation and clustering of the exposed filler particles, which eventually lead to initiation of tracking and a subsequent failure of the insulator\textsuperscript{34}.

However, dry band arcing only occurs when the hydrophobicity is reduced, since a hydrophobic surface will have no leakage currents\textsuperscript{35}. Thus on a hydrophobic surface, such as a silicone rubber, corona was suggested to be the initiating mechanism for electric ageing\textsuperscript{35}. Corona and dry band arcing are two very different phenomena, since corona is initiated by high electric fields, whereas dry band arcing is related to leakage currents. High electric fields, exceeding the ionisation level of air, can be caused by field enhancement by water droplets (water droplet induced corona) or by improper design of the geometry of the insulator. The effects of corona have been verified by observing surface degradation of silicone rubber housings before the detection of any leakage current pulses exceeding 0.5 mA\textsuperscript{36}. It has been shown that surface erosion can be avoided when surfaces parallel to the electric field are not exposed to fields higher than 0.4-0.6 kV/mm\textsuperscript{36,37}. This can be achieved by modifying the field distribution, i.e. the geometry of the insulator or by using corona rings. If surface hydrophobicity is lost due to the corona, water forms a conducting film by dissolving the pollution always present in an outdoor environment, followed by localised drying and subsequent dry band arcing. This will cause erosion/ablation of the silicone rubber surface. The processes will continue during the wet period, but cease upon drying. Hydrophobic recovery of the silicone rubber will then occur. This cycle will be repeated during wet periods and finally a flashover of the composite insulator may occur\textsuperscript{38}.

![Figure 2.3](image.png)

**Figure 2.3** (a) Illustration of filament formation and spot discharges on a hydrophobic silicone rubber insulator surface\textsuperscript{40}, (b) Water filaments on an aged silicone rubber insulator\textsuperscript{41}.
Shah et al. proposed a flashover mechanism initiated by interactions between water droplets and contamination on the insulator surface, forming conductive hydrophilic regions\textsuperscript{39,40}. Low leakage currents cause an ohmic (resistive) heating of the surface between these regions, making them to coalesce into larger conductive water filaments. Spot discharges (self-quenching discharges) between conductive filaments are then initiated by enhancement of the electric field. This finally led to insulator failure due to flashover along the wetted filaments\textsuperscript{40}. The mechanism is illustrated in Fig. 2.3a. An example of an aged silicone rubber insulator with inhomogeneous hydrophobicity is shown in Fig. 2.3b. High voltage outdoor insulation using silicone rubber housings has been used for over 20 years\textsuperscript{12}. However, glass and porcelain is often preferred as a first choice, due to the limited knowledge of the long-term performance and life expectancy of silicone rubber housings\textsuperscript{15,42}.

2.3 Loss and recovery of hydrophobicity: electrical discharges

The loss and recovery of hydrophobicity caused by exposing silicone rubber to electrical discharges (corona or plasma) have been investigated by many researchers. Plasma treatments have been used to increase the wettability of silicone rubber for improved compatibility to other materials, e.g. in biomedical applications and in printing technology. In these fields the hydrophobic recovery is considered as a problem and much effort has been directed to reveal the fundamental underlying mechanisms. The complexity of corona/plasma exposure is partly due to the fact that the polymer is simultaneously subjected to a mixture of energetic species and radiation, e.g. electrons, ions, UV and ozone. A great number of reactions take place. In addition, the effects of the treatments are highly dependent on the material structure and composition. The main effects of corona/plasma treatment on silicone rubber can be summarised as follows: (1) an increase of the oxygen content at the surface by the formation of silanol and carbonyl groups (2) oxidative crosslinking, (3) degradation of the network structure resulting in the formation of low molar mass cyclic compounds and medium to high molar mass PDMS. In order for oxidation reactions to occur oxygen needs to be present, either in the surrounding atmosphere, or dissolved in the polymer.

2.3.1 Loss of hydrophobicity

The hydrophobic surface properties of silicone rubber have been shown to be temporary lost by surface oxidation during exposure to corona discharges in air\textsuperscript{22-24,43,44}, radio frequency (RF) and microwave (MW) plasma treatments\textsuperscript{45-51} or salt-fog tests\textsuperscript{52-55}. The oxidation resulted in the formation of an inorganic, silica-like (SiO\textsubscript{x}) structure, i.e. silicon atoms bonded to more than two oxygen atoms\textsuperscript{23,24,53,56}. Polar silanol groups were also introduced in the surface region\textsuperscript{49,57}. Both of these formed structures increase the hydrophilicity of the surface. The mechanisms are briefly summarised below.
Hollahan and Carlson reported in 1970 that radio frequency (RF) oxygen plasma and air corona resulted in similar surface oxidation of PDMS\textsuperscript{58}. On the basis of infrared spectroscopy they suggested the formation of hydroxyl groups (Si-CH\textsubscript{2}OH) and peroxides (Si-CH\textsubscript{2}OOH) by reactions between excited oxygen atoms (O\textsubscript{2}*) and PDMS according to Scheme 1 and 2 (Fig. 2.4).

\begin{equation}
\text{Scheme 1 [58]}
\begin{align*}
\text{CH}_3 & \quad \text{O}_2^* \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{OH} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{Si} & \quad \text{O} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{Si} & \quad \text{O} \quad \text{CH}_3 \quad \text{CH}_3 \\
\end{align*}
\end{equation}

\begin{equation}
\text{Scheme 2 [58]}
\begin{align*}
\text{CH}_3 & \quad \text{O}_2^* \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{OH} \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{Si} & \quad \text{O} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{Si} & \quad \text{O} \quad \text{CH}_3 \quad \text{CH}_3 \\
\end{align*}
\end{equation}

\begin{equation}
\text{Scheme 3 [59]}
\begin{align*}
\text{CH}_3 & \quad \text{UV} \quad \text{CH}_3 \quad \text{OH} \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{Si} & \quad \text{O} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{Si} & \quad \text{O} \quad \text{CH}_3 \quad \text{CH}_3 \\
\end{align*}
\end{equation}

\textbf{Figure 2.4} Mechanisms leading to oxidative crosslinking.

Kim \textit{et al.} analysed silicone rubber after exposure to a salt-fog test under high electric stress by reflection infrared spectroscopy and X-ray photoelectron spectroscopy (XPS)\textsuperscript{57}. The exposure caused a decrease in the intensity of C-H absorption bands (IR) and a decrease in carbon content from 51 to 44 at.\%, combined with an increase in oxygen content from 23 to 33 at. \% according to XPS. Curve resolution of the Si 2p peak confirmed the formation of a SiO\textsubscript{x} surface layer. Formation of silanol groups was confirmed by infrared spectroscopy\textsuperscript{57}. A similar trend was observed when silicone rubber was exposed to oxygen-plasma or corona and subsequently analysed by XPS\textsuperscript{24,47}. The UV-component in the corona/plasma can introduce silanol groups by UV-induced oxidation and cleavage of methyl groups, according to a mechanism suggested by Delman \textit{et al.}\textsuperscript{59} (Fig. 2.4, Scheme 3). The strongly electropositive silicon atoms react more readily with the strongly electronegative oxygen atoms rather than with the less electronegative carbon atoms\textsuperscript{59}. Hence, the active ≡Si· will form Si-O-Si crosslinks (SiO\textsubscript{x}). Condensation of silanol groups will also result in the formation of SiO\textsubscript{x}\textsuperscript{49,60}. This is schematically illustrated in Fig. 2.5.

\begin{equation}
\text{Figure 2.5} \text{ Condensation of silanol-groups, forming oxygen crosslinks.}
\end{equation}
Lacoste et al. showed that ethylene groups (the crosslink obtained by a hydrosilylation reaction between vinylsiloxane and hydro-siloxane) were converted by photo-oxidation to hydroxyl and carbonyl groups. Corona discharges in air produces products such as NO, HNO2 and HNO3 which may dissolve in water present on the PDMS surface. The acidic water may influence the hydrolysis of the polymer chains in the surface region.

2.3.2 Hydrophobic recovery
Hydrophobic recovery of silicone rubber occurs after exposure to corona/plasma. The wide differences in the recovery kinetics reported in many research papers indicate that the phenomenon is a complex process. Differences in raw materials, curing methods, conditions prevailing during the loss of hydrophobicity and the conditions prevailing during the recovery period all affect the hydrophobic recovery kinetics. Owen et al. summarised the plausible mechanisms for hydrophobic recovery of silicone rubbers after exposure to corona or plasma:

4. Reorientation of polar groups at the surface into the bulk.
5. Condensation of silanol groups at the surface.
6. External contamination of the surface.
7. Changes in surface roughness.
8. Loss of volatile oxygen-rich species to the atmosphere.
9. Migration of low molar mass species from the bulk to the surface.

The large segmental flexibility of unoxidised and lightly oxidised PDMS enables fast reorientation of polar groups. The driving force for this hydrophobic recovery is the thermodynamic requirement of minimising the surface free energy. Extensively oxidised silicone rubber with a glassy SiOx surface layer shows a low hysteresis in contact angles, i.e. a small difference between advancing and receding contact angles. The polar groups have, in this structure, small possibilities to reorient due to their restricted environment. Reorientation of surface segments is a local process and is not believed to explain the full recovery of hydrophobicity of oxidised silicone rubber. It has been shown experimentally that it is less likely that external contamination of the surface is causing the hydrophobic recovery in silicone rubber. Hydrophobic recovery in a clean room environment occurred at the same rate as under normal conditions. Owen et al. and Morra et al. proposed that silanol groups present in the surface reacted via a condensation mechanism under the liberation of water (Fig. 2.5). However, this would not increase the hydrophobicity, since the Si-O-Si crosslinks also are polar in nature. Even though many corona-treated surfaces have been eroded, which could be a major factor in the wettability changes during exposure, this was considered less likely to affect the recovery process. Loss of volatile species may be a factor in high-vacuum conditions, but not under atmospheric pressure. Migration of low molar mass PDMS is undoubtedly the process that most researchers in the field believe is the dominant mechanism for hydrophobic recovery.
Lee and Homan\textsuperscript{43} were probably the first to suggest migration of low molar mass species from the bulk to the surface as the dominant mechanism for hydrophobic recovery. They studied a copolymer based on dimethylsiloxane and methyl-hydrogen-siloxane by reflection infrared spectroscopy and found that the intensity of the Si-H absorbance band decreased markedly upon corona exposure and that it recovered gradually during the subsequent rest period. They then proposed that a recovered sample had a thin film of liquid silicone above a layer of silica-like (SiO\textsubscript{x}) material; according to them the latter may have been cracked to permit transport of low molar mass species\textsuperscript{43}.

Smith et al.\textsuperscript{23} later reported very useful information and more direct proof for the mechanism suggested by Lee and Homan. HTV and RTV silicone rubbers were exposed to corona discharges in air and the specimens were analysed with contact angle measurements and XPS\textsuperscript{23}. The oxidised samples initially exhibited (just after the cessation of the corona treatment) a silica-like surface layer. Further resting led to the formation of a top layer of mildly oxidised PDMS, which was located above the silica-like layer. They proposed that the top layer was rich in low molar mass species that had migrated from the bulk to the surface of the specimen\textsuperscript{23}. Tóth et al. estimated the thickness of the liquid-like top layer to be less than 3 nm using angle-dependent XPS measurements\textsuperscript{24}. GC/MS data revealed that the migrating substances were rich in cyclic oligomeric dimethylsiloxanes, ranging from 4 to 23 repeating units. Removal of extractable species prior to the corona treatment resulted in a higher degree of surface oxidation\textsuperscript{24}.

Owen and coworkers\textsuperscript{46,50} used scanning electron microscopy to determine the depth of the cracks in specimens exposed to plasma treatment\textsuperscript{50}. The depth of the cracks was typically 0.3-0.5 μm. The depth of the silica-like layer was assessed by XPS to \textasciitilde10 nm\textsuperscript{46,50} and the conclusion drawn by the authors was that the cracks penetrated into the unoxidised material. Heavily oxidised specimens showed a cracked silica-like layer and Fritz and Owen\textsuperscript{46} showed that a rapid increase in the hydrophobic recovery rate occurred at the onset of cracking of the brittle surface layer. The recovery rate was always faster in cracked specimens than in specimens lacking surface cracks. Such surface cracking in silicone rubber samples exposed to oxygen-plasma was also reported by Hettlich\textsuperscript{65}.

The temperature dependence of the recovery rate provides information about the apparent activation energy of the recovery process. Morra et al.\textsuperscript{49} reported an activation energy for the recovery of oxygen-plasma-treated specimens of 48 kJ mol\textsuperscript{-1}. Kim et al. reported that the activation energies for the hydrophobic recovery of corona-exposed silicone rubber decreased from 42 to 35 kJ mol\textsuperscript{-1} by increasing the voltage of the applied corona discharges\textsuperscript{66}. The reported activation energies for the hydrophobic recovery are thus at least twice the reported activation energy for the diffusion of low molar mass PDMS in silicone rubber\textsuperscript{67}: 6-7 kJ mol\textsuperscript{-1} for cyclic oligomeric dimethylsiloxanes (D\textsubscript{4} and D\textsubscript{5}); \textasciitilde16 kJ mol\textsuperscript{-1} for PDMS with \textasciitilde40 000 g mol\textsuperscript{-1}. This is an indication that the hydrophobic recovery, if it is controlled by migration, is not a bulk process and that the
properties of the oxidised surface layer of exposed samples are different from those of the bulk.

(a)  
(b)  

Figure 2.6 Illustration of the transport of low molar mass siloxanes through a continuous (a) or cracked (b) silica-like surface layer.

The recovery process is summarised in Fig. 2.6. A hydrophilic silica-like surface layer is formed during exposure to corona/plasma. The layer retards diffusion of low molar mass PDMS to the surface, resulting in a low recovery rate. However, cracking of the SiO$_x$ layer enhances the rate of hydrophobic recovery by facilitating migration of low molar mass PDMS, ultimately forming a continuous liquid layer on top of the silica-like (SiO$_x$) layer.

2.4 Thermal degradation of polydimethylsiloxane

Low molar mass PDMS is believed to migrate from the bulk to the silicone rubber surface resulting in a hydrophobic recovery. A very important question is whether only a limited amount of low molar mass PDMS exists in the rubber or if low molar mass PDMS is continuously generated by scission of the polymer network. Deng and Hackam$^{64}$ found that the effects of heat and electrical discharges, such as dry band arcing, were similar on silicone rubber. Temperatures up to 3000°C can be obtained locally in "hot spots" during dry band arcing$^{68}$. Thus the thermal degradation behaviour of PDMS gives valuable information to address this issue, at least concerning high voltage applications.

Another very important question is whether chain scission or crosslinking is the dominant mechanism during thermal degradation of PDMS. Oxygen-free (inert atmosphere or vacuum) ageing causes mainly chain scission whereas ageing in oxygen-containing media results in both crosslinking and chain scission. Oxidation of the methyl groups leads to increased branching and at later stages, to a crosslinked gel structure. This phenomenon was illustrated by Doyle when he described the formation of a brittle surface layer on an air-aged (135-240°C) silicone rubber$^{69}$. The development of the brittle surface layer caused a significant decrease in weight loss rate. Removal of the surface layer led to re-establishment of the weight loss rate of the virgin sample. Evidently the brittle layer was less permeable to low molar mass PDMS. Doyle also found that chain scission was favoured with reference to crosslinking at higher ageing temperatures$^{69}$. Thomas reported a few years later that thermal ageing of silicone rubber in air led to a brittle surface layer, which he proposed to be due to oxidative crosslinking$^{70}$.
It has been widely demonstrated that oxygen-free thermal ageing of PDMS liquids results in the formation of almost exclusively cyclic oligomeric dimethylsiloxanes of the general formula $D_n = [(\text{CH}_3)_2\text{SiO}]_n$, were $n$ is the number of repeating units. Early work by Lewis showed that the elemental composition was unchanged after oxygen-free thermal ageing of PDMS. This finding suggests that crosslinking reactions (which do cause a change in the elemental composition) were not occurring under these conditions. The formation of cyclic oligomers, predominantly containing three ($D_3$) and four ($D_4$) repeating units, during oxygen-free, dry thermal ageing has been revealed by a number of research groups using gas chromatography.

![Figure 2.7 Mechanisms for chain scission reactions: (Ia) random formation of cyclic PDMS, (Ib) end-initiated formation of cyclic PDMS, (II) intermolecular chain scission.](image)

The different possible mechanisms for chain scission reactions without any net change in the number of covalent bonds before and after the reaction is schematically shown in Fig. 2.7. Scheme I yields short cyclic molecules either from a short cyclic formation along the polymer chains (Ia) or at the chain ends (Ib). Intermolecular reactions also take place (Scheme II). The intermolecular reaction may also yield high molar mass cyclics but these molecules are probably topically hindered to migrate in a network structure.

The kinetics of the chain scission reactions (in vacuum) of linear PDMS by thermo-gravimetric analysis was performed by Thomas and Kendrick. They concluded that the mass loss rate obeyed Arrhenius temperature dependence with an activation energy of 180 kJ mol$^{-1}$. This is considerably lower than the dissociation energy of the Si-O bond, 445 kJ mol$^{-1}$. The mechanisms proposed by Thomas and Kendrick are shown in Scheme Ia-Ib (Fig. 2.7). According to this mechanism a cyclic transition state
(indicated by the dotted lines) was formed and a cyclic oligomer was eliminated. They proposed that the free 3-d orbital of the silicon atom enabled the formation of this transition state. Further GPC findings obtained by Thomas and Kendrick suggested that the scission reactions were randomly initiated (Figure 2.7, Scheme Ia). The randomly initiated depolymerisation was independent of molecular weight of the polymer chain and type of terminal group. Trimethylsiloxyterminated, hydroxylterminated and vinylterminated linear PDMS has demonstrated this behaviour. The main product formed during depolymerisation is D₃, especially at higher temperatures, > 450°C.

Thomas and Kendrick further suggested that impurities may alter the reaction scheme and enable strict unzipping (“back biting”) of the PDMS chain at temperatures well below the depolymerisation temperature region (Figure 2.7, Scheme Ib). This type of unzipping reaction was further discussed by Nielsen. He also proposed an end-initiated rearrangement, via a silanol-activated complex. The rate of the end-initiated depolymerisation decreased with increasing molecular weight of the polymer. In the presence of potassium ions, a catalytic “unzipping” of linear PDMS at 250°C occurred rather frequently at the fourth, fifth, etc. siloxane unit in the chain, starting from the terminal chain end. The amount of D₃ then decreased whereas the amount of larger cyclics (≥D₄) increased. This was explained by the considerable strain prevailing in the D₃ ring making it thermodynamically unstable at lower temperatures.

Impurities play a very important role for the degradation rate of PDMS. Kucera et al. made PDMS according to an anionic mechanism and found that ionic pairs present in the polymer chain promoted degradation. Potassium hydride (KOH) were found to promote depolymerisation further whereas acids (sulphuric acid and benzoic acid) suppressed crosslinking. Al₂O₃ had a stabilising effect against chain scission on these polymers.

Blazsó and Garzó investigated the influence of branching by pyrolysis of branched PDMS using gas chromatography. The original linear segments degraded into cyclic oligomers whereas the branching points transformed into polycyclic fragments. The ratio of the amounts of cyclic and bicyclic products correlated with the concentration of branching points in the virgin polymer. Depolymerisation of PDMS, yielding cyclic oligomers, has also been reported by γ-radiation of PDMS.

### 2.5 Influence of environmental factors on hydrophobicity

During service, silicone rubber outdoor insulation is exposed to water, in the form of rain or fog, and UV-radiation from the sunlight. The influence of these factors on hydrophobicity is summarised in this section.
2.5.1 Water immersion
The weight gain of pure PDMS immersed in pure water at room temperature is \( \approx 0.07 \text{ wt.\%} \). Filled silicone rubbers, on the other hand, shows non-Fickian water sorption and the water uptake can be at least one order of magnitude higher than that of pure PDMS. Long-term immersion of silicone rubber in water leads to a gradual reduction of hydrophobicity. This effect has been attributed to hydratisation of the PDMS backbone, hydrolysis of siloxane bonds which creates hydrophilic silanol-groups or surface erosion and depletion of fillers in the surface region (\( \approx 0.1 \mu\text{m} \)). Other researchers emphasise that a decreased hydrophobicity during water immersion is not an indication of hydrolysis, but caused by an increased surface heterogeneity due to water penetration into the surface and / or reorientation of polar groups. The hydrolysis rate of PDMS in an aqueous environment is catalysed by clay minerals. These minerals are generally not used as filler in silicone rubber formulations used for outdoor insulation applications. They may, however, be present in the pollution layers on the insulator surfaces.

2.5.2 UV radiation
PDMS does not absorb UV light in the 300-400 nm region. Since only wavelengths longer than 290 nm reach the surface PDMS is very stable towards UV radiation from sunlight. It has, however, been reported that silicone rubber insulators were less hydrophobic on the parts what were shielded from the sunlight. Sirat et al. reported that the hydrophobicity of silicone rubber insulators increased steadily during the first year in a tropical climate. It was suggested that additional PDMS oligomers were formed by UV induced chain scission reactions.
3. EXPERIMENTAL

3.1 Materials

3.1.1 HTV silicone rubber (Paper I)
The high-temperature vulcanised silicone elastomer, Elastosil 420/60 from Wacker Chemie, Germany, was based on PDMS. The elastomer contained approximately 20 wt.% of silica filler. 1 wt.% of PMBP-50-PSI (a mixture of 50 wt.% methylated benzoylperoxide and 50 wt.% of silicone oil) from Peroxidchemie, Germany, was mixed into the silicone elastomer using a Brabender internal mixer at 20 rpm for two minutes and thereafter at 25 rpm for five minutes at room temperature. The temperature in the mixer never exceeded 50°C. Films with a thickness of 1.6 mm and a diameter of 110 mm were compression moulded and cured between Mylar sheets in a Schwabenthan Polystat 400 press at 135°C and 6 MPa for 20 minutes. The films were then stored in dry air at 23°C in a desiccator prior to the corona treatments.

3.1.2 ‘Exact’ PDMS networks (Papers II-IV, VI)
Vinylidimethyl-terminated PDMS of different molecular weights were crosslinked in a hydrosilylation reaction, using a (30-35%) methylhydro-(65-70%) dimethylsiloxane copolymer (M_w = 2100 g mol^-1) as crosslinker. The ratio of hydride to vinyl groups was 2:1 in order to achieve fully crosslinked network structure. A platinum divinyltetramethyl disiloxane complex was used as a catalyst at a concentration of 30 ppm. The chemicals were purchased from United Chemical Technologies Inc., USA, and were used as received. The molar mass distribution of the vinylidimethyl-terminated PDMS was assessed by Size Exclusion Chromatography. Sheets of crosslinked PDMS with a thickness of 1 mm and a diameter of 210 mm were prepared in a Schwabenthan Polystat 400S compression moulding machine at 135°C and 6 MPa pressure for 15 min. Post-curing was performed at 120°C for 12 h in a hot-air oven. Specimens with a diameter of 30 mm were cut from the moulded sheets. Low molar mass species were removed from the specimen by Soxhlet extraction during 72 h, using hexane (bp 68°C) as solvent. The specimens were then slowly deswollen in air, dried in a vacuum-oven, and kept in dessicators. The number average molar mass of the chain segments between the crosslinks (M_c) of the PDMS networks are assumed to be equal to number average molar mass (M_n) of the particular vinylidimethyl-terminated PDMS used. The codes used for the different PDMS networks are as follows: P0.7: M_c = 700 g mol^-1; P8: M_c = 7500 g mol^-1; P12: M_c = 11 600 g mol^-1; P17: M_c = 16 500 g mol^-1 and P38: M_c = 38 300 g mol^-1.
The polydispersity ($\frac{M_w}{M_n}$) of the vinyldimethyl-terminated PDMS's were 1.1 (P0.7), 1.5 (P8), 1.6 (P12), 1.9 (P17) and 1.5 (P38).

P17 was also diluted in heptane (Merck, >99% purity) to a 5 wt.% solution. The solution was filtered through a filter with a pore size of 0.45 µm and spin-coated onto silicon wafers at 3000 rpm where it was allowed to spin + dry over a period of 30 s. The silicon wafers were cleaned with ethanol and acetone before spin coating. The specimens were subsequently cured in a dust-free hood at 130°C for 4 h.

3.1.3 Field aged HTV silicone rubber formulations (Paper VII)
The silicone rubbers formulated from Powersil 310 (Wacker Chemie, Germany), was based on PDMS and approximately 20 wt.% of reinforcing silica filler. 2,5-bis(t-butylperoxy)-2,5-dimethylhexane (C6) was used as crosslinking agent (2 phr). Silanised aluminum trihydrate (ATH) with a median particle size of 1.3-2.6 µm and the geometrical form of pseudo-hexagonal platelets was added (Martinal OL-104/S, Martinwerk, Germany). The silicone oil added was based on linear PDMS ($\bar{M}_n$ : 14 000 g mol$^{-1}$) (AK 350 from Wacker Chemie, Germany). The formulations were mixed in a Brabender internal mixer at 65°C. Rods, with a diameter of 25 mm and a length of 220 mm were then injection-moulded at 185°C during 45 minutes. The initial injection pressure was 1 Mpa and then it was kept at a constant load of 0.2 MPa. The post-curing was performed during 10-15 h at 185°C in a hot-air oven.

3.2 Conditions during exposure to electrical discharges

3.2.1 Corona discharges
The experimental set-up consisted of two circular electrodes mounted in a sealed glass vessel. The geometry of the upper electrode was designed to achieve a homogeneous electric field over the specimen by using the two-dimensional version of the electric field calculation program “ACE”$^{97}$. Views of the electrode from the side (Fig. 3.1) and from below (Fig. 3.2). The electrode had a diameter of 87 mm. The length of the seven innermost needles was 12 mm, the 12 middle needles 11 mm and the 12 outer needles 9 mm. The tips of the needles had a radius of 56 µm with a standard deviation of 4.2 µm$^{98}$. The lower circular electrode had a diameter of 140 mm and was connected to ground. The applied voltage was 20 kV peak to peak at 50 Hz. The integrated corona charge transfer (in Watts), hereafter referred to as the power of the electrode, was obtained according to a method described by Dakin et al.$^{99}$ Two different geometries were used. The films were either positioned directly on the electrode ground plate, resulting in a power of 1.5 W, or on circular glass plates (thickness: 3 mm; diameter: 120 mm) which were then positioned on the electrode ground plate. The latter geometry resulted in a power of 2.6 W. This set-up was consequently used, unless the effect of 1.5W is stated.
3.2.2 Radio-frequency plasma (RF)
Radio-frequency plasma treatments were performed in a bell-jar reactor, type LCD-1200-400A from Shimadzu, Japan, with a volume of approximately 75x10^{-3} m^3. Treatments were performed at a pressure of 26.6 Pa of ultra pure oxygen (Scotts Special Gases Inc., USA) and a gas flow rate of 4.37x10^{-6} m^3 s^{-1}. The frequency was 13.56 MHz and the power was 40 W. The disk was rotated in order to achieve a uniform plasma exposure of the specimens.

3.2.3 Microwave plasma (MW)
Microwave treatments were performed in a V15-G microwave frequency reactor from Plasma-Finish GmbH, Germany. The treatments were performed in 27 Pa of ultra pure oxygen or dry air (AGA, Sweden) and a
gas flow of $8.3 \times 10^{-7}$ m$^3$ s$^{-1}$. The frequency was 2.45 GHz and the power was 40 or 100W.

### 3.3 Characterisation techniques

#### 3.3.1 Contact angle measurements
The contact angle measurements were performed using a Ramé Hart goniometer using the sessile drop technique\textsuperscript{100}. Deionised water (Millipore, resistivity: 18.4 M$\Omega$ cm) was used. Each data point given was based on at least 8 contact angle measurements at four different positions on the specimen. The advancing contact angles were obtained by keeping the needle in the water droplet after positioning it on the surface and by carefully adding more water until the advancing angle appeared to be maximal. The receding angle was obtained by withdrawing water from the drop until the three-phase line started to recede. All measurements were performed with the needle remaining in the droplet.

#### 3.3.2 Wilhelmy balance
The dynamic contact angle was measured by a fully computer-controlled, automated tensiometer Sigma 70 (KSV Instruments, Finland). Distilled and deionised water was poured into a beaker and placed inside a closed test chamber together with the specimen, to minimise pollution from the air. The speed of immersion and withdrawal was 5 mm/min. Each individual specimen was used for one measurement only.

#### 3.3.3 Reflection infrared spectroscopy (IR)
HTV silicone rubber (Paper I): a Perking Elmer 1760 spectrometer equipped with a nitrogen-cooled MCT detector was used. The spectra were based on 100 scans with a resolution of 4 cm$^{-1}$. A KRS-5 crystal with 45° beam incidence angle from Spectra Tech was used. The spectrum of the KRS-5 crystal was subtracted from all the spectra.

HTV silicone rubber (Paper VII): a Perkin Elmer 2000X, equipped with a "Golden Gate" single reflection ATR unit with a diamond crystal was used. The angle of incidence was 40°. Each spectrum was an average of 10 scans with a resolution of 4 cm$^{-1}$.

#### 3.3.4 X-ray photoelectron spectroscopy (XPS)
Before XPS analyses the specimens were extracted in CHCl$_3$ or hexane in order to remove low molar mass siloxanes, formed during exposure to corona/air-plasma, and subsequently degassed in a vacuum oven. The XPS spectra were obtained using an AXIS-HS spectrometer from Kratos Analytical. The monochromatic Al K$_\alpha$ radiation used was operated at 15 kV and 300 W. The pressure in the sample chamber was between $5 \times 10^{-6}$ and $1 \times 10^{-5}$ Pa. Survey spectra were recorded at a 80 eV pass energy and the high resolution spectra of the Si 2p peak at 20 or 25 eV pass energy. The spectra were referenced to the O1s-line (binding energy = 532.0 eV). A low-energy electron flow gun was used to neutralise sample charging. The
high resolution spectra of the Si 2p peaks were either resolved in two components: one peak at 103.8 eV associated with an inorganic silica-like (SiOₓ) phase, i.e. a component with Si atoms bonded to more than two oxygen atoms. The other component was positioned at 102.1 eV, assigned to an organic silicone phase (PDMS)²⁴. Alternatively the Si 2p peak was resolved into three components in accordance with Alexander et al.¹⁰¹. Si bound to two oxygen at 102.1 eV, Si bound to three oxygen at 102.8 eV and Si bound to four oxygen (SiO₂) at 103.4 eV. The accuracy of these fits was estimated to be ± 5%¹⁰¹.

3.3.5 Scanning Electron Microscopy (SEM)
A Jeol JSM-5400 scanning electron microscope was used operated at 10-15 kV acceleration voltage. The specimen were coated with Au/Pd (60:40) before examination, using a Desk II from Denton Vacuum, operated at 45 mA for 2 x 10 s. The specimen were kept in vacuum at least one hour prior to sputtering and were thereafter analysed instantaneously, in order to avoid cracking of the sputtered layer caused by release of residual dissolved gases from the bulk.

3.3.6 Atomic Force Microscopy (AFM)
AFM measurements were performed at the Institute for Surface Chemistry, Stockholm, Sweden using a Nanoscope IIIA Multimode Atomic Force Microscopy. The scan rate was 1.5 Hz.

3.3.7 Neutron reflectivity measurements
The neutron scattering experiments on spin-coated specimens were performed at the Missouri University Research Reactor (MURR), University of Missouri-Columbia, U.S.A. This instrument featured a monochromatic beam (λ = 0.235 nm) used in an angle-dispersive configuration with a single ³He detector. The reflected intensity data, normalised to unit incident intensity were measured as a function of the change in neutron momentum transfer normal to the surface (Q = (4π/λ) sinθ, where λ is the wavelength of the incident neutron beam and θ is the incident angle). The profile of the scattering length density as a function of layer depth (z) was varied to fit the experimental data using an asymmetric interfacial width error function.

3.3.8 Optical microscopy
The fracture characteristics of the silica-like surface layers was assessed using an uniaxial tensile tester (Fig 3.2) mounted on a Leitz Ortholux POL BK II optical microscope. The size of the specimen was 6 ± 0.5 x 10 ± 0.5 mm².
A small prestrain was applied to assure that the specimen was aligned properly which induced an uncertainty of about 0.5% strain ($\varepsilon = d/l_0$, where $d$= displacement and $l_0$= initial length of specimen) in the measured values. The strain was increased stepwise by strain steps of 2% after an initial step of 1% strain. The strain rate was $50 \pm 10 \, \mu m \, s^{-1}$ in each strain step. The time interval between the steps was 4 minutes. During this period the fragmentation lengths were determined using a micrometer scale in the microscope.

3.3.9 Size exclusion chromatography (SEC)
Size Exclusion Chromatography was used to assess the molar mass distributions of the PDMS. A Waters 717 Plus autosampler and a Waters model 510 apparatus equipped with three PLgel 10 µm mixed-B columns, 300×7.5 mm (Polymer Labs) was used. Chromatograms were recorded using a PL-ELS 1000 evaporative light scattering detector (Polymer Labs). Data was processed using Millenium version 3.20 software. Chloroform was used as eluent, at a flow rate of 1.0 ml min$^{-1}$. PDMS standards with narrow molar mass distributions and $M_n$ between 2000 and 85 000 g mol$^{-1}$ were used for calibration. The solutions were filtered with 45 µm Teflon filters before being injected into the column.

3.3.10 Gas chromatography – mass spectrometry (GC-MS)
The low molar mass fraction was analysed by GC-MS, using a Finnigan GCQ gas chromatograph/mass spectrometer (EI mode). The GC was equipped with a Cp-Sil 8 capillary column (5% phenyl-95% polydimethylsiloxane, 30 m × 0.25 mm, 0.25 µm) from Chrompack, Sweden. Helium was used as carrier gas at a flow rate of 40 ml min$^{-1}$. The temperature program of the column was 40°C for 1 min followed by a temperature rise from 40 to 250°C (10°C/min). The injector temperature was kept at 220°C. The mass spectrometer was operated at 70 eV.
4. EXPOSURE TO ELECTRICAL DISCHARGES

This chapter addresses the effect of silica-like surface layers on the hydrophobic recovery of silicone rubbers after exposure to electrical discharges. Two types of were used, commercial peroxide cured (HTV) silicone rubber and addition cured ‘exact’ PDMS networks. Five networks, differing only in crosslink density, were investigated. The first part of the chapter discusses the build up of a silica-like surface layer when HTV silicone rubber is exposed to corona and the effects of ‘mechanical deformation’ on the subsequent hydrophobic recovery. ‘Exact’ PDMS networks were then exposed to corona or air-plasma (MW) in order to investigate the influence of crosslink density on the hydrophobic recovery rate. The difference in surface oxidation caused by the low energetic corona (2.6 W), compared to the highly energetic air-plasma (100 W) was investigated. Finally, the long-term stability of the hydrophobic recovery was assessed by repeated corona treatments of two ‘exact’ PDMS networks. All treatments were performed in an air-environment. In the second part of the chapter, an ‘exact’ PDMS network was exposed to oxygen-plasma (RF or MW) and the influence of atmospheric contamination and migration of mobile siloxane species on the hydrophobic recovery was addressed. Furthermore the thickness and composition of the silica-like surface layer was assessed using neutron reflectivity measurements. In the third part the migrating siloxanes were characterised using chromatographic methods.

4.1 HTV silicone rubber: corona (Paper I)

4.1.1. Loss of hydrophobicity
The hydrophobicity gradually decreased with exposure time when the HTV silicone rubber was exposed to corona discharges (Fig. 4.1). The use of the higher effect of 2.6W resulted in a faster loss of hydrophobicity. The corona discharges caused a uniform surface oxidation, as indicated by the small bars associated with the 90% confidence interval. The decreasing contact angle hysteresis, i.e. difference between advancing and receding contact angles indicated a decreased segmental mobility of the molecules in the surface region. In order to investigate the hydrophobic recovery after corona as a function of exposure time, silicone rubber specimens were exposed to corona during 0.3 h, 1 h and 200 h.
4.1.2. Recovery of hydrophobicity

The hydrophobic recovery was initiated directly after the end of the corona exposure. The increase in hydrophobicity was generally more pronounced in the early stages and levelled off, approaching the values of the virgin, unexposed surfaces (Fig. 4.2). Specimens subjected to a small mechanical deformation (<1% strain) directly after exposure to corona for 1 h or more recovered their hydrophobicity faster than untouched specimens kept under identical conditions (Fig. 4.2). The increase in recovery rate after deformation was most pronounced after exposure to 200 h corona. The contact angle hysteresis of the ‘undeformed’ films was lower compared to the deformed ones, indicating a lower degree of segmental mobility of molecules in the surface region of these films.

4.1.3. Contact Angle Measurement

Contact angles for HTV silicone rubber exposed to 0.3 h (a) and 1 h (b) of corona plotted versus storage time at 25°C; ‘mechanically deformed’ specimen: advancing (■) and receding (○); ‘undeformed’ specimen: advancing (❐) and receding (●). The dotted lines indicate the initial advancing (a.a₀) and receding (r.a₀) contact angles.
The hydrophobic recovery increased with increasing storage temperature, where the deformed specimens followed an Arrhenius temperature relationship. The calculated activation energies of the hydrophobic recovery after exposure to corona were: 0.3 h: 57 and 54 kJ mol\(^{-1}\), 1 h: 52 and 33 kJ mol\(^{-1}\) and 200 h: 36 and 39 kJ mol\(^{-1}\). The values are based on the times to full recovery of the advancing and receding contact angles, respectively. The activation energies of the recovery thus decreased with increasing dose of corona. This was in accordance with data of corona-exposed silicone rubber reported by Kim et al. where the activation energy of hydrophobic recovery decreased from 42 to 35 kJ mol\(^{-1}\) by increasing the voltage of the applied corona discharges\(^{66}\). The calculated activation energies were at least twice the activation energies of the diffusivity of low molar mass PDMS in silicone rubbers, ranging between 3-16 kJ mol\(^{-1}\) depending on molar mass of the diffusing species\(^{67}\). These results indicated that the hydrophobic recovery, if it was controlled by the diffusivity of low molar mass siloxanes, was not a bulk process and that the properties of the oxidised surface were different from those of the bulk.

The hydrophobic recovery of ‘undeformed’ specimens, with the exception of specimen exposed to 0.3 h corona, was slower compared to the deformed ones, and the kinetics of the recovery showed a large variation under identical conditions and did not obey any clear Arrhenius temperature relationship.

### 4.1.3 X-ray photoelectron spectroscopy

The atomic surface composition was analysed using angle-resolved XPS (Table 4.1). The estimated depth of penetration was 8-10 nm at normal angle (\(\phi=0^\circ\); \(\phi\) is the angle between the direction of emitted photoelectrons to the analyser and the surface normal) and 2 nm at grazing angle (\(\phi=60^\circ\))\(^{24}\).

<table>
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<th>Angle ((\phi))</th>
<th>Atomic comp. (at.%)</th>
<th>Ratio</th>
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</tbody>
</table>

Short-term (0.3 h) exposure to corona led to a pronounced increase in oxygen content to 41-45% and a decrease in the carbon content to 29-33%. The 2 nm top layer showed a lower oxygen content and higher carbon content than the top 8-10 nm. After 1 h corona, the amount of oxygen increased to 53-56% and the carbon content dropped to 15-19% with even greater changes in the top 2 nm layer (Table 4.1). The composition of the surface of the specimen exposed to 200 h corona, was similar to that exposed for 1 h of corona (Table 4.1). This means that the atomic
composition of the surface layer remained essentially constant after the initial hour of corona exposure. The lower oxidation of the 2 nm layer (φ = 60°) can be explained by diffusion of mobile PDMS which covered the oxidised surface. The Si 2p peak was resolved into two components: one at 102.1 eV, assigned to an organic silicone phase, and one at 103.8 eV, associated with an inorganic silica-like (SiOₓ) phase, i.e. a component with silicon atoms bonded to more than two oxygen atoms (Table 4.2).

<table>
<thead>
<tr>
<th>Exposure time (h)</th>
<th>C 1s (eV)</th>
<th>Si 2p (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>284.5</td>
<td>286.5</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>0.3</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>92</td>
<td>8</td>
</tr>
<tr>
<td>200</td>
<td>95</td>
<td>5</td>
</tr>
</tbody>
</table>

The first hour of exposure caused most of the irreversible changes towards the formation of an inorganic silica-like phase. A small silica peak (constituting 8% of the area of the Si 2p peak) was present in the unexposed specimen, most likely due to the amorphous silica filler added to this material. The content of oxidised carbon atoms (binding energy = 286.1 eV) showed only a minor increase in the exposed specimen and never exceeded 8% of the carbon content (Table 4.2). This suggests that oxidation in the 8-10 nm top layer mainly involved the formation of linkages between Si and O atoms.

4.1.4 Reflection infrared spectroscopy
The effect of corona was further studied by reflection infrared spectroscopy (Fig. 4.3). The depth of the assessed surface layer was in the range of 0.45 to 4.5 μm, depending on the wavelength of the IR radiation. The spectra obtained are thus not related to the surface in the strictest sense, compared to “true” surface methods such as XPS. The increase of the broad absorption peak centred at 3300 cm⁻¹ after exposure to corona indicated the formation of hydroxyl groups. According to XPS data, the resolution of the C 1s peak demonstrated only the presence of minor amounts of oxidised carbon atoms. This suggested that the majority of hydroxyl groups formed were bonded to Si-atoms (i.e. silanol groups) and not to carbon atoms. The absorption bands from C-H stretching at 2963 cm⁻¹ and bending at 1463 cm⁻¹, originating from the substituted methyl groups remained almost unchanged, even after 200 h of continuous corona, indicating an almost unchanged content of methyl groups in the HTV silicone rubber within the observed penetration depth. The depletion of carbon atoms detected by XPS was obviously associated with a very thin surface layer (~10 nm) which was hardly noticeable by infrared spectroscopy. Corona treatment led only to a very minor increase in the carbonyl absorption peak between 1650-1700 cm⁻¹. This suggested that, during surface oxidation, only low amounts of carbonyl groups were formed compared to the formation of silanol groups. These findings, combined with the data obtained by contact angle measurements, strongly
support the idea of a thin surface layer with inorganic, silica-like structure in corona-treated HTV silicone rubber.

Figure 4.3 Reflection infrared spectroscopy of HTV silicone rubber surfaces after exposure to corona.

4.2 'Exact' PDMS networks: corona and air-plasma (MW) (Paper III)

The results presented in Paper I demonstrated that corona exposure of a HTV silicone rubber resulted in the gradual formation of a silica-like surface layer, which decreased the rate of hydrophobic recovery. In order to investigate the influence of the crosslink density of the PDMS networks on the formation of such surface layers and the hydrophobic recovery rate, five 'exact' PDMS networks were prepared. Furthermore the mechanical properties of the silica-like surface layers were investigated. The abbreviations used for the PDMS networks, differing only in crosslink density \( \rho / M_c \) were as follows: P0.7: \( M_c = 700 \) g mol\(^{-1} \); P8: \( M_c = 7500 \) g mol\(^{-1} \); P12: \( M_c = 11600 \) g mol\(^{-1} \); P17: \( M_c = 16500 \) g mol\(^{-1} \) and P38: \( M_c = 38300 \) g mol\(^{-1} \). The materials were exposed to either corona or air-plasma (MW). The air-plasma was used to investigate the influence of a surface treatment with a high intensity (100W) on the degree of surface oxidation and the subsequent hydrophobic recovery.

4.2.1 Hydrophobic recovery

Influence of exposure time

The reproducibility of the hydrophobic recovery rate after exposure to corona was investigated by exposing three different specimens of P17 to 1h corona. The specimens were exposed to corona at three separate occasions. It was found that the measured contact angles generally were within the confidence interval of the contact angle measurements (Fig. 4.4). The materials were then exposed to corona during 0.5 h, 1 h or 3 h in order to investigate the influence of crosslink density on the subsequent hydrophobic recovery. It was observed that the recovery was independent of the crosslink density of the materials exposed to 0.5 h corona (Fig. 4.5a
and b). For the materials exposed to 1 h corona, the recovery rate increased with increasing crosslink density (Figs. 4.5c and d). The recovery data of materials exposed to 3 h corona resembled those obtained for the specimens exposed to 1 h corona, where the hydrophobic recovery rates increased with increasing crosslink density. The scatter in the contact angle data was however larger after the 3 h corona exposure. The hysteresis was only 2-5° directly after the corona exposures and it increased gradually with recovery time to ~10°. The small hysteresis in freshly exposed samples reflects the low segmental mobility of the oxidised (silica-like) surface layer.

![Figure 4.4 Reproducibility of the hydrophobic recovery at 22°C after exposure to 1 h corona, illustrated by three different specimens of P17. (a): advancing contact angle ($\theta_a$), (b): receding contact angle ($\theta_r$). The error bars indicate a confidence interval of 90%. The dotted lines indicate the initial contact angles.](image)

The hydrophobic recovery of materials exposed to air-plasma (MW) of higher intensity, compared to corona, showed no systematic dependence on material crosslink density (Fig. 4.6) at any of the used doses (30-720 s air-plasma). The times to recover the initial hydrophobicity were shorter for the specimens exposed to air-plasma than for the specimens exposed to corona. Furthermore the variation in recovery times between different materials increased progressively with increasing dose of air-plasma. The contact angle hysteresis was 2-5° directly after exposure to the air-plasma and increased gradually with the recovery time to finally reach 25°.

**Temperature dependence**

The temperature dependence of the hydrophobic recovery was investigated by ageing the exposed materials at four different temperatures (22-114°C). The hydrophobic recovery of all materials exposed to corona showed an Arrhenius temperature dependence. The Arrhenius diagram shown in Figure 4.7 was obtained by plotting the logarithm of the reciprocal time to reach $\theta_r = 70°$ versus the reciprocal temperature. The recovery rate data for a series of materials exposed to 1 h corona are shown.
Figure 4.5  Advancing ($\theta_a$) and receding ($\theta_r$) contact angles of PDMS networks as a function of the recovery time at 22°C after corona exposure during 0.5 h corona (a-b) and 1 h (c-d) for the following materials: P0.7 (○), P8 (●), P12 (△), P17 (▲) and P38 (●). The dotted lines indicate the range of the advancing and receding contact angles for unexposed specimens. The error bars indicate a 90% confidence interval.

Figure 4.6  (a): Advancing ($\theta_a$) and (b): receding ($\theta_r$) contact angles of PDMS networks as a function of the recovery time at 22°C after corona exposure during 120 s air-plasma for the following materials: P0.7 (○), P8 (●), P12 (△), P17 (▲) and P38 (●). The error bars indicate a 90% confidence interval.
Specimens that were deformed to 15% strain in order to cause a fragmentation of the surface layer (Section 4.2.3) showed an increased recovery rate by almost 2 orders of magnitude (Fig. 4.7). The activation energy ranged between 30 and 60 kJ mol\(^{-1}\) with an average of 42 kJ mol\(^{-1}\) and a standard deviation of 10 kJ mol\(^{-1}\). The activation energy was independent of crosslink density (average including all exposure times): P0.7: 43 kJ mol\(^{-1}\); P8: 45 kJ mol\(^{-1}\); P12: 41 kJ mol\(^{-1}\); P17: 41 kJ mol\(^{-1}\); P38: 35 kJ mol\(^{-1}\)) and corona exposure time (average ± standard deviation): 40±8 kJ mol\(^{-1}\) (0.5 h); 49±10 kJ mol\(^{-1}\) (1 h); 42±13 kJ mol\(^{-1}\) (3 h). The specimens deformed to 15% strain showed similar activation energies, average ± standard deviation: 38±8 kJ mol\(^{-1}\). This indicated that the same mechanism was dominating, even though cracks were initiated in the silica-like layer. The specimens exposed to air-plasma showed a very pronounced deviation from the Arrhenius law.

**Figure 4.7** The reciprocal of the logarithm of the time to reach a receding contact angle of 70° after 1h corona: P0.7 (○), P8 (●), P12 (△) P17 (▲) and P12 subjected to 15% strain after exposure (▼). The error bars indicate a 90% confidence interval.

**Figure 4.8** The reciprocal of the logarithm of the time to reach a receding contact angle of 70° after 180 s air-plasma. Material: P8. The error bars indicate a 90% confidence interval.
All the data conformed to the curve form shown in Figure 4.8 with a steep slope at low temperatures and a flat line at the higher temperatures. This 'non-Arrhenius' temperature dependence is further discussed in Section 4.2.5.

4.2.2 X-ray photoelectron spectroscopy
The elemental composition of the 8-10 nm top layer was assessed by XPS and the data are presented in Tables 4.3-4.5. The elemental composition is presented as the ratio between the atomic concentration of carbon and oxygen (C/O). The unexposed materials showed C/O ratios close to 2.2. The silicon content remained essentially constant between 24–28 at.% for all analysed materials.

Table 4.3 Atomic C/O ratio of the surface from XPS data after exposure to corona or air-plasma.

<table>
<thead>
<tr>
<th>Material</th>
<th>Corona</th>
<th></th>
<th>120 s air-plasma</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5 h</td>
<td>1 h</td>
<td>3 h</td>
<td></td>
</tr>
<tr>
<td>P0.7</td>
<td>0.87</td>
<td>0.83</td>
<td>0.41</td>
<td>0.48</td>
</tr>
<tr>
<td>P8</td>
<td>1.20</td>
<td>1.08</td>
<td>0.79</td>
<td>0.82</td>
</tr>
<tr>
<td>P12</td>
<td>1.46</td>
<td>1.11</td>
<td>0.90</td>
<td>0.92</td>
</tr>
<tr>
<td>P17</td>
<td>1.69</td>
<td>1.32</td>
<td>1.01</td>
<td>1.08</td>
</tr>
<tr>
<td>P38</td>
<td>1.56</td>
<td>1.48</td>
<td>1.04</td>
<td>1.17</td>
</tr>
</tbody>
</table>

The corona/air-plasma treatment led to a gradual decrease in the C/O ratio with increasing exposure time (Table 4.3). It is also evident from the data presented in Table 4.3 that the C/O ratio decreased with increasing crosslink density at every corona exposure time. This shows that the C-C bonds were more sensitive towards oxidation than the methyl groups substituted on silicon.

Table 4.4 Results of the curve resolution of Si 2p peak for the materials studied after corona exposure.

<table>
<thead>
<tr>
<th>Material</th>
<th>Corona exposure time (h)</th>
<th>Intensity (%) of Si 2p peaks</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5</td>
<td>102.1 eV</td>
<td>102.8 eV</td>
</tr>
<tr>
<td>P0.7</td>
<td>0.5</td>
<td>36</td>
<td>30</td>
</tr>
<tr>
<td>P0.7</td>
<td>1</td>
<td>41</td>
<td>23</td>
</tr>
<tr>
<td>P0.7</td>
<td>3</td>
<td>38</td>
<td>18</td>
</tr>
<tr>
<td>P8</td>
<td>0.5</td>
<td>59</td>
<td>19</td>
</tr>
<tr>
<td>P8</td>
<td>1</td>
<td>47</td>
<td>31</td>
</tr>
<tr>
<td>P8</td>
<td>3</td>
<td>39</td>
<td>27</td>
</tr>
<tr>
<td>P12</td>
<td>0.5</td>
<td>56</td>
<td>32</td>
</tr>
<tr>
<td>P12</td>
<td>1</td>
<td>52</td>
<td>27</td>
</tr>
<tr>
<td>P12</td>
<td>3</td>
<td>49</td>
<td>19</td>
</tr>
<tr>
<td>P17</td>
<td>0.5</td>
<td>69</td>
<td>20</td>
</tr>
<tr>
<td>P17</td>
<td>1</td>
<td>69</td>
<td>15</td>
</tr>
<tr>
<td>P17</td>
<td>3</td>
<td>58</td>
<td>12</td>
</tr>
<tr>
<td>P38</td>
<td>0.5</td>
<td>73</td>
<td>17</td>
</tr>
<tr>
<td>P38</td>
<td>1</td>
<td>67</td>
<td>20</td>
</tr>
<tr>
<td>P38</td>
<td>3</td>
<td>46</td>
<td>25</td>
</tr>
</tbody>
</table>

33
The silicon atoms are electron withdrawing (electropositive), thus polarising the methyl groups which makes them less susceptible to radical attack\(^1\). The broad Si 2p peak was resolved into three peaks at different binding energies (eV) according to a method described by Alexander et al.\(^101\) (Table 4.4). The 102.1 eV peak is associated with Si bound to two oxygen atoms (unoxidised PDMS), the 102.8 eV peak is associated with Si bound to three oxygen atoms (partly oxidised PDMS) and the 103.4 eV peak is associated with Si bound to four oxygen atoms (SiO\(_2\)). All materials showed a similar trend in the changes in surface structure with increasing corona exposure time (Table 4.4). The SiO\(_2\) content increased and the fraction of unoxidised PDMS decreased with increasing exposure. At low crosslink densities the increasing oxidation was almost linear with crosslink density whereas it saturated at higher degrees of crosslinking.

The oxidation induced by the air-plasma proceeded at a much higher rate compared to corona. Already after 10 s air-plasma treatment of P8 the C/O ratio was reduced from 2.16 to 1.30 (Table 4.5), which was comparable to 0.5 h corona treatment (C/O: 1.20). Curve resolution of the Si 2p peak showed that 25% of PDMS had transformed into an oxidised state already after 10 s air-plasma, consisting mainly of partially oxidised PDMS (Table 4.5). The total amount of oxidised silicon increased with treatment time, reaching a value of 60%, mainly consisting of SiO\(_2\) (38%). This was comparable to the SiO\(_2\) content after 3 h corona for this particular material. Higher doses of air-plasma (>180 s) led to no further change in the surface composition. The ratio C/O remained essentially constant at \(\approx 0.65 \pm 0.05\) (Table 4.5).

**Table 4.5** Atomic C/O ratio and results of curve resolution of the Si 2p peak of the surface layer of material P8 from XPS data after exposure to air-plasma.

<table>
<thead>
<tr>
<th>Plasma treatment time (s)</th>
<th>C/O</th>
<th>Intensity (%) of Si 2p peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>102.1 eV</td>
</tr>
<tr>
<td>10</td>
<td>1.30</td>
<td>75</td>
</tr>
<tr>
<td>30</td>
<td>1.28</td>
<td>70</td>
</tr>
<tr>
<td>120</td>
<td>0.82</td>
<td>57</td>
</tr>
<tr>
<td>180</td>
<td>0.70</td>
<td>45</td>
</tr>
<tr>
<td>360</td>
<td>0.65</td>
<td>42</td>
</tr>
<tr>
<td>720</td>
<td>0.60</td>
<td>40</td>
</tr>
</tbody>
</table>

The finding by XPS that all exposed surfaces of ‘exact’ PDMS materials contained a significant fraction of unoxidised PDMS (at least 40%) was important. This was valid also for HTV silicone rubber, even though the content of unoxidised PDMS was lower; after 200 h of continuos corona, 13% of the silicone remained unoxidised (Table 4.2). Since the curve-fitting procedures of the Si 2p peaks differed between ‘exact’ PDMS materials and HTV silicone rubbers, the proportion of oxidised/unoxidised PDMS is not directly comparable. It is believed that only a small part of the unoxidised silicone is due to migration of low molar mass species, due to the extraction procedures after the exposures. Hence, there must be a limiting factor of physical and/or chemical nature that prohibits oxidation over a certain limit. One possibility is that the extensive crosslinking accompanying oxidation reduces the segmental mobility also of the
unoxidised species. At some critical low value in segmental mobility further oxidation should be impossible. Grassie and Scott\textsuperscript{106} stated that polymers oxidise more rapidly above their glass transition temperature than in the glassy state primarily due to the faster rate of diffusion of oxygen and to the so-called ‘cage effect’ (recombination of nearby radicals). Dan and Guillet\textsuperscript{107} showed that the quantum yield (number of molecules reacting in a particular process/number of quanta absorbed by the system) for chain scission induced by UV radiation showed a pronounced jump at the glass transition temperature for a variety of fully amorphous polymers. An implication of this view is that the oxidised and unoxidised components must be mixed on a fine (submicrometer) scale. If the oxidised and unoxidised species formed separate, larger domains (micrometer - size), the segmental mobility within the unoxidised domains would be unaffected.

Generally the ‘exact’ PDMS materials exhibited a lower degree of oxidation compared with HTV silicone rubbers exposed to the same dose of corona (1 h). This has previously been reported by Smith et al.\textsuperscript{23}. They suggested that the surfaces of peroxide-cured (HTV) silicone rubbers were more silica-like after exposure to corona whereas the surfaces of addition-curing silicone rubbers contained a higher content of oxidised polymer chains which had the capability of restructuring readily in response to environmental changes\textsuperscript{23}. Residues of the peroxides used for crosslinking of HTV silicone rubbers, substituted on the polymer backbone, may also be sensitive to oxidation and initiate further oxidative crosslinking reactions.

4.2.3 Tensile testing

Tensile testing was used to assess the mechanical properties of the formed silica-like layer. Specimens of P0.7 were not included in these studies because of their brittle mechanical properties (fracture strain < 2%). The onset of cracking and the subsequent fragmentation process was determined as a function of strain (Fig. 4.9). The fracture patterns appeared as sharply defined cracks oriented perpendicular to the direction of the applied stress (Fig. 4.12). The surface crack pattern was characterised by the fragmentation length ($L$), which was defined as the distance between two adjacent parallel cracks. Cracks with random orientation, often initiated from defects or edges were not considered in the statistical analysis of the crack pattern. Further it should be noted that micro-cracking/pores (voids on the sub-micrometer level) may be initiated below the observed onset of fragmentation. We thus made the assumption that a decreasing onset of fragmentation also indicated a decreasing onset for initiation of such micro-cracks/pores.

After 0.5 h corona, only a fraction of the specimens showed fragmentation (dotted lines in Fig. 4.9a) whereas the material with the lowest crosslink density (P38) showed no fragmentation at all. Specimens exposed to 1 h corona, showed curves that were essentially shifted along the strain axis depending on their particular crosslink density with the material with highest crosslink density shifted to the lowest strains (Fig. 4.9b). Further exposure to corona (3 h) led to a fragmentation length-strain relationship almost independent of the crosslink density (Fig. 4.9c).
Figure 4.9 Average fragmentation length ($<\ell>$) as function of strain after exposure to: (a) 0.5h corona, (b) 1h corona, (c) 3h corona for the following materials: P8 (◇), P12 (●), P17 (□) and P38 (■). The error bars indicate a 90% confidence interval.

Specimens exposed to air-plasma showed the same basic pattern as after exposure to corona: the strain for the onset of cracking increased with decreasing dose of plasma and decreasing crosslink density. The specimens exposed to 30 s air-plasma showed no surface cracks, whereas they started to appear on some of the specimens exposed to 120 s (P17 and P38) and on all specimens exposed to 180 s air-plasma (Fig. 4.10). The fragmentation length showed a strain dependence similar to specimens exposed to corona.

Figure 4.10 Average fragmentation length ($<\ell>$) as function of strain after exposure to: (a) 120 s air-plasma, (b) 180 s air-plasma for the following materials: P8 (●), P12 (△), P17 (▲) and P38 (■). The error bars indicate a 90% confidence interval.
Figure 4.11 shows a summary of the fracture strain of the different oxidised layers as function of the ratio (C/O) by XPS. The fracture strain increases, as expected, with increasing C/O ratio. At the same degree of oxidation (C/O) the strain for the onset of fragmentation decreased with decreasing crosslink density. This was likely due to the increased difference in modulus between the surface layer and the bulk. Surface cracking occurred at much lower strains for the specimens exposed to corona than for those exposed to air-plasma oxidised to the same C/O level. This difference in fracture behaviour indicated the presence of a thinner silica-like layer in the air-plasma exposed specimens.108

![Figure 4.11](image)

**Figure 4.11** The fracture strain as a function of the carbon-to oxygen (C/O) ratio after exposure to corona: P8 (●), P12 (■), P17 (▲) and P38 (◆) or air-plasma: P8 (○), P17 (△) and P38 (◇). The dotted lines are added as guides for the eye.

4.2.4 **Atomic force microscopy**

Further details about the fragmentation patterns and surface roughness of the silica-like layers were obtained by atomic force microscopy. Only specimens of P8 were included in this study. The specimens were exposed to corona (1 h or 3 h) or air-plasma (120 s).

![Figure 4.12](image)

**Figure 4.12** Atomic force micrograph of deformed P8 exposed 1 h corona (15% strain). The inserted arrow indicates the direction of applied strain.
Some of the specimens were subjected to 15% strain prior to the AFM analysis, in order to initiate cracking of the silica-like layers. Long and almost parallel cracks oriented perpendicular to the applied stress were observed in the deformed specimens exposed to 1 and 3 h corona (Figs. 4.12 and 4.13). Great many fibrils with a diameter of approximately 10 nm bridged the cracks (depth > 30 nm) in the specimens exposed to 1 h corona (Fig. 4.13 a). The cracks in the specimen exposed to 3 h corona exhibited sharper edges and only a few bridging fibrils (Fig. 4.13b). The crack depth was ~100 nm. The base of the crack appeared to be of the same phase as the surface, indicating that the cracks did not penetrate down to the fully unoxidised PDMS. The depth of the cracks formed after 120 s air-plasma was ~10 nm, but may certainly be deeper since the bases of the cracks were not detected. The surface roughness of the regions between the parallel cracks was generally low (Ra < 1 nm) for all specimens.

![Atomic force micrographs of deformed P8 exposed to: (a) 1 h corona (15% strain), (b) 3 h corona (15% strain).](image)

The thickness of the brittle silica-like layer thus increased with the dose of corona/air-plasma, due to the proceeding vitrification (the glass transition temperature shifts above 22°C), from a few 10 nm’s to maximum of ~100 nm. This is in the same order as the characteristic depth of penetration of UV-radiation, which is the dominating factor of the radiative energy transfer from a plasma to the polymer matrix. No absolute proof of micro-porosity in the silica-like layer was obtained by AFM. However, in one case (P8 exposed to 1 h corona), the surface roughness (a possible sign of micropores) of the regions between the cracks decreased if the surface layer was cracked. The release of the tensile stresses in the surface led possibly to the closing of the pores. Specimens exposed to 3 h corona or 120s air-plasma showed, however, no such jump in the surface roughness accompanying surface cracking. It is possible that these more highly oxidised surfaces possessed a more rigid pore structure.
4.2.5 Mechanisms of hydrophobic recovery of ‘exact’ PDMS networks

Corona

The ductile behaviour of the surface layer evident from the tensile testing (Fig. 4.9 a), in combination with the XPS data (Tables 4.3 and 4.4) showing a relatively low content of oxidation products, suggested that the silica-like layer was not fully developed in P8, P12, P17 and P38 after 0.5 h corona. The hydrophobic recovery rates (Figs. 4.5 a and b) were essentially the same for all the materials suggesting that the same mechanism, diffusion of low molar mass siloxanes through an uncracked, less oxidised surface layer, was prevailing in all the materials. Due to the absence of a crosslinked silica-like structure, reorientation of methyl/silanol-groups in the surface may also contribute to the recovery process.

Corona exposure for 1 h led to the formation of a vitrified silica-like layer, most prominently in the materials with the denser networks (Tables 4.3 and 4.4). The strain for the onset of fragmentation increased with increasing \( M_c \) (Fig. 4.9 b). Hence, the materials with the densest networks were more oxidised and they had more developed silica-like layers that cracked more readily. The hydrophobic recovery curves were different depending on the crosslink density; materials with lowest \( M_c \) showed the fastest recovery (Figs. 4.5 b and c). It is suggested that the faster hydrophobic recovery in the materials with the denser network structures was due to transport of oligomers through cracks/pores in the vitrified surface layer. These specimens were not cracked by an applied stress (deformation). Instead self-cracking on the sub-micrometer scale is suggested. This tendency increased with decreasing crosslink density.

Longer corona exposure (3 h) led to further oxidation and even more brittle silica-like layers (fragmentation occurred at ~3% strain), which also showed self-cracking. The trend in the hydrophobic recovery data was similar to that after 1 h corona. All these recovery processes obeyed an Arrhenius temperature dependence (Fig. 4.7).

Air-plasma

The hydrophobic recovery of the materials exposed to air-plasma was essentially independent of the crosslink density of the materials (Fig. 4.6). The oxidation rate (by XPS) increased with decreasing \( M_c \), even though the oxidation rate was higher using the air-plasma compared to corona (Tables 4.3-4.5). More important is that the lowest strain required to cause fragmentation was 10% in the case of 120 s air-plasma, which was considerably higher than the ~5% obtained for the materials exposed to 1 and 3 h corona. Thus, the silica-like layer in the materials exposed to air-plasma showed higher fracture toughness than in the corresponding (i.e. with the same elemental composition according to XPS) materials exposed to corona. This difference in fracture toughness can be traced back to AFM data showing that the vitrified layer was thinner in the air-plasma exposed specimens than in corona exposed specimens with the same degree of surface oxidation as revealed by XPS. It is thus suggested that self-cracking was a rare event in the specimens exposed to air-plasma for 30, 120 and 180 s and that the small differences in hydrophobic recovery
rate were due to differences in the degree of oxidation of the uncracked silica-like surface layer. The recovery process did not obey an Arrhenius temperature dependence. Similar observations were reported previously for some of the ‘untouched’ HTV silicone rubbers exposed to corona (Section 4.1.2).

It may thus be concluded that the non-Arrhenius behaviour is a characteristic feature of specimens with silica-like layers with little self-cracking and can be explained by the following scheme: the glassy, defect free, layer acts as an effective barrier for transport of oligomers at 22°C. Long recovery times are then observed. If the glass transition temperature of this layer is in the range between 22-60°C, the transformation from a glassy to a rubbery state will increase the oligomer diffusion rate significantly. Fast recovery rates are then observed. This transition will also occur in cracked surfaces, but the impact on the hydrophobic recovery rate will be less significant due to the previous transport through the cracks to the surface. The lower apparent activation energies of the recovery at higher temperatures (Fig. 4.8) are in agreement with the transport of oligomers through a semi-rubbery state. Another factor to consider is the mismatch of the coefficient of thermal expansion of PDMS and SiOx. This mismatch may cause micro-cracking and/or buckling110 of the silica-like layer, which promotes transport of low molar mass siloxanes. This results in a faster rate of hydrophobic recovery than expected at elevated temperatures, whereas no corresponding cracks initiate at room temperature. This phenomenon will also result in a non-Arrhenius temperature dependence.

4.3 ‘Exact’ PDMS networks: hydrophobic long-term stability after exposure to corona (Paper VI)

In Section 4.2 it was shown that surface oxidation increased with increasing crosslink density of the ‘exact’ PDMS networks and furthermore with increasing exposure time. Two of these materials, a highly crosslinked (P0.7) and a less crosslinked, (P12) were exposed to repetitive corona treatments. After each exposure the materials were allowed to recover hydrophobicity. The purpose was to investigate if the hydrophobic recovery rate gradually decreased or even was lost after exposure to a certain dose of corona discharges, caused by the gradual vitrification of the silica-like layer.

4.3.1 Long term stability of hydrophobicity
The long-term stability of hydrophobic recovery was investigated by subjecting specimens of P0.7 and P12 to repeated 4 h exposures of corona. After each exposure, the specimens were allowed to recover hydrophobicity for at least 1000 h. The specimens were exposed to 6 (P0.7) and 9 (P12) repetitive corona treatments, respectively. For clarity, only contact angle measurements after 1, 6 and 9 treatments (P12) and 1, 3, 5 and 6 treatments (P0.7) are shown (Figs. 4.14 and 4.15). After the initial 4 h corona, P12 exhibited a lower rate of hydrophobic recovery compared to
P0.7. This difference in recovery rate, depending of crosslink density, was discussed in Paper III (Section 4.2.1). However, after the initial 4 h treatment, the recovery rates of P12 were almost independent of the dose of corona, even after 9 x 4 h of exposure (Fig. 4.14). P0.7 exhibited a fast recovery after the first 4 h treatment, thereafter the hydrophobic recovery rate decreased gradually after each treatment (Fig. 4.15). Furthermore, the onset of hydrophobic recovery (receding angle) was gradually delayed; from 1 h after the initial treatment, up to 200 h after 6 x 4 h of corona.

The surface oxidation was characterised using XPS (Table 4.6). After 6 x 4 h corona, P0.7 exhibited a ratio C/O ≈ 0.6, which is close to the limiting value reached after 720 s of air-plasma (Section 4.2.2). P12 exhibited a (C/O) ratio of 1.23 after 9 x 4h corona, higher than the value reached after
exposure to 1 h corona (C/O = 1.11). The low degree of surface oxidation in combination with the constant recovery rate suggested the presence of mobile siloxanes on the surface of P12.

**Table 4.6** Surface composition obtained by XPS.

<table>
<thead>
<tr>
<th>Material</th>
<th>Corona exposure time (h)</th>
<th>Atomic composition (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>0</td>
<td>C  52.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  24.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si  23.0</td>
</tr>
<tr>
<td>P0.7</td>
<td>6 x 4</td>
<td>C  30.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  48.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si  21.5</td>
</tr>
<tr>
<td>P12</td>
<td>9 x 4</td>
<td>C  43.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  35.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si  21.0</td>
</tr>
</tbody>
</table>

**Figure 4.16** Scanning electron micrograph showing surface cracking of corona-treated PDMS (P0.7) after 6x4 h exposure.

**Figure 4.17** Scanning electron micrograph showing surface cracking of corona-treated PDMS (P12) after 6x4 h exposure.
Scanning electron microscopy revealed spontaneous surface cracking after a certain dose of corona (4 – 8 h), for both materials. The appearance of these cracks was, however, very different for P0.7 and P12. The spontaneously formed cracks in P0.7 appeared to be initiated in a brittle manner (Fig. 4.16) They were narrow (< 1 µm) with a regular shape, often close to 90° angle to each other. P12 exhibited more ductile fractures, i.e. irregular, curved shapes. These cracks were also broader (> 5 µm), compared to the ones initiated on P0.7 (Fig. 4.17). During repeated exposure, vitrification of the freshly unexposed PDMS within the cracks occurred. New cracks were then initiated within the older cracks. It is suggested that this type of cracking facilitated transport of low molar mass siloxanes more than the type of cracking exhibited by the glassy material (P0.7). The crosslink density of commercial HTV silicone rubbers is in the range of 9000 g mol⁻¹. A commercial formulation should thus exhibit recovery kinetics similar to the material with the lower crosslink density (P12) used in this study. All materials were extracted in order to remove the low molar mass siloxanes prior to exposure. Since it has been shown that extraction of the low molar mass siloxanes prior to exposure to an oxygen-plasma increases the degree of oxidation, the performed experiments may be referred to as a “worst case scenario”. In real applications a reservoir of low molar mass siloxanes is always present in the rubber formulation.

4.4 ‘Exact’ PDMS networks: oxygen-plasma (RF and MW) (Paper II)

Oxygen-plasma treatments, using RF and MW plasma, were used as an alternative method of accelerated surface oxidation. The similarity between oxygen and air-plasmas on surface oxidation of polymer surfaces has been widely demonstrated. By exposing an ‘exact’ PDMS network to oxygen plasma, three questions were addressed: (1) possible effects of adsorption of contamination as a mechanism of hydrophobic recovery, (2) the diffusion of mobile siloxanes to the surfaces, (3) thickness and chemical composition of the silica-like layers. Thin films of P17 (thickness: 200 nm), spin-coated on silicon wafers were used. The films were not extracted prior to exposure.

4.4.1 Influence of atmosphere on hydrophobic recovery
One of the suggested mechanisms of hydrophobic recovery is adsorption of contamination from the surrounding air. This hypothesis was investigated by exposing spin-coated P17 to 80 s of MW oxygen-plasma, followed by ageing in different atmospheres: dry air, argon and vacuum (Fig. 4.18). The similarity in hydrophobic recovery of specimens in different atmospheres showed conclusively that the recovery was not due to contamination through adsorption from the surrounding atmosphere.

4.4.2 Hydrophobic recovery assessed by XPS
The elemental composition of spin-coated P17, by XPS is shown in Table 4.7. All specimens were exposed to 80 s MW oxygen plasma and aged for
different times in dry air at 22°C. The decrease in oxygen content and increase in carbon content with increasing ageing time showed that migration of PDMS, supposedly of low molar mass, occurred. Thus, the oxidised surface layer, which gradually recovered hydrophobicity (Fig. 4.18), was gradually coated with a thin liquid film of low molar mass PDMS.

![Figure 4.18](image)

**Figure 4.18** Contact angle as a function of the ageing time of spin-coated P17 exposed to 80 s of MW oxygen plasma followed by ageing in different atmospheres: advancing angle, dry air (○); receding angle, dry air (●); advancing angle, argon (■); receding angle, argon (▲); advancing angle, vacuum (△); receding angle, vacuum (◆). The error bars indicate a 90% confidence interval. Initial contact angles: advancing (-----) and receding (-- --).

<table>
<thead>
<tr>
<th>Ageing time (h)</th>
<th>Si</th>
<th>C</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>20.3</td>
<td>35.2</td>
<td>44.4</td>
</tr>
<tr>
<td>93</td>
<td>21.2</td>
<td>43.3</td>
<td>35.5</td>
</tr>
<tr>
<td>260</td>
<td>21.7</td>
<td>46.9</td>
<td>31.4</td>
</tr>
</tbody>
</table>

**Table 4.7** Elemental composition (at. %) by XPS of specimens exposed to MW oxygen plasma for 80 s and after different times of storage in dry air at room temperature.

4.4.3 Thickness and composition of the oxidised surface layer

The thickness of the oxidised surface layers formed on spin-coated P17, after exposure to a RF oxygen plasma was assessed using neutron reflectivity (NR). A schematic figure of the experiment is shown in Figure 4.19.

![Figure 4.19](image)

**Figure 4.19** Schematic figure of a spin-coated PDMS film on a silicon wafer after plasma exposure, showing oxidised and unoxidised layers. The angle of incidence (θ) of neutrons is shown.
Figure 4.20a shows the neutron reflectivity as a function of neutron momentum transfer normal to the surface (Q) for unexposed spin-coated PDMS, where only the supporting silicon wafer was detected. The insert figure depicts the profile of the scattering length density (nb) as a function of depth (z). Since (nb) for unoxidised PDMS was low (0.06×10^-4 (nm)^2), PDMS was almost indistinguishable from air. The silicon substrate had a (nb) value of 2.11×10^-4 (nm)^2. The smooth character of the log R-Q curve indicates that the spin-coated PDMS layer was of uniform composition along the layer depth (z) direction. The specimens exposed to RF oxygen-plasma showed small but distinct oscillations in the reflectivity as a function of Q (Fig. 4.20b). The oscillations characterised a discrete layer with a different scattering length density (i.e. a different chemical composition) than of unoxidised PDMS, which appeared after plasma treatment.

![Figure 4.20](image)

**Figure 4.20** Neutron reflectivity as a function of the scattering vector (Q = (4π/λ)⋅sinθ). The insert figures show the profile of scattering length density (nb) as a function of the layer depth (z). The continuous lines displayed in figures a-b, show the best fits to the experimental data: (a) unexposed specimen; (b) specimen directly after 180 s of RF oxygen plasma (λ= wavelength of the incident neutrons).
The spacing ($\Delta Q$) between successive peaks in the ripple was used to estimate the thickness ($d$) of this layer: $d = \frac{2\pi}{\Delta Q}$. The continuous lines shown in Figure 4.20 represent the fitted reflectivity, calculated using an asymmetric error function for the scattering length density profile at the interfaces. The neutron reflectivity data for specimens treated with RF oxygen plasma is summarised in Table 4.8. The thickness of the chemically modified layer decreased from 158 nm after 80 s exposure to 130 nm after 180 s exposure (Table 4.8). It is suggested that the decrease in thickness was caused by a gradual densification of the surface material, caused by the oxidative crosslinking reactions. The obtained thickness of the oxidised surface layer was slightly higher as the results obtained by AFM of ‘exact’ PDMS networks exposed to 3 h corona, $\approx 100$ nm (Section 4.2.4).

**Table 4.8** Fitted parameters from the neutron reflectivity measurements.

<table>
<thead>
<tr>
<th>Plasma exposure time (s)/Ageing time (h)</th>
<th>Layer</th>
<th>$n_b$ (nm)$^{-2}$</th>
<th>Thickness $^a$ (nm)</th>
<th>Roughness of interface $^a$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80/144</td>
<td>Oxidised</td>
<td>$1.21 \times 10^{-4}$</td>
<td>157±2</td>
<td>10±2$^b$</td>
</tr>
<tr>
<td></td>
<td>Unoxidised</td>
<td>$0.06 \times 10^{-4}$</td>
<td>90±3</td>
<td>46±2$^c$</td>
</tr>
<tr>
<td>80/288</td>
<td>Oxidised</td>
<td>$1.27 \times 10^{-4}$</td>
<td>158±3</td>
<td>10±2$^b$</td>
</tr>
<tr>
<td></td>
<td>Unoxidised</td>
<td>$0.06 \times 10^{-4}$</td>
<td>92±3</td>
<td>38±2$^c$</td>
</tr>
<tr>
<td>180/0</td>
<td>Oxidised</td>
<td>$1.33 \times 10^{-4}$</td>
<td>126±3</td>
<td>14±2$^b$</td>
</tr>
<tr>
<td></td>
<td>Unoxidised</td>
<td>$0.06 \times 10^{-4}$</td>
<td>80±3</td>
<td>36±2$^c$</td>
</tr>
<tr>
<td>180/144</td>
<td>Oxidised</td>
<td>$1.33 \times 10^{-4}$</td>
<td>131±3</td>
<td>14±2$^b$</td>
</tr>
<tr>
<td></td>
<td>Unoxidised</td>
<td>$0.06 \times 10^{-4}$</td>
<td>85±3</td>
<td>46±2$^c$</td>
</tr>
<tr>
<td>180/288</td>
<td>Oxidised</td>
<td>$2.11 \times 10^{-4}$</td>
<td>127±3</td>
<td>18±2$^b$</td>
</tr>
<tr>
<td></td>
<td>Unoxidised</td>
<td>$0.06 \times 10^{-4}$</td>
<td>82±3</td>
<td>64±2$^c$</td>
</tr>
</tbody>
</table>

$^a$ Optimum value ± accuracy.

$^b$ Roughness of interface between air and oxidised layer.

$^c$ Roughness of interface between oxidised and unoxidised layers.

The roughness data shown in Table 4.8 refer to the two interfaces: i.e. the interface between air and the oxidised layer - interface 1 or to the interface between the oxidised and unoxidised layers - interface 2 (Fig. 4.19). The roughness of the interfaces remained relatively unchanged with increasing storage times after exposure.

After RF oxygen-plasma exposure for 80 s, the scattering length density ($n_b$) of the oxidised top layer remained essentially constant with storage time in air at 22°C (Table 4.8). After plasma treatment for 180 s, the scattering length density for the treated layer increased with increasing ageing time, from $1.33 \times 10^{-3}$ (nm)$^2$ immediately and 144 h after the oxygen-plasma exposure to $2.11 \times 10^{-4}$ (nm)$^{-2}$ after 288 h. The latter value is high compared to the aforementioned values. This result could, however, be consistent with additional reactions, such as condensation of silanol groups forming Si-O-Si bridges$^{49}$.

**Table 4.9** Calculated scattering length densities for different repeating units.

<table>
<thead>
<tr>
<th>Structure of repeating unit</th>
<th>Scattering length $n_b$ (nm)$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-Si(CH$_3$)$_2$O-</td>
<td>$0.06 \times 10^4$</td>
</tr>
<tr>
<td>-Si(CH$_2$OH)$_2$O-</td>
<td>$0.95 \times 10^4$</td>
</tr>
<tr>
<td>-Si(CH$_3$O)O-</td>
<td>$1.15 \times 10^4$</td>
</tr>
<tr>
<td>-Si(OH)$_2$O-</td>
<td>$1.85 \times 10^4$</td>
</tr>
<tr>
<td>-SiO$_2$-</td>
<td>$3.80 \times 10^4$</td>
</tr>
</tbody>
</table>
By calculating scattering length densities for different chemical compositions of the repeating unit, replacing the methyl groups by oxygen-containing species, the average composition of the formed species was assessed. The chemical structures and their scattering length densities are shown in Table 4.9. If it was assumed that all the plasma-conversion products were SiO₂, the measured (nb) implied a ~30% conversion of PDMS to SiO₂. As a comparison to the values obtained by neutron reflectivity, XPS was used to analyse the surface composition of spin-coated P17 exposed to oxygen-plasma (MW). Curve resolution of the Si 2p peak of the specimen first exposed to 180 s of plasma and then aged for 260 h in dry air suggested a mixture of species: -Si(CH₃)₂-O- (59%), -Si(O,CH₃)-O- (23%), and SiO₂ (18%). The calculated (nb) value for this mixture of species using the values displayed in Table 4.9 amounted to ≈1.0 x10⁻⁴ (nm)⁻², which was in the same range as the experimental data obtained (1.21-1.33x10⁻⁴ (nm)⁻²). Furthermore, it was obvious that the surface of the analysed specimen was “contaminated” by diffusing low molar mass PDMS species (Table 4.7) and that the virgin oxidised layer should contain more SiOₓ. It should be noted that NR was based on RF oxygen plasma whereas XPS was based on MW oxygen-plasma. The power of the plasma and the oxygen pressure during the treatments was, however, identical.

4.5 Characterisation of migrating low molar mass PDMS (Paper IV)

In the previous Sections (4.1-4.4) the hydrophobic recovery of PDMS after exposure to electrical discharges has been examined and related to the properties of oxidised silica-like surface layers. It was demonstrated that the recovery was mainly dependent on the migration of low molar mass siloxanes to the surface through the oxidised silica-like layer. In this section these migrating low molar mass siloxanes are characterised using Size Exclusion Chromatography (SEC) and Gas Chromatography-Mass Spectrometry (GC-MS). The low molar mass siloxanes were extracted from ‘exact’ PDMS networks after exposure to corona.

4.5.1 Extraction procedure
Since the intention was to dissolve preferably the mobile siloxanes in the surface region of the films, an extraction time as short as possible was used: 60 s. A few films were extracted during 20 minutes for comparison. The extractions were performed at 22°C using CHCl₃. Materials P0.7, P12 and P38 were allowed to recover close to their original hydrophobicity before extraction (storage time: 240 h (P0.7 and P12), 850 h (P38)) whereas P8 and P17 was extracted after only 70-90 h after corona exposure. The advancing contact angles then ranged between 35-45° and the receding contact angles between 25-35°. The initial advancing and receding contact angles were 100-106° and 74-80°, respectively. Further details can be found in Section 4.2.1.
4.5.2 Identification of the low molar mass PDMS

The extractables of the materials were analysed by SEC and consisted only of low molar mass species (<1000 g mol\(^{-1}\)). They were identified by GC-MS as a homologous series of cyclic oligomeric dimethylsiloxanes of the general formula \(D_n = [(\text{CH}_3\text{SiO})_n, \text{ where } n \text{ is the number of repeating units. These low molar mass cyclic PDMS will be referred to as oligomeric dimethylsiloxanes (ODMS). The sizes of the extracted ODMS generally ranged between 3-10 repeating units (Fig. 4.21).}

![Gas chromatogram showing the presence of a homologous series of ODMS. Material P 12, exposed to 1 h corona.](image)

Low amounts (<9% wt. % in extractable ODMS) of linear ODMS with 3 repeating units (L\(_3\)) was also identified. The L\(_3\) content was not influenced significantly by exposure to corona, suggesting that it was present in the virgin networks as a residual structure which was too short to cyclise readily, as has been proposed by Thomas and Kendrick\(^{73}\). The absence of fragments from the carbon crosslinks suggests a complete oxidation of these units to volatile species, such as carbon dioxide or methane. Cyclic ODMS, mainly D\(_5\)-D\(_8\), was also isolated by extraction from the unexposed materials, although these species had been carefully extracted prior to exposure to corona. The molar mass distribution of the cyclic ODMS of both unexposed and corona-exposed materials was independent of the crosslink density (Figs. 4.22). Furthermore, the molar mass distributions showed no systematic change with increasing corona exposure time (0.5 - 3 h).

However, the recovery time after exposure to corona influenced the molar mass distribution. For the fully recovered materials the distributions of cyclic ODMS were either identical to that of the
extractables of the unexposed molar mass (P0.7) or shifted towards a higher content of larger cyclics, D_6-D_7 (P12 and P38) (Fig. 4.22). Since these materials were extracted approximately 240 h (P0.7 and P12) and 850 h (P38) after the corona exposure, it is suggested that an equilibrium in composition of cyclics between the bulk and surface of the exposed specimen was established.

![Graphs showing cyclic ODMS content](image)

**Figure 4.22.** Number of repeating units (n) in cyclic ODMS, extracted from the surface region of 'exact' PDMS networks exposed to corona: unexposed (●), 0.5h corona (◇), 1h corona (○), 3h corona (□) for the following materials: (a) P0.7, (b) P8, (c) P12, (d) P17, (e) P38. The error bars indicate a 5% standard deviation. Lines are guidance for the eye only.

The additional amounts of D_6-D_7 may have been formed during the exposure to corona. The materials which were not given sufficient time to fully recover their original hydrophobicity (P8 and P17) contained higher proportions of D_6-D_8 in their extractables than the corresponding unexposed materials. This suggests that the initial hydrophobic recovery (<100 h) was more controlled by transport of these smaller cyclics, whereas the larger cyclics (>D_6) appeared at later stages in the recovery process. The low amounts of D_3 found in the studied systems may be a
result of the strained ring structure which makes $D_3$ thermodynamically unstable at 22°C in favour of larger, unstrained cyclic oligomers.

The amount of ODMS increased with increasing dose of corona, especially after more than 0.5 h corona (Fig. 4.23) and furthermore with increasing recovery time after corona exposure. However, the amounts of ODMS extracted from P8 and P17, before complete hydrophobic recovery, were in the same order as the for the corresponding unexposed materials. A correlation between an incomplete hydrophobic recovery and low amounts of ODMS could thus be seen. The trend of decreasing amounts ODMS after 3 h corona compared to 1 h corona may be caused by the scatter in data. The total amount of low molar mass siloxanes extracted from the surfaces was considerably lower (maximum 0.5 ng cm$^{-2}$) than the calculated amount necessary to form a monolayer of siloxanes (53 ng cm$^{-2}$). This strongly suggests that the 60 s extraction was of low efficiency, and only free cyclics on the very surface was dissolved. ODMS may also have been adsorbed to the oxidised surface layer, making them less willing to dissolve in the unpolar solvent (CHCl$_3$). Furthermore, the low amounts of extractable siloxanes suggest that oxidative crosslinking was the dominant degradation mechanism of PDMS during corona exposure, compared to depolymerisation processes. The presence of ozone, formed by ionisation of oxygen during the corona, may well accelerate the oxidative crosslinking.

![Figure 4.23](image-url)

**Figure 4.23** Total amount of identified low molar mass PDMS per area extracted (ng cm$^{-2}$) as function of exposure time to corona discharges for the PDMS networks: P0.7 (○), P8 (●), P12 (△), P17 (▲) and P38 (❖). The error bars indicate a variation of 35% in amounts, found between replicates.

After extracting materials during 20 minutes and subsequent analysis using SEC, also siloxanes of higher molar masses were found, both prior and after exposure to corona discharges. An example is shown in Figure 4.24. P38 were extracted after 3100 h (1 h corona) and 7000 h (3 h corona) storage time after exposure, respectively. The molar mass distribution of unexposed P38 was initially bimodal, consisting of a low molar mass fraction (<1000 g mol$^{-1}$) and a higher molar mass fraction of $M_c = 52 000$ g mol$^{-1}$, most probably originating from residual uncrosslinked PDMS. After exposure to corona a broadening of the peaks was observed.
Figure 4.24 Molar mass distributions of P38: unexposed, 1h and 3h corona, respectively. Extraction time: 20 min. LMM = low molar mass fraction.

This was due to the formation of additional amounts of low molar mass siloxanes, resulting in a shift towards longer retention times. Further, siloxane bond interchange reactions resulted in a shift towards higher molar masses\textsuperscript{111}. Since these high molar mass siloxanes were not found in the extractables after the short-time extraction (60 s), it is less likely that these species were involved in the initial hydrophobic recovery (< 800 h) after exposure to corona.

4.5.3 Estimation of the probed extraction depth
The probed extraction depth ($r$) was estimated from the Einstein relationship\textsuperscript{112} for diffusion in one dimension:

$$r = \sqrt{2Dt}$$

where $D$ is the diffusivity of the extractables (oligomers) and $t$ the extraction time. For the unexposed (unoxidised) specimens the extraction depth can be estimated from the diffusivity data of Gedde et al.\textsuperscript{67}: $1 \times 10^{-8}$ cm$^2$ s$^{-1}$ (PDMS, $M_n = 18 400$ g mol$^{-1}$) and $20 \times 10^{-8}$ cm$^2$ s$^{-1}$ ($D_5$) to $r=10$-50 µm (60 s) and $r=50$-220 µm (20 min). This calculation will largely overestimate the extraction depth in the specimens exposed to corona, because these contain a surface layer of oxidised and sometimes vitrified silica-like material (Section 4.1-4.4). The diffusivity of the oligomers through this layer is much lower than through the unoxidised material. The calculations assume that the extraction is controlled only by diffusion. The transport of free oligomers at the surface to the main liquid phase will take some (unknown) time and hence the practical extraction depths should be smaller than the values obtained calculation above.
5. FIELD AGING OF AC/DC ENERGISED HTV SILICONE RUBBER FORMULATIONS

This chapter addresses the ageing mechanisms of HTV silicone rubber formulations, which have been aged during 18 months in a coastal environment under AC/DC voltage at the Anneberg test station, Sweden. It should be noted that the experimental set-up used at the Anneberg test station was designed to avoid corona discharges. Instead the accelerating factor was a high electrical stress, 100 V/mm (30% of the creepage distance normally used for ceramic insulators at this location) and 50 V/mm. The knowledge gained from the laboratory by exposing silicone rubber surfaces to electrical discharges was used to assess and evaluate the ageing mechanism of the silicone rubber formulations tested at Anneberg. Only analysis of the rods exposed to 100 V/mm is presented here.

5.1 Background to the field test

Field studies on the long-term performance of high voltage outdoor insulation have pointed out the necessity of focus the investigations on well-defined material formulations41. Further, to get a wider acceptance for accelerated ageing methods, performed in a laboratory, a good correlation between field ageing and laboratory tests must be verified. This requires field-ageing using samples in which the material formulations are well known. The dominant ageing mechanisms can then be determined and compared to results from laboratory tests, performed under well-defined conditions.

This study has been conducted in a coastal environment on silicone rubbers with known differences in their composition. To address the influence of the level of aluminium trihydrate (ATH) filler and the addition of silicone oils on the electric long-term performance, two different levels of (ATH) and silicone oil were chosen as parameters (Table 5.1). The question how the applied electric stress affected the rate and the mechanism of ageing was assessed by exposing the materials to AC or DC voltage using two different creepage paths (100 and 50 V/mm). By designing the test using short creepage distances and electrical field control, where less than 20 mm of each sample was exposed a tangential electrical field exceeding 0.4 kV/mm and never exceeding 0.8 kV/mm, corona was avoided. In order to eliminate the influence of insulator geometry, the investigations were performed on cylindrical samples (diameter: 25 mm, length: 100mm (100 V/mm) or 200 mm (50 V/mm)). Regular visual inspections, together with continuos on-line measurements
of leakage current (LC), have been carried out to monitor the performance\textsuperscript{113,114}. In order to elucidate the degree of surface degradation as well as ageing mechanisms, chemical analyses were performed after the field exposure of 18 months. Only analysis of the rods exposed to 100 V/mm is presented here.

Table 5.1 Selected material compositions of silicone rubber with high (+) or low (-) level of ATH filler and silicone oil (AK350), phr = parts per hundred rubber.

<table>
<thead>
<tr>
<th>Formulation: ATH (+)/AK350 (+)</th>
<th>Formulation: ATH (-)/AK350 (-)</th>
<th>Formulation: ATH (-)/AK350 (+)</th>
<th>Formulation: ATH (+)/AK350 (-)</th>
<th>Formulation: ATH (+)/AK350 (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>50</td>
<td>100</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>4</td>
</tr>
</tbody>
</table>

5.2 Field observations and electric measurements

Since this thesis is focused on the chemical analyses of the aged materials, only a brief summary of the electrical measurements is presented here. Additional details can be found elsewhere\textsuperscript{113,114}.

Leakage current measurements and visual observations showed that the high content of AK 350 and ATH initially caused an earlier onset of electric activity along the surfaces. It is possible that the higher surface roughness, caused by the higher amount of ATH, and the increased pollution trapping by the added silicone oil caused the earlier surface activities. On prolonged exposure, however, both extra AK 350 and ATH decreased the rate of surface erosion. During severe weather conditions (i.e. salt-storms, heavy rain or fog) DC-energised rods exhibited the highest reduction in hydrophobicity, compared to AC-energised rods. The total number of leakage current peaks (> 4 mA) was significantly higher for the DC-energised rods, compared to the AC-energised ones. However, AC-energised rods exhibited melted spots on their electrodes, originating from localised discharges of short duration and high power densities. At the end of the test all DC-energised rods with a low ATH content showed a powdery whitish surface and exhibited a high electric activity during severe weather conditions.

5.3 Surface characterisation

5.3.1 Scanning electron microscopy

Surface erosion caused by electrical discharges was observed on all formulations, but the appearance was different for AC and DC energised samples, respectively. Generally, erosion caused by DC voltage resulted in large homogeneously eroded areas (of the order of cm\textsuperscript{2}) which often exhibited a lower surface roughness than the surface of the unexposed samples. The erosion process thus proceeded in a polishing manner. Samples with low content of ATH also exhibited discharge channels with a width of 10-30 µm, parallel to the electric field (Fig. 5.1 a).
Erosion occurring during AC voltage was more localised and appeared generally in the form of irregular channels and pits mixed with uneroded areas. Samples with traces of melted spots on the electrodes also exhibited ‘craters’ (extensive pitting) in the surface. The formulation [ATH(+) / AK 350(+)] exhibited the highest density of such ‘craters’, the larger were in the order of 100 µm (Fig. 5.1 b). The correlation between these craters and melted spots on the electrodes suggested that the craters were formed due to single hot discharges of short duration (not detected with the leakage current system used).

5.3.2 Reflection infrared spectroscopy
Reflection infrared spectroscopy was used to assess the ageing of the energised silicone rubber surfaces. A typical infrared spectrum of an aged surface is shown in Fig. 5.2, illustrating chemical changes between eroded and non-eroded areas, before and after cleaning (removal of surface contamination). For non-cleaned surfaces, an increase in absorbance from non-ordered hydroxyl groups was observed in the region 3400-3600 cm\(^{-1}\). The dehydration of the ATH filler was characterised by a decrease in the absorption peaks in the interval 3300 – 3650 cm\(^{-1}\) (Region I), correlated to the hydroxyl groups bonded within the filler. For an estimation of the degree of dehydration of the ATH in the surface region, the area of the largest related absorption peak (3435 cm\(^{-1}\)) was calculated and normalised against the corresponding bulk peak (Table 5.2). The dehydration of ATH was higher in samples exhibiting the highest amount of leakage currents. Further, the dehydration was most pronounced in the eroded areas. Finally, samples with a low level of ATH exhibited the highest relative loss of ATH. The ATH reference peak was recovered by cleaning the surface with acetone. This was attributed to a removal of loosely attached particles encapsulated by low molar mass siloxanes. A broadening of the absorption peaks in the 1000–1130 cm\(^{-1}\) region, originating from the Si-O bonds was observed (Region II), due the formation of additional oxygen bridges between silicon atoms\(^{49}\).
Figure 5.2 Infrared spectra of an silicone rubber surface aged under AC voltage [ATH(+)/AK350(-)].

Table 5.2 Remaining ATH, as detected by infrared spectroscopy, on the surfaces of AC/DC-energised samples.

<table>
<thead>
<tr>
<th></th>
<th>Not eroded, not cleaned (%)</th>
<th>Not eroded, cleaned (%)</th>
<th>Eroded, not cleaned (%)</th>
<th>Eroded, cleaned (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC</td>
<td>ATH(-)/AK350(-)</td>
<td>80.1</td>
<td>79.0</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>ATH(-)/AK350(+)</td>
<td>83.6</td>
<td>77.7</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>ATH(+)/AK350(-)</td>
<td>92.7</td>
<td>94.0</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>ATH(+)/AK350(+)</td>
<td>78.1</td>
<td>99.4</td>
<td>10.2</td>
</tr>
<tr>
<td>AC</td>
<td>ATH(-)/AK350(-)</td>
<td>49.2</td>
<td>75.8</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>ATH(-)/AK350(+)</td>
<td>70.1</td>
<td>79.3</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>ATH(+)/AK350(-)</td>
<td>56.7</td>
<td>93.9</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>ATH(+)/AK350(+)</td>
<td>72.3</td>
<td>92.9</td>
<td>22.3</td>
</tr>
</tbody>
</table>

5.3.3 X-ray photoelectron spectroscopy (XPS)

The degree of surface oxidation of the AC/DC-energised rods was further assessed by XPS. The atomic composition of the analysed surfaces consisted exclusively of carbon (C), oxygen (O), silicon (Si) and low contents of aluminium (Al). The aluminium originated from the ATH filler. The degree of surface oxidation is presented as the ratios between the atomic composition of (O/Si) and (C/Si), to separate the individual variation of oxygen and carbon. The amount of Al is presented in atomic (at.)%. Analysis of the bulk of virgin formulations, having the highest respectively the lowest filler to polymer ratio, yielded the following ratios: [ATH(+)/AK350(-)]: O/Si=1.35, C/Si=2.19 and Al: 1.6 at.%; [ATH(-)/AK350(+)]: O/Si=1.15, C/Si=2.05 and Al: 0.5 at.% The surface oxidation as a function of the distance from the energised end was analysed. The carbon content gradually decreased towards the energised end. Less
expected was a decrease also in oxygen content. Generally, an increase in oxygen content is observed when silicone rubbers are exposed to electrical discharges.\(^{23,49,50,57}\) It is suggested that the decrease in oxygen content was a result of the dehydration of the ATH filler, thereby decreasing the amount of oxygen. The decrease then compensated for the increased oxygen content caused by a possible mild oxidation of the silicone rubber surfaces. In order to minimise the number of samples, each rod was analysed at two positions at the energised end only, where the highest degree of oxidation occurred (Table 5.3). If the surface exhibited a darker band of contamination, one specimen was taken from this side (‘cont.’) and the other from the least contaminated (‘clean’) side.

<table>
<thead>
<tr>
<th></th>
<th>DC</th>
<th>AC</th>
<th>DC</th>
<th>AC</th>
<th>DC</th>
<th>AC</th>
<th>DC</th>
<th>AC</th>
</tr>
</thead>
<tbody>
<tr>
<td>O/Si, cont.</td>
<td>1.19</td>
<td>1.27</td>
<td>1.21</td>
<td>1.29</td>
<td>1.37</td>
<td>1.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C/Si, cont.</td>
<td></td>
<td></td>
<td>1.77</td>
<td>1.77</td>
<td>1.85</td>
<td>1.55</td>
<td>1.63</td>
<td>1.76</td>
</tr>
<tr>
<td>Al, cont.</td>
<td></td>
<td></td>
<td>0.2</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>O/Si, clean</td>
<td>1.20</td>
<td>1.25</td>
<td>1.21</td>
<td>1.15</td>
<td>1.18</td>
<td>1.27</td>
<td>1.28</td>
<td>1.14</td>
</tr>
<tr>
<td>C/Si, clean</td>
<td>2.14</td>
<td>1.71</td>
<td>1.81</td>
<td>2.05</td>
<td>1.92</td>
<td>2.00</td>
<td>2.04</td>
<td>2.00</td>
</tr>
<tr>
<td>Al, clean</td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td>-</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Generally, the oxidation was more uniform on the DC-energised samples, even though it was less severe compared to some of the contaminated areas of the AC-energised samples. The ratio (O/Si) again remained essentially unchanged, or showed a slight decrease for all analysed specimens whereas the ratio (C/Si) decreased. Al was present only on AC-energised samples, no trace (< 0.1 at.%) was found on DC-energised ones. Since Al was quantified in virgin silicone rubber formulations this indicated that the more uniform erosion of the DC-energised rods, as assessed by SEM, resulted in the loss of the outermost layer of ATH/Al\(_2\)O\(_3\). The XPS data showed that the surfaces only exhibited low degrees of surface oxidation after the test period. This indicated that oxidative crosslinking of silicone rubbers, observed after exposure to corona discharges, as described in Chapter 4 or salt-fog tests, was not a dominant mechanism during the ageing at the Anneberg test station.

### 5.4 Characterisation of siloxanes within the pollution layer

#### 5.4.1 Size exclusion chromatography

The hydrophobic pollution layers were removed from the aged test rods, and the siloxanes responsible for the hydrophobic transfer were extracted using CHCl\(_3\). The molar mass distributions of the extracted PDMS, are shown in Figure 5.3. The molar mass distributions of the extractable siloxanes present in the virgin rubber formulations are included for comparison ("bulk"). The approximate peak values (\(\overline{M}_n\)) of the molar mass for the distributions are displayed above the chromatograms.
Three distributions were found: a low molar mass ('LMW') fraction (<1000 g mol⁻¹), a molar mass fraction ranging between 12-14 000 g mol⁻¹, originating from the added AK 350 and a high molar mass fraction ranging between 38-100 000 g mol⁻¹. The origin of the mass fraction at 38-43 000 g mol⁻¹ was most likely siloxanes, which were not successfully crosslinked into the polymer network, since they were present also in the bulk. The fraction between 83-100 000 g mol⁻¹ was not present in the bulk samples and was thus formed during ageing under both AC and DC conditions. It is likely that this fraction originated from siloxane interchange reactions, involving condensation of formed silanol groups⁷³,¹¹¹.

The amount of extracted higher molar mass PDMS was estimated to 0.2-2 µg/mg of extracted contamination. Only low amounts of siloxanes were found in the pollution layers on both energised and virgin samples of the formulation ATH(+)/AK350(-). This indicated that the addition of extra ATH filler resulted in a decrease of the amount of extractable siloxanes, which is in accordance with findings reported by Deng and Hackam¹¹⁵. No clear correlation between the amounts of higher molar mass siloxanes found in the pollution layer and an extra addition of AK 350 to the rubber was obtained. The higher amounts of low molar mass siloxanes ('LMW') (<1000 g mol⁻¹) on the surfaces of AC-energised samples, compared to the corresponding DC-energised ones, indicated that depolymerisation reactions were more dominant during AC conditions than during DC conditions. This was consistent with the field observations made, which showed that DC-energised samples lost their hydrophobicity whereas the AC-energised samples generally maintained the hydrophobicity during severe weather conditions. The higher electric activity on DC compared to AC-energised samples¹¹¹, may also have degraded the low molar mass fraction further into volatile species¹¹⁶. Since SEC can not discriminate

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**Figure 5.3** Molar mass distribution of the PDMS in the pollution layer compared to the distribution in virgin samples (bulk): (a) ATH(-)/AK350(-), (b) ATH(-)/AK350(+), (c) ATH(+)/AK350(-), (d) ATH(+)/AK350(+).
between the different oligomers (< 1000 g mol⁻¹), they were not possible to quantify using this method. The scale of the intensity in Figure 5.3 is thus adjusted in order to emphasise the higher molar mass fractions.

5.4.2 Gas chromatography - mass spectrometry

The oligomeric dimethylsiloxanes (ODMS), extracted from the pollution layers were analysed by GC-MS. Samples were taken from the areas containing the highest amount (cont.) and lowest amount (“clean”) of contamination. The low molar mass fraction consisted exclusively of a homologous series of cyclic ODMS: \( D_n = [(\text{CH}_3\text{H})_2\text{SiO}]_n \), (Tables 5.4 and 5.5). Low amounts of unidentified carbon compounds from the pollution layer were also detected. No trace of linear siloxanes was found. The distribution of the number of repeating units of the cyclic PDMS in the pollution layer differed significantly from the bulk extracts, which consisted mainly of \( D_6 \) and larger cyles (Table 5.4 and 5.5). Homma et al. identified siloxanes diffusing from a virgin RTV silicone rubber through a carbon coating. The siloxanes were found to be \( D_6 \)–\( D_{15} \), with the highest concentration at \( D_{12} \). This is in agreement with the GC-MS data of the virgin rubbers.

Table 5.4 Content (wt. %), of ODMS, transferred from the rubber to the contamination layer, DC-energised samples.

<table>
<thead>
<tr>
<th>LMW PDMS</th>
<th>Virgin rubber</th>
<th>Cont. / Clean</th>
<th>Cont. / Clean</th>
<th>(+) / (-)</th>
<th>(+) / (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_3</td>
<td>&lt;1</td>
<td>19 / 8</td>
<td>21 / 10</td>
<td>18 / 13</td>
<td>16 / 13</td>
</tr>
<tr>
<td>D_4</td>
<td>&lt;1</td>
<td>53 / 17</td>
<td>38 / 18</td>
<td>58 / 27</td>
<td>24 / 26</td>
</tr>
<tr>
<td>D_5</td>
<td>&lt;1</td>
<td>10 / 16</td>
<td>42 / 20</td>
<td>11 / 21</td>
<td>32 / 24</td>
</tr>
<tr>
<td>D_6</td>
<td>7</td>
<td>7 / 22</td>
<td>&lt;1 / 15</td>
<td>6 / 23</td>
<td>18 / 15</td>
</tr>
<tr>
<td>D_7</td>
<td>23</td>
<td>3 / 18</td>
<td>&lt;1 / 5</td>
<td>3 / 6</td>
<td>6 / 6</td>
</tr>
<tr>
<td>D_8</td>
<td>24</td>
<td>1 / 6</td>
<td>&lt;1 / 1</td>
<td>3 / 3</td>
<td></td>
</tr>
<tr>
<td>≥ D_9</td>
<td>46</td>
<td>6 / 14</td>
<td>&lt;1 / 26</td>
<td>3 / 6</td>
<td>1 / 13</td>
</tr>
</tbody>
</table>

The contaminated areas generally contained higher amounts of \( D_3 \) and \( D_4 \), compared to the less contaminated (clean) areas on the same rod (Tables 5.4 and 5.5). This difference was, however, less pronounced for DC-energised samples compared to AC-energised ones.

Table 5.5 Content (wt. %), of ODMS, transferred from the rubber to the contamination layer, AC-energised samples.

<table>
<thead>
<tr>
<th>LMW PDMS</th>
<th>Virgin rubber</th>
<th>Cont. / Clean</th>
<th>Cont. / Clean</th>
<th>(+) / (-)</th>
<th>(+) / (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_3</td>
<td>&lt;1</td>
<td>26 / 6</td>
<td>31 / 4</td>
<td>27 / 4</td>
<td>17 / 11</td>
</tr>
<tr>
<td>D_4</td>
<td>&lt;1</td>
<td>53 / 18</td>
<td>54 / 13</td>
<td>50 / 15</td>
<td>32 / 26</td>
</tr>
<tr>
<td>D_5</td>
<td>&lt;1</td>
<td>21 / 32</td>
<td>16 / 33</td>
<td>22 / 28</td>
<td>23 / 15</td>
</tr>
<tr>
<td>D_6</td>
<td>7</td>
<td>&lt;1 / 22</td>
<td>&lt;1 / 31</td>
<td>&lt;1 / 33</td>
<td>9 / 20</td>
</tr>
<tr>
<td>D_7</td>
<td>23</td>
<td>&lt;1 / 9</td>
<td>&lt;1 / 12</td>
<td>&lt;1 / 11</td>
<td>&lt;1 / 10</td>
</tr>
<tr>
<td>D_8</td>
<td>24</td>
<td>&lt;1 / 4</td>
<td>&lt;1 / 4</td>
<td>&lt;1 / 6</td>
<td>&lt;1 / 4</td>
</tr>
<tr>
<td>≥ D_9</td>
<td>46</td>
<td>&lt;1 / 10</td>
<td>&lt;1 / 3</td>
<td>&lt;1 / 2</td>
<td>19 / 12</td>
</tr>
</tbody>
</table>
It has been shown that the formation of D₃ is facilitated by non-catalytic, depolymerisation reactions at elevated temperatures, > 450°C. At lower temperatures (250°C), or in the presence of contamination, such as alkali ions, a catalytic depolymerisation also takes place. The amount of D₃ then decreases whereas the amount of larger cyclics increases (≥ D₄). It is proposed that the different composition of ODMS in the pollution layers was a result of the level of local electric activity. High contents of D₃ indicated high electrical activity (spot discharges), occurring at localised areas. Lower power densities facilitated the formation of the more stable cyclics, D₄-D₆. Eldrige et al. identified mainly D₆-D₁₅ in a virgin RTV coating. However, weathered and energised coatings of the same RTV contained predominately D₃-D₆, which is in agreement with the data presented in this paper. Furthermore, increased amounts of D₅-D₇ and a corresponding decrease of D₈-D₁₂ was found in silicone rubber housings used for arresters, after service during 4.5 years.

5.5 Mechanisms of surface ageing

The erosion caused during DC voltage resulted in large homogeneously eroded areas whereas erosion caused during AC voltage was more localised and appeared generally in the form of irregular channels and pits close to uneroded areas. The low degree of surface oxidation in combination with the large amounts of formed low molar mass siloxanes suggests that thermal depolymerisation, initiated by electrical discharges of high energy density, was the dominating mechanism of the ageing of the silicone rubber formulations, both under AC and DC conditions. This is also supported by the surface depletion of ATH, as shown by reflection infrared spectroscopy. The low molar mass siloxanes formed were mainly D₃-D₆. The highest amounts of D₃-D₆ were found in the eroded/contaminated regions. This indicated that the formation of these species was facilitated by high electrical activity. One might conclude that oxidative crosslinking, normally associated with corona discharge activities (Ch. 4) have not played a major role in the surface degradation. However, this might be a consequence of how this test has been designed, to avoid the initiation of corona discharges.
6. CONCLUSIONS

6.1 Accelerated testing using corona or plasma

6.1.1 Oxidised surface layers
When exposed to corona or air/oxygen-plasma, an oxidised surface layer was gradually formed on HTV silicone rubbers as well as addition-cured 'exact' PDMS networks. XPS showed that surface oxidation was faster in more highly crosslinked polymers. This was explained by the higher susceptibility to oxidation of the C-C bonds in the crosslinks than of the repeating unit of the polymer. Addition-cured PDMS exhibited a lower degree of oxidation, compared to HTV silicone rubber, after identical corona exposures. Microscopy confirmed the presence of a brittle, microporous silica-like layer, with an organic silicon content of at least 13-40% according to XPS, within the oxidised surface region. The origin of the organic silicon content may partly be due to migration of siloxanes to the surface in the vacuum environment during analysis, but may also be due to a dispersion of oxidised and unoxidised components mixed on a fine (submicrometer) scale. It is suggested that the unoxidised regions are shielded from further oxidation by the surrounding oxidised (vitrified) phase, which acts as a cage for active radicals. The surface roughness of the layers was low, generally less than 1-10 nm.

Neutron reflectivity showed that the thickness of the oxidised layer in PDMS exposed to oxygen-plasma (RF) was in the order of 130-160 nm and that the thickness did not increase with increasing plasma dose. The thickness of the silica-like layer increased gradually with increasing corona exposure time, reaching a thickness of approximately 100 nm after 3 h corona, which is of the same order of magnitude as the thickness of the oxidised layer. Specimens exposed to air-plasma (MW) developed thinner silica-like layers than those exposed to corona with the same degree of surface oxidation. The strain at which the silica-like layer cracked decreased with increasing corona/air plasma exposure time. After prolonged exposure to corona/plasma self cracking of the silica-like layers occurred. When exposed to repeated corona treatments continuous cracking was initiated within older cracks, due to the oxidation of the previously unexposed PDMS.

The hydrophobic recovery following the corona/plasma exposure occurred at a slow pace by diffusion of oligomers through the micro-porous but uncracked silica-like layer or at a much higher pace by transport of oligomers through cracks in the silica-like layer. The hydrophobic recovery of specimens exposed to corona obeyed Arrhenius temperature dependence with activation energies of 30-60 kJ mol$^{-1}$ both for mildly oxidised
specimens without a glassy silica-like layer and for specimens with a cracked silica-like layer. The hydrophobic recovery of the specimens exposed to air-plasma (MW) showed a pronounced curvature in the Arrhenius diagram. It is suggested that this behaviour is characteristic for specimens with thin, uncracked silica-like layers; a steep slope in the Arrhenius diagram at low temperatures features the glassy state and a flatter part at high temperatures a more rubber-like state.

6.1.2 Low molar mass siloxanes
The migrating siloxanes responsible for the initial hydrophobic recovery after corona was identified as a homologous series of cyclic oligomeric dimethylsiloxanes (ODMS), with 4-10 repeating units (D₄-D₁₀). Low amounts of ODMS were present in unexposed PDMS, despite careful extraction. However, additional amounts were formed during corona treatments. The extractable content of ODMS further increased with increasing recovery time after corona.

6.2 Field ageing using high electric stress as accelerating factor
HTV silicone rubber formulations were aged during 18 months in a coastal environment under AC/DC voltage. Surface erosion, caused by thermal depolymerisation was the dominating ageing mechanism. This depolymerisation was initiated by hot surface discharges. The depolymerisation resulted in the formation of additional amounts of mobile siloxanes, of which the low molar mass fraction consisted of a homologous series of cyclic oligomeric dimethylsiloxanes, mainly D₃-D₇. The highest amounts of D₃-D₄ were found in the eroded/contaminated regions. This indicated that the formation of these species was facilitated by high electrical activity (spot-discharges). Oxidative crosslinking, resulting in the formation of silica-like surface layers was not observed. DC-energised samples, with a low content of aluminium trihydrate (ATH) filler and no addition of extra silicone oil, exhibited the highest degree of surface erosion in the end of the test. High levels of ATH and silicone oil improved the long-term stability of the materials.

6.3 ‘Life-time’ of hydrophobic recovery
In Chapter 1 a hypothesis of the lifetime of the hydrophobic recovery of PDMS was given which suggested that after a certain incubation time (or dose of energetic species) a glassy, silica-like layer was formed which inhibited the transport of low molar mass siloxanes to the surface. This would result in a severely retarded rate of hydrophobic recovery. The ‘end of the life of hydrophobic recovery’ was then reached. The hypothesis was tested by exposing silicone rubber to high doses of corona. It was shown that the long-term stability was dependent of the crosslink density of the rubber. The recovery rate of a highly crosslinked (glassy) silicone rubber gradually decreased, whereas the recovery rates of less crosslinked
silicone rubbers (having crosslink densities in the same order as commercial silicone rubbers) remained essentially constant when exposed to repeated doses of corona. However, the hydrophobicity was not permanently lost for any of the tested materials. Scanning electron microscopy showed that the silica-like layer cracked spontaneously after a certain dose of corona (degree of oxidation) or by mechanical deformation of the specimen. This preference for silica-like layers to crack indicated that they would not act permanently as an effective barrier against the transport of low molar mass siloxanes to the surface. This result suggests that the proposed hypothesis was not suitable to describe the long-term stability of the hydrophobic recovery rate of silicone rubbers.

It was observed that the cracking of the silica-like surface layer proceeded by the initiation of new cracks within older ones upon repeated corona exposure. This was caused by vitrification of the older cracks. The hydrophobic recovery rate of these materials was independent the dose of corona. It is suggested that as long as this type of cracking occurs, transport of low molar mass siloxanes through the freshly formed cracks is facilitated. Since new cracks are continuously initiated the hydrophobic recovery rate, i.e., migration of siloxanes is independent of dose of corona. However, this vitrification process will come to a stop when the cracks reach a certain depth where the polymer matrix is shielded from the corona discharges. No new cracks are then initiated. The recovery process will then occur at a slower pace, by transport of siloxanes through the older, oxidised cracks. Further, it is suggested that the highly crosslinked material, which exhibited the presence of deep cracks, had reached this state. Based on this discussion, a revised 'life-time' criteria of the long-term stability of the hydrophobic recovery of silicone rubber after exposure to corona/plasma is suggested (Fig 7.1).

![Figure 6.1](image-url)

**Figure 6.1** Schematic representation of the revised hypothesis of 'hydrophobic life-time' of a silicone rubber surface exposed to corona/plasma, based on a continuous cracking of the silica-like surface layer.

If \( \tau \) is the incubation time to initiate a crack in a brittle surface layer and \( a \) is the crack depth when cracking occurs, either spontaneously or by mechanical deformation, the propagation rate of cracking is: \( \frac{a}{\tau} \). If a
criterion for end of desired properties is set, here as a critical value of the crack depth \((b)\), the ‘life-time of hydrophobic recovery’ of a silicone rubber surface is: \((b/ a)\). This model should be applicable to unfilled PDMS networks with low initial surface roughness. The critical value of the surface roughness must be verified experimentally. If silicone rubber is exposed to hot discharges the same scheme may be applicable. However, a gradual removal of the formed silica-like layer is likely to occur due to the high energy involved, resulting in a continuous erosion of the surface region.

6.4 Regeneration of low molar mass PDMS

The long-term stability of the hydrophobic recovery is also dependent on the presence of mobile siloxanes within the silicone rubber. It was shown that additional amounts of cyclic oligomeric dimethylsiloxanes were formed by depolymerisation reactions during the exposure to electrical discharges. This strongly suggests that the ‘reservoir’ of these species will not be depleted in silicone rubber formulations used as high voltage outdoor insulation.
7. ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to my supervisor, Professor Ulf Gedde and Dr. Mats Leijon, ABB Corporate Research, Västerås, for initiating this project and for accepting me as a student. Ulf, I am also very grateful for your support and enthusiasm throughout this work, making this an educational and fun period in my life.

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8. REFERENCES


