Degradation of Biomedical Polydimethylsiloxanes During Exposure to *In Vivo* Biofilm Environment Monitored by FE-SEM, ATR-FTIR, and MALDI-TOF MS

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ABSTRACT: Polymers used for biomedical purposes in medical devices are usually requested to be inert to degradation. This article describes that slow irreversible changes were observed in silicone surfaces exposed to *in vivo* biofilms even if silicone, in general, is supposed to have excellent long-term properties. Tracheostomy tubes made of silicone rubber were exposed to *in vivo* biofilm environments in clinical tests for periods of 1, 3, and 6 months. The chemical degradation was monitored by MALDI-TOF MS, ATR-FTIR, and FE-SEM. In addition, the physical changes were monitored by contact angle and hardness measurements. Cyclic polydimethylsiloxane (PDMS) was detected on the surfaces of new (unaged) silicones. On the surfaces of the *in vivo* samples new compounds, presumably linear methyl-hydroxyl-terminated PDMS, were detected in addition to cyclic PDMS. These compounds may be formed as a result of the hydrolysis of linear dimethyl terminated PDMS, which is also present in the silicone rubber. ATR-FTIR spectroscopy confirmed that hydrolysis had indeed occurred during the *in vivo* exposure, since Si—OH groups were detected. Furthermore, significant changes in the topography were detected by FE-SEM, indicating the initiation of degradation. No significant changes in the contact angle of the *in vivo* used samples were observed, but this information may be shielded by the fact that biofilm may remain on the surface, despite the thorough cleaning before the analysis. It is also possible that the surface hydrophobicity was recovered by the diffusion of linear low-molecular-weight compounds from the bulk. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 802–810, 2010

Key words: biocompatibility; degradation; MALDI; FTIR; polysiloxanes

INTRODUCTION

Silicone medical devices are made of polydimethylsiloxane (PDMS) with the repeating unit structure: —$Si(CH_3)_2O)_n$—. This polymer is often found in biomedical products made for tubing purposes (tracheostomy tubes, catheters, etc.) since it has good biostability and no toxicity.[1] Silicones are in general regarded as resistant to degradation, but slow changes do occur in, for example outdoor or strongly acidic environments.[2,3] PDMS is a hydrophobic material and normally surface changes result in increased wettability of the polymer surface.

In recent studies, several degradation products were found during environmental degradation of PDMS, for example dimethylsilandiol $(CH_3)_2Si(OH)_2$ was identified in "soil aged" silicone.[4] On the surface of PDMS electrical insulators, that were degraded in outdoor environments, linear molecules with different end groups were formed by ring-opening of the cyclic constituents.[5] In addition, linear low-molecular-weight (LMW) compounds already exist in the bulk of the material and migrate to the surface when chain scission occurs (e.g., by discharge). Chain scission results in loss of hydrophobicity (since hydrophilic groups are formed) and the migrating LMW compounds are responsible for the hydrophobic recovery of the surface.[6–10] These LMW compounds were found to be linear PDMS with methyl and/or hydroxyl end groups.[11,12]

In medical use of silicone rubber there are two factors which are the main reasons for degradation. One is the acidic environment which is caused by body fluids (e.g., gastric acid pH $\sim$ 1) and results in hydrolysis.[3] The other is the biofilm that is formed on the surface of the material through permanent attachment of microorganisms.[13,14] The biofilm may

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penetrate into the material, which leads to degradation. Biofilm formation takes place when free-floating cells attach to the surface through weak van der Waals forces. At this initial stage, if the cells are not immediately separated from the surface, they anchor themselves permanently using cell adhesion structures like pili. In the second stage more cells arrive and the colonization begins. In this stage newly arrived cells are providing more diverse adhesion sites and begin to build the matrix that holds the biofilm together. Mostly, cell division and recruitment takes place during the colonization. The final stage is known as development where only the shape and the size of the biofilm may change. Cells become inactive and tend to have higher resistance against antibiotics.

Silicone tracheostomy tubes are used for patients suffering from different respiratory disorders. The tube is inserted into the trachea right under the vocal cords to ensure the breathing of the patient. Tubes are inspected once a month and if there is no visible sign of degradation they are inserted again. Signs of degradation have been monitored in tracheal tubes made of silicone rubber, polyvinylchloride, and polyurethane by infrared spectroscopy and electron microscopy.[15] Already after 1 month *in vivo* use cracks, pits and erosion to varying degrees were detected on the tracheal tubes.

The objective of this study was to, in detail, describe and explain the chemical and physical degradation of PDMS during exposure to *in vivo* environments. The correlation of the changes in the hydrophobicity, morphology and chemical structure were done based on, field-emission scanning electron microscopy (FE-SEM), contact angle and hardness measurements and attenuated total reflectance Fourier-transform-infrared spectroscopy (ATR-FTIR). The chemical structure of the LMW compounds present on the surface of the degraded silicones were identified by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS).

EXPERIMENTAL

Materials

Bivona® TTS™ silicone rubber tracheostomy tubes with Superslick® layer were purchased from Smiths Medical International Limited (Hythe, United Kingdom). Sodium-trifluoroacetate (NaTFA) (purum, ≥98.0%), heptane (puriss. p.a., ≥99.5%), and 2-(4-hydroxyphenylazo)-benzoic acid **(**HABA) (puriss. p.a., matrix substance for MALDI-MS, ≥99.5%) were purchased from Fluka (Stockholm, Sweden). Chloroform (≥99%), tetrahydrofurane (THF) (Chromasolv® Plus, for HPLC, ≥99.9%), 2,5-dihydroxybenzoic acid (DHB) (puriss. p.a., matrix substance for MALDI-MS, >99.0%), were purchased from Sigma Aldrich (Stockholm, Sweden).

TABLE I
The Medical Records of the Patients[15]

Patient no.	Tube no.	Inhaled drugs	Note
1	SIL-205 SIL-206 SIL-208	–	Aspirate
2	SIL-209 SIL-210 SIL-212	–	–
3	SIL-213 SIL-214 SIL-216	–	–
4	SIL-217 SIL-218 SIL-220	Budesonide; ipratropium bromide monohydrate	+ Oxygen; aspirate
5	SIL-221 SIL-222 SIL-224	–	Aspirate

Tracheostomy tubes

The tubes came from the National Respiratory Center (NRC), Danderyds hospital, Stockholm, Sweden, a national referral clinic for outpatients with long-term tracheostomy which customizes annually ~ 800 tracheostomy tubes. The tubes were exposed in human patients for 1, 3, and 6 months.[15] Silicone rubber tubes had a so-called superslick layer on the surface which may be composed of a poly-phenylmethyl siloxane according to FTIR-analysis (unpublished results). The phenyl group on the molecule is responsible for the enhanced slipperiness of the surface which supposed to repel bacteria or inhibit the biofilm formation. Five patients took part in the experiment, and all analytical data are presented as average results. The diagnosis and the most important details of the patients are presented in Table I, where also the sample codes are given.

After the exposure, the tubes were cleaned at Danderyd Hospital, Stockholm, Sweden by the following procedure: all tubes were washed both outside and inside by soaking in warm water with perfume free detergent containing surfactants (Nilfisk-Advance, Stockholm, Sweden) and water. After that the tubes were rinsed under running water for 30 s. Finally, the tubes were soaked in a disinfected cup containing 0.5% chlorhexidine alcohol for 1 min and then rinsed in another disinfected cup with 0.9% sterile saline for 1 min.[15]

After the cleaning, three pieces were cut from three different areas on each tube. These areas are presented in Figure 1. Area 1 is at the neck plate where the tube penetrates into the airway. Usually

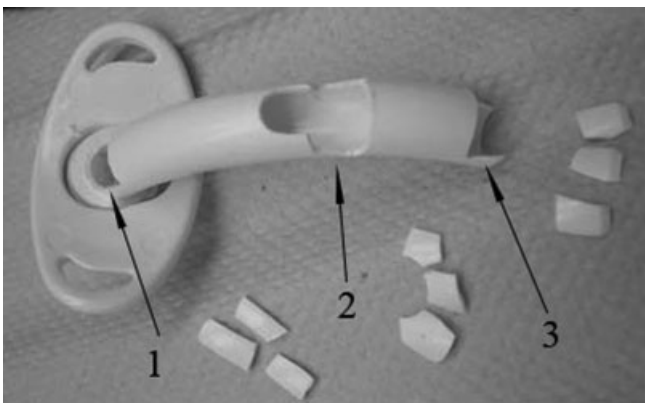

Figure 1 Sample preparation scheme of the samples from the tracheostomy tubes, samples were cut from the areas indicated 1, 2, and 3.[16]

tracheostomy tubes have a fenestration to allow the patient to be able to talk while wearing the tube. Area 2 is at the fenestration site. Area 3 is the end of the tube which is located closest to the lungs. All *in vivo* samples were compared with a reference tracheostomy tube which consisted of a tracheostomy tube from a newly opened package.

Scanning electron microscopy

SEM micrographs from each sampling area at the different exposure times were taken with a Hitachi S-4800 Ultra-High Resolution FE-SEM (Hitachi High Technologies Europe GmBH, Krefeld, Germany) at 400× and 600× magnification. The samples were first coated with gold/palladium. The thickness of the coating layer was $\sim$ 10 nm.

Contact angle measurements

Contact angle measurements were carried out on a CAM 200 instrument from KVS Instruments Ltd. (Helsinki, Finland). MilliQ grade water from a Synergy 185UV Ultrapure water system (18.2 MΩ cm, Millipore AB, Solna, Sweden) was used for the measurements. The contact angle was determined from the average of three pieces from each area where five droplets were analyzed on each piece, that is a total number of 15 droplets. Ten images were taken for each droplet with a speed of 10 ms/frame.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry

A Bruker Ultraflex MALDI-TOF MS instrument with a SCOUT-MTP laser source from Bruker Daltonics (Bremen, Germany) was used. The instrument was equipped with a nitrogen laser (337 nm), a grid less ion source and a reflector. The spectra were collected in the reflector positive ion mode with an acceleration voltage of 25 kV and a reflector voltage of 26.3 kV. The mass range of the detector was set between m/z 900 and 3000. The laser power was set slightly above the threshold. The samples for MALDI-TOF MS were spotted on a MTP 384 ground steel target plate (Bruker Daltonics, Bremen, Germany).

The LMW silicone compounds were extracted from the surface of the tube pieces by rinsing with 5 mL heptane. The heptane extracts were collected in glass vials. After evaporation of the heptane, the residue was dissolved in 1 mL chloroform.[11] HABA and DHB, both at a concentration of 10 g/L in THF, were used for MALDI sample preparation. The analyte and the matrix solutions were mixed in equal ratios, 10 + 10 μL. All analyte/matrix mixtures were doped with 4 μL NaTFA at a concentration of 1 g/L in THF. Approximately 0.3 μL of the mixture was then spotted onto the target plate. Three pieces from each sampling area of the tube were analyzed and three spots were prepared on the target plate per extract. The mass spectra were accumulated from 500 laser shots.

Attenuated total reflection Fourier transform infrared spectroscopy

The tube surfaces were analyzed using a Spectrum 2000 FTIR spectrometer from PerkinElmer (Wellesley, MA) equipped with a Golden Gate single-reflection accessory for ATR. A total number of three pieces from each area were analyzed and 16 scans per piece between 4000 cm^{-1} and 600 cm^{-1} were averaged at intervals of 1 cm^{-1} with a resolution of 4 cm^{-1}.

Hardness measurement

Shore A hardness measurements were done by a Zwick/Roell Shore Digital Hardness Tester (Zwick GmbH & Co. KG, Ulm, Germany) according to DIN 53505, ISO R 868, NFT 51109, ASTM D 2240, and BS 903 Part A26 standards.

RESULTS AND DISCUSSION

SEM was used to study the surface structure of reference and *in vivo* used tubes. Figure 2 shows typical micrographs from areas 1, 2, and 3 after different exposure times. The material surface structure shows significant changes on after *in vivo* use.

Figure 1 represents the SEM micrograph of the surface of the reference material which has never been exposed to human body. The typical "worm-like" silicone rubber pattern was observed. After 1 month exposure, the surface of the samples [Fig. 2(b–d)] were similar to the reference material [Fig.

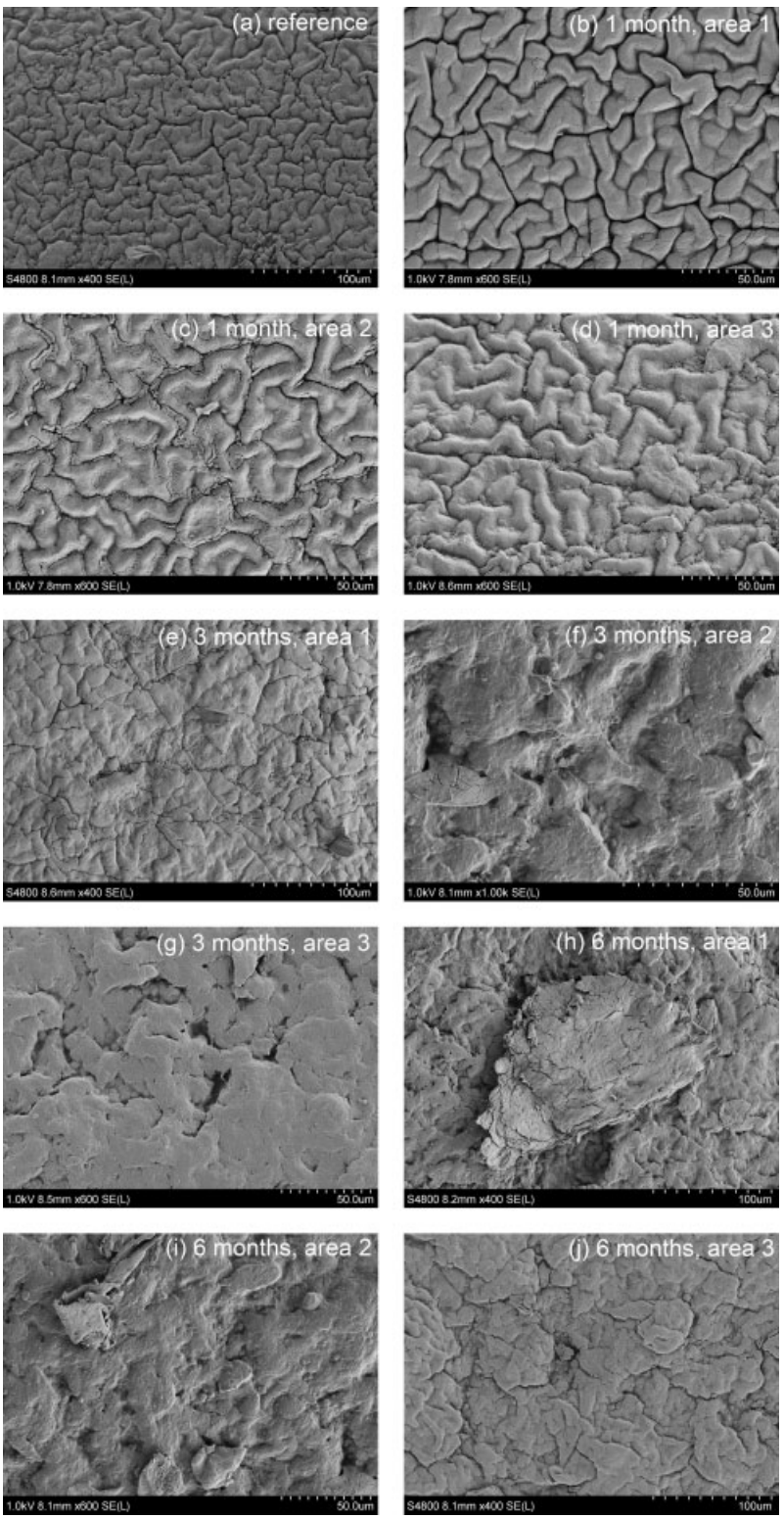

Figure 2 SEM micrographs from the surface of silicone rubber: (a) Unexposed sample; (b–d) area 1, 2, and 3 of 1-month *in vivo* used sample; (e–g) area 1, 2, and 3 of 3-month *in vivo* used sample; and (h–j) area 1, 2, and 3 of 6-month *in vivo* used sample.

2(a)]. No significant surface changes were observed, which indicates that during the first month either no degradation takes place or the influence of it cannot be detected. After 3 months [Fig. 2(e–g)], the surfaces of areas 1, 2, and 3 were significantly altered compared with the reference surface. On the topography of area 1 [Fig. 2(e)], a network of cracks had formed on the surface. Since the shape of the cracks

TABLE II
The Contact Angle Measurement Results of Unexposed and *In Vivo* Used Silicone Rubber Tracheostomy Tubes

	Contact angle (°)			
Sample	Area 1	Area 2	Area 3	Exposure time (month)
SIL-reference	115	115	115	0
SIL-205	118	113	101	1
SIL-206	116	111	114	3
SIL-208	111	107	108	6
SIL-209	110	110	109	1
SIL-210	115	113	111	3
SIL-212	122	118	122	6
SIL-213	123	111	112	1
SIL-214	119	120	118	3
SIL-216	115	114	114	6
SIL-217	117	122	120	1
SIL-218	115	109	116	3
SIL-220	107	105	107	6
SIL-221	124	114	92	1
SIL-222	116	112	113	3
SIL-224	114	112	115	6

were irregular, it seems likely that this surface alteration is not due to mechanical stress. However, the typical "worm-like" pattern of silicone rubber is still recognizable. On area 2 [Fig. 2(f)], the pattern of silicone smoothened and became unrecognizable compared with the reference sample [Fig. 2(a)]. The surface of area 3 [Fig. 2(g)] is similar to area 2 [Fig. 2(f)], but the pattern became much smoother and almost vanished. Similar surface changes were also observed after 6 months exposure. On the surface of area 1 [Fig. 2(h)], a part of a biofilm or some other biological media was occasionally detected. In addition the surface pattern of silicone is not recognizable. The same surface alterations were observed on area 2 [Fig. 2(i)] which indicates higher degree of degradation. On area 3 [Fig. 2(j)], the silicone pattern smoothened as well, but still recognizable. It was observed from the SEM micrographs [Fig. 2(j)] that the degree of degradation in this area based on the surface pattern might be between the degradation of the 3 months sample area 1 [Fig. 2(e)] and 3 [Fig. 2(g)].

Contact angle measurements were performed to detect any changes in surface hydrophobicity on the tubes. Table II shows the individual measured contact angles from the areas 1, 2, and 3 for various exposure times, whereas Figure 3 shows the average values from all patients as a function of time for each area. The standard deviation varied between 1.4° and 9°.

As can be seen in Figure 3, no significant trend was observed in the contact angle measurements. In some cases, for example sample SIL-212 area 1, the measured contact angle was higher than for the reference tube, whereas in other cases the contact angle

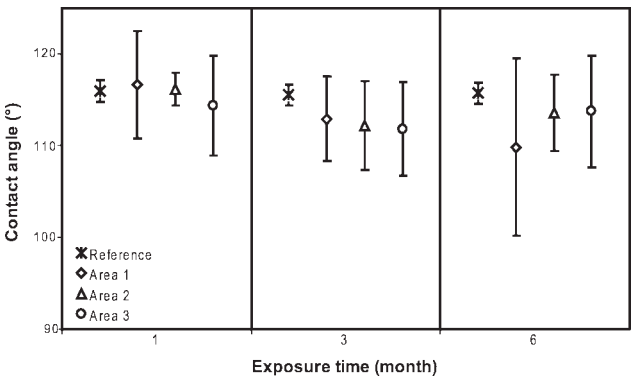

Figure 3 The contact angle measurement results of the reference sample and *in vivo* used samples (according to sampling area 1, 2, and 3) as a function of exposure time.

was lower compared with the reference. A possible explanation to the increase phenomenon could be that the biofilm was not completely removed from the surface during the cleaning. It is known that the surface of biofilms is hydrophobic to protect the contained microorganisms from the surrounding environment.[14,17]

Several parameters, some of which may also be due to post *in vivo* treatment, for example cleaning of the tubes, may influence the results. It was expected that the surface hydrophobicity would decrease due to wear of the hydrophobic "Superslick" coating and/or changes in the chemical structure of the polymer molecules at the tube surface. An explanation for the increase in contact angle could be the "self-healing" phenomenon which has been observed in silicone rubbers. It has been shown that diffusion of hydrophobic linear LMW silicon molecules from the bulk to the surface of the plastic could increase the contact angle.[6–10]

The slight decrease of the contact angle could be a result of decrosslinking and chain scissions on the surface. Degradation of silicone rubbers in a strongly acidic environment,[3] which is present inside the human body, predominantly occurs through

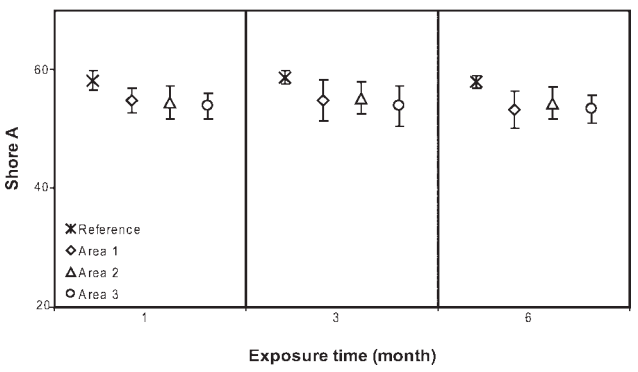

Figure 4 Shore A hardness measurement results of unexposed and *in vivo* used silicone rubber tracheostomy tube.

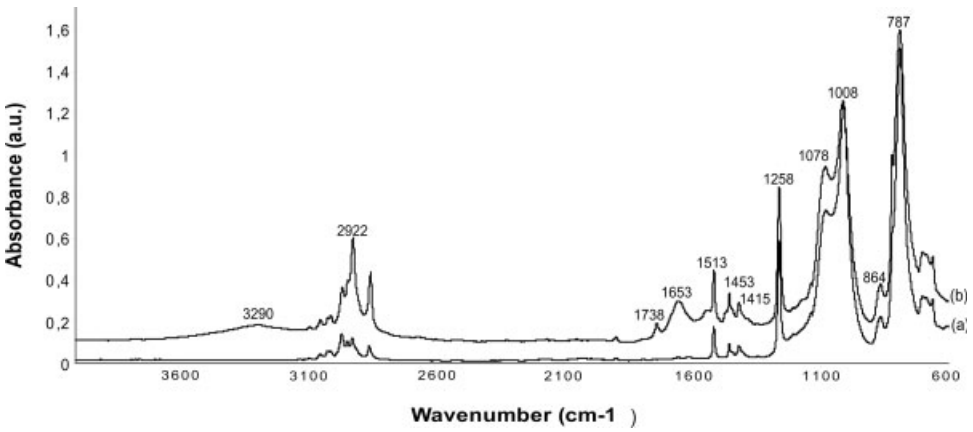

Figure 5 Comparison of ATR-FTIR test results of an unexposed reference (a) and *in vivo* used tracheostomy tube (b).

hydrolysis. Thus, relatively hydrophilic hydroxyl-terminated compounds are formed. In addition, besides linear LMW compounds cyclic compounds are also formed. These are known to be hydrophilic and therefore the presence of these molecules may be another reason for the decreased contact angle.

Every human environment is unique and, therefore, it is hard to compare and to draw general conclusions from the contact angle results. However, it is clear that the surface hydrophobicity remained fairly constant during 6 months *in vivo* use. This can be attributed to the silicone rubber, which is believed to be biostable and a good material for *in vivo* applications, for example for tubing purposes.

Figure 4 represents the individual results of the hardness measurements of all areas and exposure times. The Shore A hardness of the reference materials was $\sim$ 58. It could be determined that the hardness of all samples decreased slightly. However, the difference of hardness values between the *in vivo* used and unexposed material is significant only for a few cases, and the values do not follow any trend. The standard deviation of the samples varied between 0.5 and 3.2 Shore A hardness. A decreased hardness can be due to decrosslinking in the material.

A significant difference between the different sampling areas was expected, however, the results showed no indication on that.

ATR-FTIR spectroscopy was performed on *in vivo* used and unexposed reference material and the results were compared. Figure 5 shows the IR spectra of the reference and an *in vivo* used sample. The strongest peak was observed at 787 cm^{-1}, which corresponds to Si—C stretching vibration. The peaks between 1008 cm^{-1} and 1078 cm^{-1} are due to the Si—O—Si stretching vibration, which corresponds to the polymer backbone. Bending and rocking vibrations of Si—CH_3 were found at 1258 cm^{-1} and 864 cm^{-1}, respectively.[2,3,18,19] Because of the Superslick layer, peaks at 1513 cm^{-1}, 1453 cm^{-1}, and 1415 cm^{-1} were observed, which corresponds to the vibration of Si-Ph.[19,20] In the higher wavelength region between 2800 cm^{-1} and 3100 cm^{-1}, the stretching of —CH_3 was detected.[2,3,18–20]

During the exposure, in most cases, a new peak between 3200 cm^{-1} and 3600 cm^{-1} was detected in the IR spectra (Fig. 6). This corresponds to the stretching vibration of the Si—OH bond. In addition, it was shown that the peak which corresponds to the —CH_3 functional group increased during exposure. The migration of LMW silicone compounds to the surface is a possible explanation for this phenomenon.

In most of the *in vivo* used samples, new, "protein-like" peaks were observed between 1525 cm^{-1} and 1760 cm^{-1} (Fig. 7). Biofilm is usually consisting of a polysaccharide gel hosting micro-organisms such as bacteria. Although the tubes were cleaned with anionic and nonionic surfactants it is likely that some remains of the biofilm are left. The peaks, which were observed in region 1500–1800 cm^{-1} indicated presence of biofilm and traces of cell wall material from bacteria.[21–26]

MALDI-TOF MS was used to study chemical changes on the surface of the materials. The mass spectra from extracts of *in vivo* samples were

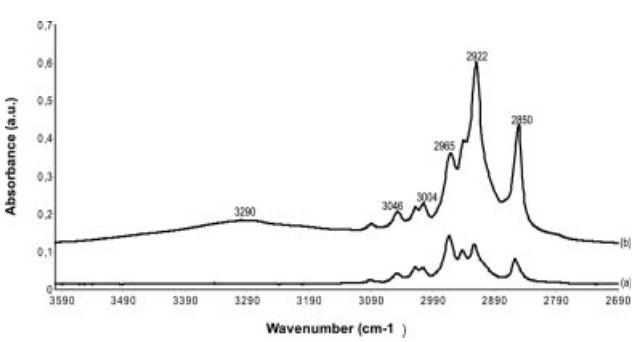

Figure 6 Comparison of ATR-FTIR test results of an unexposed reference (a) and *in vivo* used silicone rubber tracheostomy tube (b) in region 2690–3590 cm^{-1}.

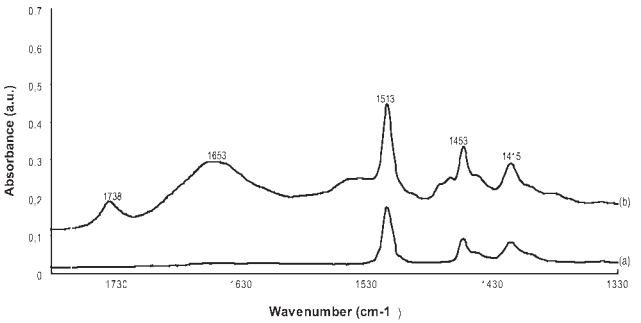

Figure 7 Comparison of ATR-FTIR test results of an unexposed reference (a) and *in vivo* used silicone rubber tracheostomy tube (b) in region 1320–1720 cm^{-1}.

compared with those from reference material. MALDI sample preparation with DHB as matrix and THF as solvent resulted in higher resolution mass spectra. Therefore, this preparation method was chosen for further analysis. Figure 7 shows the MALDI mass spectra of an extract from a reference sample. In the spectrum (Fig. 8) peaks in the m/z range 1000–2600 were detected. The difference in m/z between two adjacent peaks is m/z 74, which corresponds to the mass of one repeating unit. The peaks at m/z 1059 + n74 (n = 0,1,2,...) correspond to sodium adducts of cyclic PDMS molecules. On the surface of reference sample, only cyclic PDMS molecules were found. The shortest cyclic PDMS chain was detected at m/z 1059 (14 repeating units) and the longest one at m/z 2539 (34 repeating units). However, no linear compounds were detected in the reference samples.

This is somewhat surprising as the material is comprised of both cyclic and linear PDMS. Nevertheless, the molar mass of the linear polymer is much higher (~ 250,000 g/mol) than that of the cyclic. MALDI sample preparation for analysis of high molar mass compounds (~ >50,000 g/mol) is different than that for compounds with low molar mass (~ >10,000 g/mol). In addition, detailed chemical structure analysis, for example analysis of the degree of polymerization (DP) and end-group analysis, becomes impossible at higher molar mass due to instrumental and chemical factors, that is peaks originating from molecules of neighboring DP cannot be separated due to the increasing influence of natural isotope distributions with increasing molar mass. Therefore, the aim of this study was to focus on chemical structure analysis of low molar mass compounds in PDMS.

Peaks at m/z +16 compared with the peaks from cyclic molecules were occasionally detected in the MALDI-TOF mass spectra of extracts of *in vivo* used tubes (Fig. 9). These could originate from linear molecules with methyl and hydroxyl end groups (Fig. 10), but could also be due to adduct formation with potassium. To rule out the possibility to potassium adducts the samples were doped with silver trifluoroacetate. In the spectra from doped samples (where silver ion adducts were detected) the m/z +16 peaks were still observed. Therefore, these peaks most likely do not originate from cyclic molecules. If linear PDMS (with methyl end groups) undergoes hydrolysis, the mass of the product oligomers will match the m/z of the unknown peaks. The cyclic PDMS is also sensitive to hydrolysis and if this should occur, peaks at m/z +18 compared with the peaks originating from cyclic PDMS would appear. However, due to overlap of the isotopic envelope, we could not detect any hydrolysis products from cyclic PDMS. Therefore, we believe that these peaks originate from linear products from hydrolysis of linear PDMS. Because of the hydrolysis, decrosslinking could also occur.[3,27] However, in the MALDI

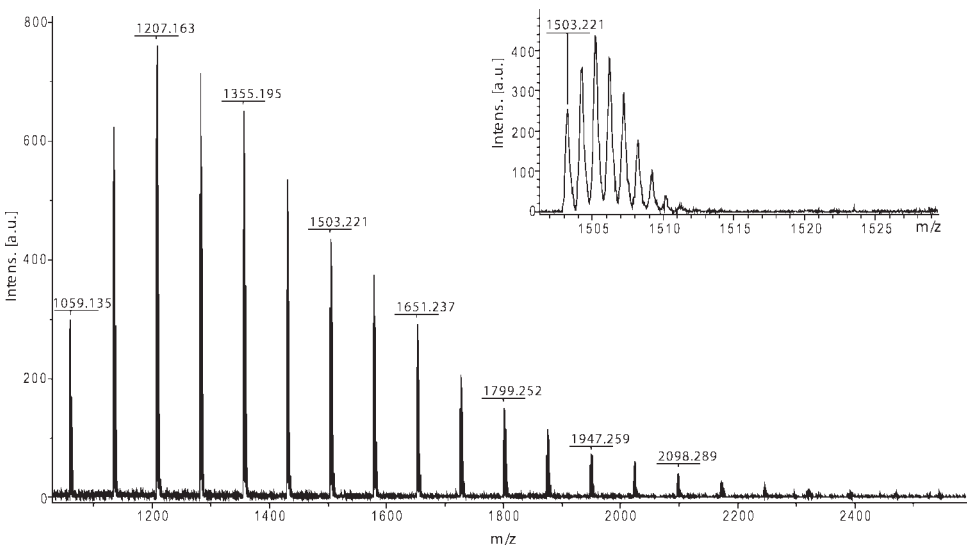

Figure 8 MALDI TOF mass spectrum of a residue extracted from unexposed silicone rubber tracheostomy tube.

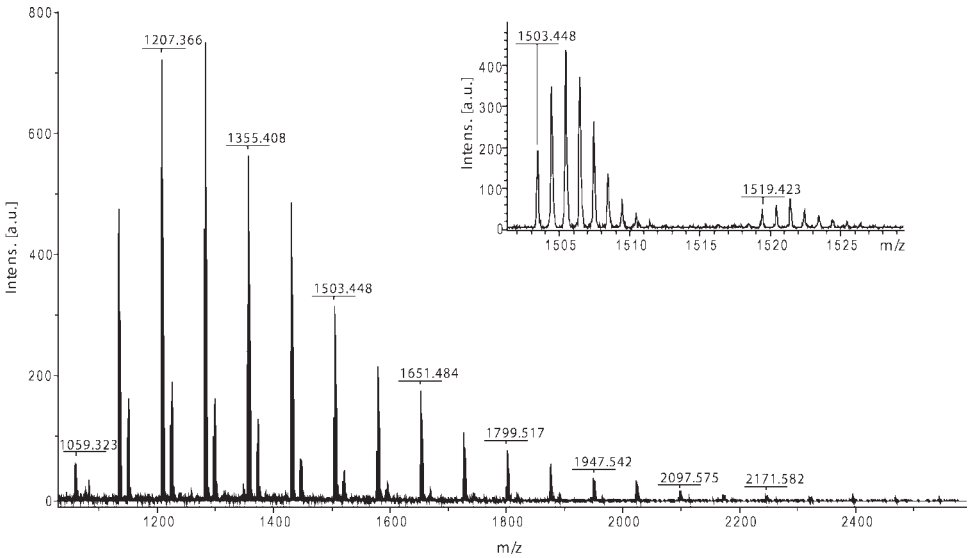

Figure 9 MALDI TOF mass spectrum of a residue extracted from an *in vivo* used silicone rubber tracheostomy tube.

TOF mass spectra no indications on this could be detected.

It is known that some of the patients were aspirating, which could be reason for the hydrolysis. Although the backbone of the silicone rubber [Fig. 10(a)] is stable, hydrolysis could occur (Fig. 11) in the strong acidic environment (pH $\sim$ 1–2) originating from the gastric acid.[3,28]

In summary, hydroxyl-containing compounds were detected in both ATR-FTIR spectroscopy and MALDI-TOF MS. Thus, it seems clear that hydroxyl compounds were formed on the tubes during the *in vivo* exposure. The formation of these molecules confirms that the silicone rubber has been degraded by hydrolysis. Presence of biofilm on silicone surfaces has been demonstrated in other applications, for example outdoors high voltage insulators.[26] Once a surface has been in contact with water, inorganic and/or organic particles a colonization of microorganisms occur. The environment at the interphase between a biofilm and a polymeric surface could be very aggressive and combinations of degradation mechanisms most likely combine resulting in chemical and/or biological degradation. Even if silicone is inert to biodegradation, the biofilm formation resulted in a slow hydrolysis and a change in surface characteristics which may lead to a decreased life-time of the material in question.

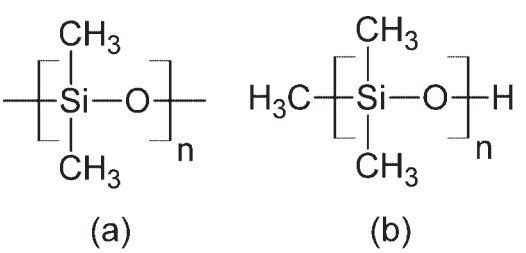

Figure 10 The chemical structure of cyclic (a) and methyl-hydroxy-terminated polydimethylsiloxane (b).

CONCLUSIONS

This study demonstrates that although silicone rubber is generally regarded as inert to biodegradation, initiation of degradation is observed already after 1 month *in vivo* exposure.

Furthermore, after 1 month of *in vivo* exposure, new linear LMW PDMS compounds were detected on the silicone surfaces by MALDI-TOF MS. These compounds, we believe, are linear hydroxyl-terminated PDMS molecules, which are formed during the *in vivo* exposure, probably by hydrolysis of linear high-molecular weight dimethyl terminated PDMS. The ATR-FTIR results confirmed that hydrolysis of PDMS had occurred during the *in vivo* exposure of the materials, since peaks corresponding to the vibration of Si—OH bonds were detected in the spectra.

SEM micrographs showed significant differences in the topography between the *in vivo* and the new (unaged) samples. The typical "worm-like" surface structure of the Superslick layer started to vanish after 3 months and was almost totally lost after 6 months exposure. The hardness of the samples decreased, however, this change was significant only

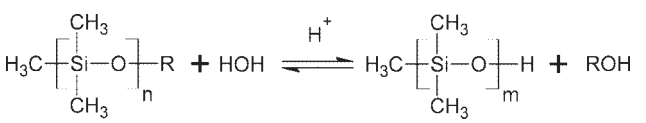

Figure 11 Scheme of acid-catalyzed hydrolysis of linear polydimethylsiloxane.

in a few cases. The decrease in hardness indicated decrosslinking of the material. No significant trend was seen in the wettability experiments.

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