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High-Magnification SEM Micrograph of Siloxanes

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Abstract

SEM is a powerful and efficient microscopy for the analysis of nanomaterials. Although this imaging technique is common and several standard methods exist for chemical analysis, questions remain about the optimal magnification and voltage to be used. The chemical molecules are relatively sensitive to the electron beam. HMDS is as often as possible utilized for surface treatment at the covering of the photosensitive material on the wafer, and trimethylsilanol is created, together with alkali, by hydrolysis of HMDS. The best viewing condition to HMDS and reaction products of organosilicons. The greatest challenges of working with organosilicons molecules are imaging and characterizing features on such a small scale by SEM. The results support the conclusion that, contrary to what is usually recommended, it is best to determine the structure of organosilicon molecules without spectroscopy. It has been a convenient method for the emergence of the structure of HMDS and reaction products. Many micro/nanofabrication technologies have been invented and developed during the past decades. Indeed, some of them have already been widely applied in the cell biology study. In this section, we introduce and emphasize on several prominent technologies, such as soft lithography, electrospinning, nanostructured patterning technologies (including dip pen, e-beam writing, nanoimprint lithography, nanoshaving, and so on), and three-dimensional fabrications. Over the past decade, nanotechnology research has shown exciting evidence that key biological processes (e.g., osteoblast proliferation, osteoblast gene expression, and initial protein adsorption that control such events) can be easily manipulated by modifying the nanotopography of Ti implants. A table is also presented to highlight the pros and cons of different major technologies.

Keywords: siloxanes, organic molecules

1. Introduction: High-magnification SEM micrograph of siloxanes

Scanning electron microscopy (SEM) is a powerful and efficient microscopy for the analysis of nanomaterials. Although this imaging technique is common and several standard methods

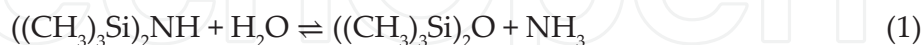
exist for chemical analysis, questions remain about the optimal magnification and voltage to be used. The chemical molecules are relatively sensitive to the electron beam. HMDS is as often as possible utilized for surface treatment at the covering of the photosensitive material on the wafer, and trimethylsilanol is created, together with alkali, by hydrolysis of HMDS. This study specifically represents the best imaging condition to HMDS and reaction products of organosilicons. The greatest challenges of working with organosilicon molecules are imaging and characterizing features on such a small scale by SEM. The results support the conclusion that, contrary to what is usually recommended, it is best to determine the structure of organosilicon molecules without spectroscopy. It has been a convenient method for the emergence of the structure of HMDS and reaction products.

The process of imaging of molecules is essential for researchers although the scale of small-molecule chemistry has brought with it, challenges. Specifically, with organic compounds having recently been detailed by spectroscopy and diffraction techniques, advances in electron microscopy have made high-resolution images a possibility. The microscopy is capable of displaying numerous small materials, nanostructured structures, and chemical molecules while not sufficiently to illustrate molecular bonds.

Although organic molecular structures are displayed by developing microscopic techniques, many organic molecule structures are yet to be revealed. The examination of a molecule from its fragments is dependent upon the precise manipulation of these molecules. Organic structure characterization is primarily based upon microscopic techniques that are largely established upon electron or X-rays. To obtain an imaging experiment, there exists various techniques such as optical microscopy (OM), transmission electron microscopy (TEM), X-ray microscopy (XRM), scanning electron microscopy (SEM), energy disperse X-ray spectroscopy (EDX), and atomic force microscopy (AFM). There is a wide earthly spectrum, from the morphology level to the atomic level. Each microscope has the ability to display only a restricted number of fields [1, 2]. The appropriate microscope should be selected for the best characterization. The imaging magnitudes of microscopes vary, as TEM, from approximate 1 Å to 10 μm ; STEM, from 1 Å to 100 μm ; AFM, from 1 nm to 1 mm; SEM, from 1 nm to 1 mm; and OM, from 100 nm to 1 cm. Scanning electron microscopy is an essentially significant technique for image acquisition in the scientific field [3]. It is vital to be able to decipher the structure of nanosized and micro-dimensional materials for characterization of the materials and to interpret the formation and mechanism. Additionally, the imaging of organic molecules and biological specimens poses a serious challenge for researchers.

The applicability of ultraviolet spectroscopy to organosilicon compounds, utilizing mass, Raman, and other spectroscopy techniques [3]. Alkyl-substituted silanes and siloxanes are not ultraviolet absorbent. SEMs are primarily used to analyze the morphology of materials on the samples [4]. The SEM observation scale ranges from microns to nanometers. The decrease of beam damage and charging proves to have an adverse impact on organics. The previous research has shown that microscopy, along with spectrometry, is highly beneficial in identifying organic components [1]. Unfortunately, these methods are destructive to the sample and make conduction of subsequent tests impossible. However, the nondestructive technique of low-voltage SEM enables the identification of organic components.

1,1,1,3,3,3-Hexamethyldisilazane (HMDS) is used as a photoresist adhesion promoter in semiconductor applications. It is often possible to locate HMDS residues in SEM images. Silazanes as HMDS are generally moisture sensitive. In addition to appropriate adhesion and photoresist properties, surface dampness, in addition, is a central point. HMDS is well known as a versatile silylation reagent with the ability to block or protect Si—H, N—H, and O—H bonds. HMDS is converted into trimethylsilanol (TMS) and ammonia by the process of hydrolysis in aqueous mediums, as in the equation $((\text{CH}_3)_3\text{Si})_2\text{NH} + 2\text{H}_2\text{O} \rightleftharpoons 2(\text{CH}_3)_3\text{SiOH} + \text{NH}_3$ or directly to hexamethyldisiloxane (HMDSO), and ammonia in an aqueous medium, as equation [5]



According to Donaldson Company, HMDS is able to be hydrolyzed in air to form TMS and ammonia at approximately 25°C, with 45% relative humidity (6–8). Sonnenfeld et al. [6] investigated atmospheric pressure dielectric barrier discharges, with HMDSO admixed into a combination of a noble gas and a molecular gas (O_2 or N_2). The reaction and molecular structure arrangement is illustrated in **Figure 1** [6].

HMDSO can be formed from a minimum number of reaction products, most likely trimethylsilanol, hexamethyldisilane, pentamethyldisiloxane, heptamethyltrisiloxane, and octamethyltrisiloxane.

HMDS, as the silazanes, is similar to siloxanes, with —NH— replacing —O— and acquired in high yield and purity. As dependent on the molecular structure, in the Si—N pillar, $\text{Si}(\text{NH})_3$ and $\text{Si}(\text{NH})_2$ are realized and the properties of the silazanes that are dependent on the molecular structure such as various functional groups (Si—H , Si—CH_3 , Si—CH=CH_2) and degrees of branching [8, 9]. The silazanes, in a process called silylation, react readily with an active hydrogen on any organic chemical (e.g., alcohol, amine, or thiol). For example, hexamethyldisilazane is composed of two silicon atoms fused to the nitrogen atom. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) is used as a photoresist adhesion promoter in semiconductor applications.

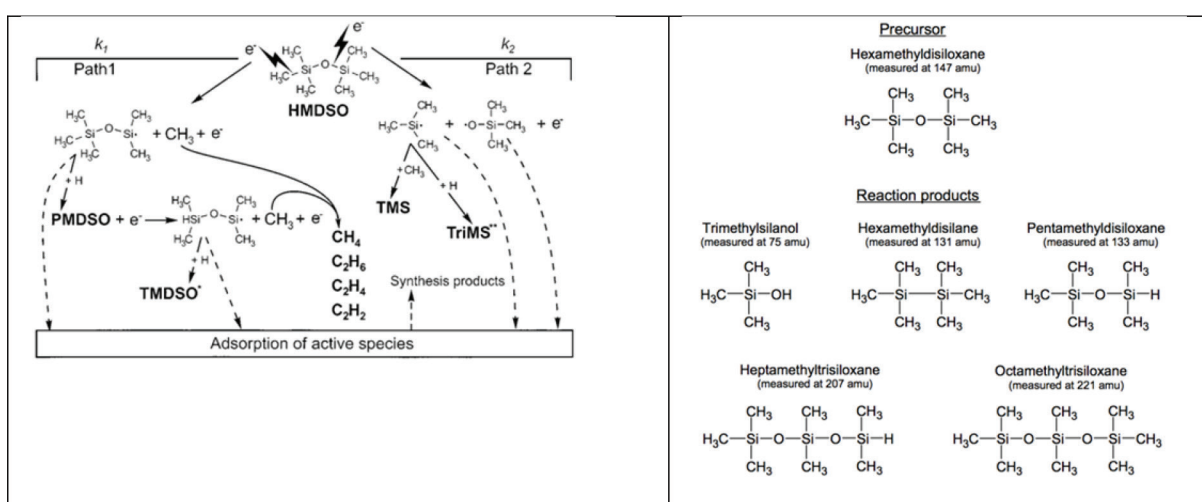


Figure 1. Scheme of the proposed HMDSO reaction chemistry (left) [6]. Possible chemical structures of the identified reaction products in comparison with HMDSO (right) [7].

The Si—O bond is a simple one, in both arrangement and cleavage, an important trait for manufactured science. Weak interactions, along with the simple arrangement and cleavage of Si—O bonded compounds, are used in the construction of supramolecular architectures. The chemistry of the Si—O bond formation is an interesting aspect for hydrolytic cleavage. The Si—O bond can also be compiled from a weak Si—H or Si—Si bond [10–12].

The residue or morphology of small chemical molecules remains unclear, as a result of a lack of high-throughput and high-resolution surface characterization methods. We demonstrate the revealed morphology of surface contaminants by SEM. This study introduces early-stage research about the ability to detect and characterize microscopic fixative residues of HMDS on a biofilm surface, by means of SEM. The results of this research reveal a new possible method of obtaining additional information from the commonly used organic molecules. The results attained from the SEM have proven to be a useful tool in detecting HMDS residues. Advancements in software may increase the abilities of currently available instruments, with microscopy images.

The samples were then dehydrated in a concentration of ethanol, ascending from 50 to 100%, and then dried in hexamethyldisilazane (HMDS, $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$, 98.5%; ABCR GmbH & Co. KG, Karlsruhe, Germany) solution overnight. After complete drying, the specimens were sputtered and coated with a thin layer of carbon. The specimen surfaces were examined under a scanning electron microscope XL 30 ESEM FEG, operating at 5 kV and under a magnification rate ranging from 2,000- to 200,000-fold. Tilt angle, spot size, and scanning mode of the electron microscope remained constant for all samples examined. The material was incidentally found when working on the biological surface. HMDS is a drying chemical used for the purpose of fixing scanning electron microscopy specimens.

2. The imaging of surface contaminant, HMDS

Identifying surface residues and contaminants on a biofilm or other biological surface using SEM imaging is seldom explored. One of the major challenges in resolving organic residues, which are the final fixation buffer on a biological surface, is caused by an overlay on top of the image, as both the contaminants and the biological surface are carbon-based materials. In **Figure 2**, HMDS, which is an SEM fixation buffer, appears on the 24 h biofilm formation surface in situ. The topographic contrast exists as a result of the uniformity of the contaminants.

Oral bacteria are visible on the rear surface, and organic residue appears at a lighter concentration on the top surface. The residues therefore prevented the surface from being made visible. The contaminant could be HMDS, and their analogous counterparts as the prepared SEM sample's fixations buffer contain Si.

The water on the biological surface was dried by the evaporation of hexamethyldisilazane. HMDS has been shown in **Figure 3**. During observation of the biological surface, HMDS and residues were measured on dental titanium by means of SEM. Specimens exhibited spontaneous separation during hydrolysis.

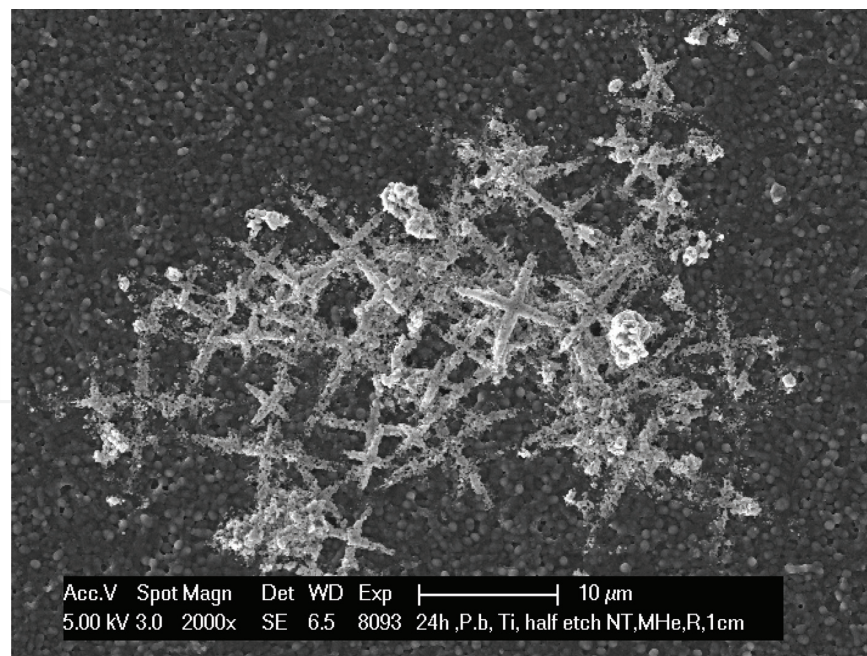


Figure 2. SEM fixative residues on 24 h in situ biofilm formation surface.

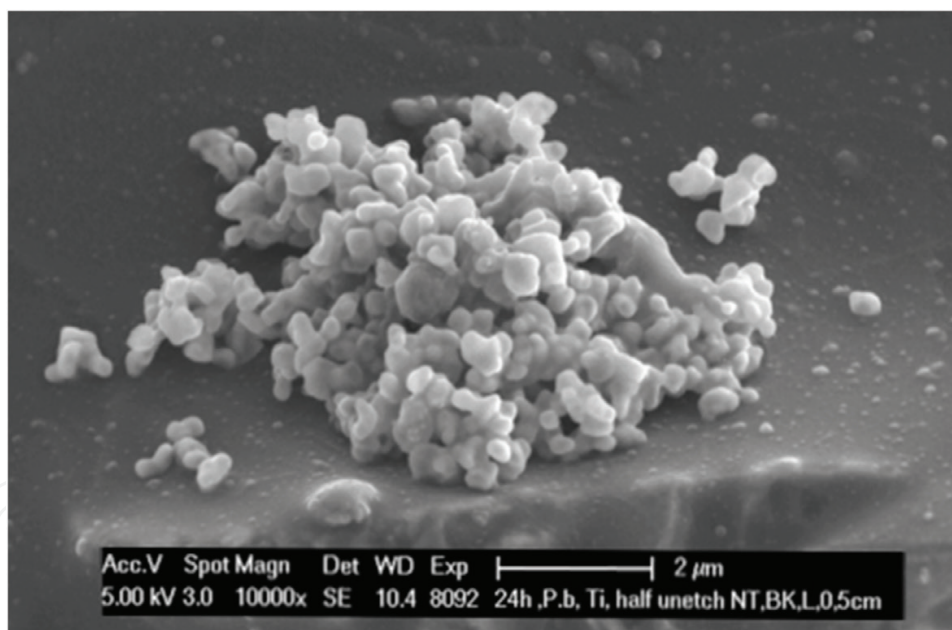


Figure 3. Closer view of the HMDS and related residues on the surface. The shapes of the molecules are seen to be different from each other.

Previous studies had established the same reported morphology for HMDS in this project. The results of this research concur with data obtained by EDX surface analysis, which reflected particle sizes in the range of 20–30 nm [13]. Previous experiments did not show details of HMDS and HMDSO photographed with an electron microscope. As a result of this, it will be a priority for future research and experimentation. Upon reviewing other studies, there is no visual information available about HMDS and HMDSO, although there exists much chemical information about it [14].

3. The imaging of HMDSO transforming into siloxanes

Siloxane molecules are cyclic siloxanes (D_3 , D_4 , D_5 , and D_6) and linear siloxanes (L_2 , L_3 , L_4 , L_5 , and L_6). **Table 1** shows that cyclic siloxanes are 2D and 3D conformer generations. In accordance with functional groups, there exist four types of siloxanes. The first of these is the monofunctional (M) units; the second is the difunctional (D) units, which are oligomers' and polymers' linear chains or cyclic compounds; the third is trifunctional (T) units; and the fourth is tetrafunctional (Q) units, which result in branched and spatially cross-linked molecules (elastomers) [2]. The characteristic of these principal structures are presented in **Figure 4**.

Environmental conditions such as temperature, air, and water contact can alter the conformation of siloxanes. The Si–O siloxane chain can be rotated under minimal force at room or higher temperature. When siloxanes are in contact with air, the methyl groups which determine the hydrophobic properties are compacted by the contact surface [16]. When the contact is made with water, the dipole of the siloxane skeleton is responsible for the interactions between the mediums, as the siloxane (silicone) elastomer becomes more hydrophilic [17]. These properties attribute the differences in adhesion properties between silicone elastomers.

Prior studies had proven that silicon does not have the ability to form stable, double bonds. During the synthesis of siloxanes, chains comprising various numbers of repeat units in the chain are formed. Siloxane reaction products [18] are available as oligomers of varying chain length and molecular weights. A single type of molecule does not form at the end of the reaction. The mixture may also contain siloxanes in the cyclic structure. HMDS, the initiator molecule, is converted to siloxanes. As is visible, regular geometric structures vary from HMDS [18] molecules. It is possible that the foliar structures present the linear form of siloxanes molecule [14] and the cyclic form of siloxane molecule, as was shown in **Figure 5**.

Technologies	Pros	Cons	Resolution	Dimension
Soft lithography	Low cost High biocompatibility	Diffusion from the ink can lower the resolution	30 nm–100 nm	2D or 3D
Electrospinning	Suitable for tissue engineering More flexibility in material requirement	Low yield	3 nm–5 μ m	3D
Dip pen	Allow the creation of biocompatible nanosized patterns	Limited suitable materials Not suitable for curved surface High cost	30 nm	2D
Electron beam writing	High resolution	Limited suitable materials Not suitable for curved surface High cost	5 nm	2D

Table 1. Summary of the pros and cons of different nanotechnologies [24].

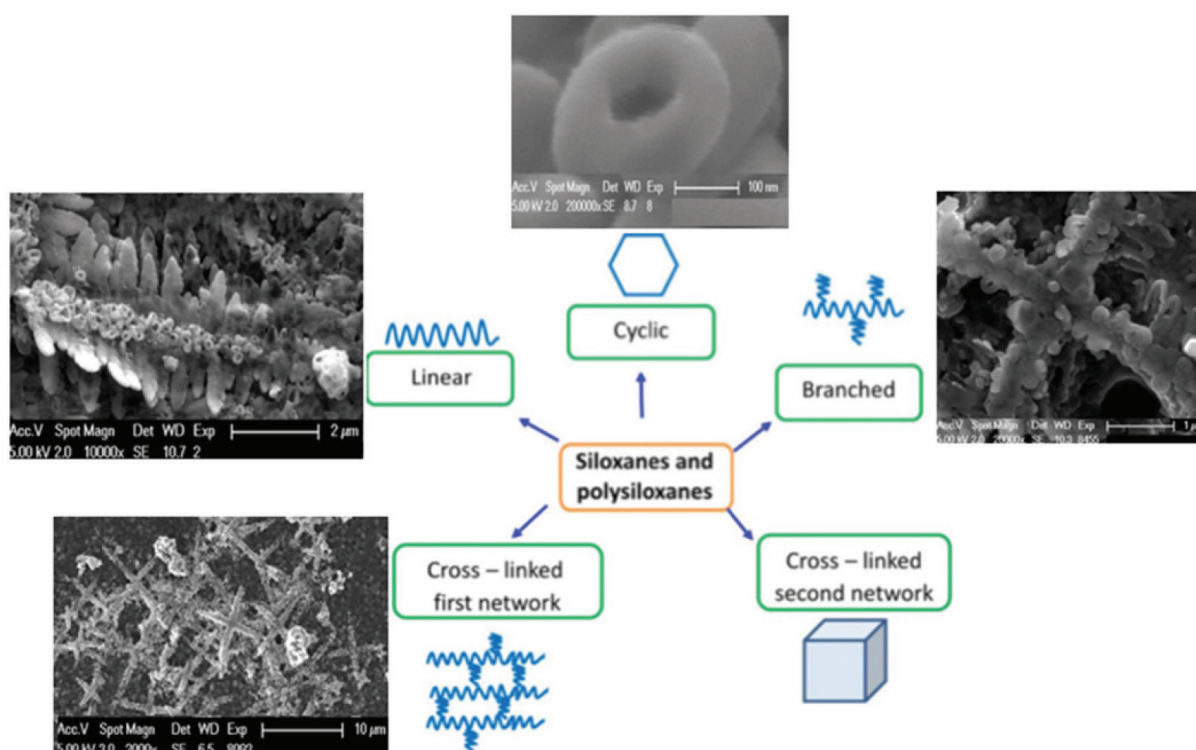


Figure 4. The characteristic and principal structures of siloxanes. The table was drawn inspired from Krystyna M [15].

When closely observing SEM images at the formation of circular structures, it can be seen how the molecule shifts from a linear (lamellar structure) to a circular form. The HMDSO is monitored from the linear structure to the circular structure that was shown in **Figure 6**.

Previous studies have reflected that siloxanes were prepared in many stages and were obtained by means of hydrolysis with excess water at temperatures ranging from 10 to 90°C. For example, continuous hydrolysis of dimethyldichlorosilane (Me_2SiCl_2) produced a mixture of cyclic and linear hydroxyl-terminated oligosiloxanes [15].

The chemical formula of all the circular structures and the electron microscopic image obtained were the groups of molecules that were shown in **Figure 7**.

It is possible to define the measurements of the molecules detected by electron microscopy. To calculate the diameter and volume of the structure, which is estimated to be the group of molecules in the circular form, as is shown in **Figure 8**. The Si—O bond length was 0.164 nm; there were approximately 253 Si—O bonds in the group of molecules.

Synthesis of siloxane elastomers occurs by cross-linking linear siloxane polymers. The process of cross-linking involves the conversion of linear polymers into spatial macromolecules, which are the result of the formation of cross-links, that is, bridges, between them. The poly addition of Si—H bonds to vinyl groups results in the formation of numerous hydrocarbon bridges linking polysiloxane chains. This was the type of cross-linking [15] that was shown in **Figure 9**.

These linear structures lead to the formation of flaccid-appearing structures at the same time. The siloxane chain has an unusually dynamic flexibility; additionally, it possesses a large

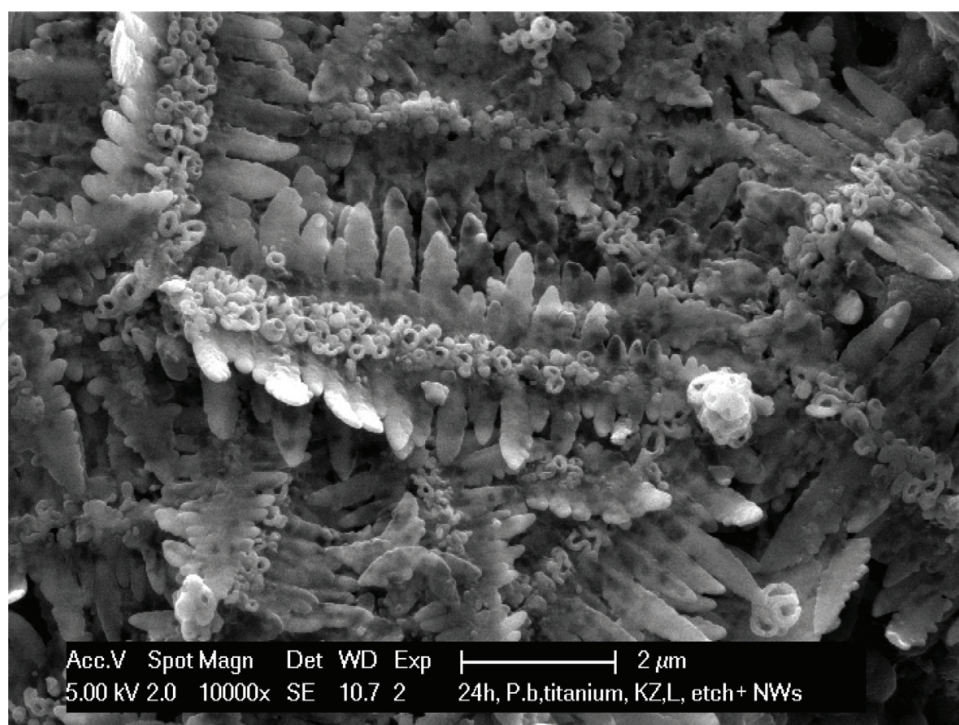


Figure 5. SEM image of different types of siloxanes structures.

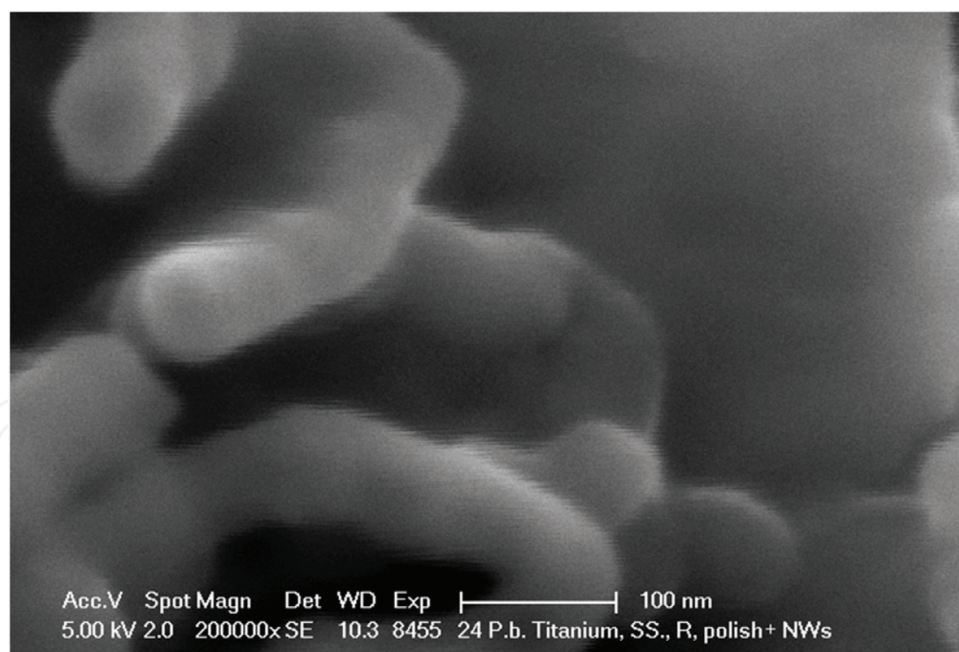


Figure 6. SEM images of HMDSO, from the linear structure to the circular structure. The form could be the groups of molecules that pack together to make these structures.

number of conformations. A conformation can be easily altered. This flexibility facilitates turning by chemical bonds [19]. The conformations may change slightly under stress, leading to the chain conformation adapting to the ambient conditions. Siloxane conformations have minimum free energy of the surface, with these properties possibly creating a thin, highly adherent layer on it (**Figure 10**).

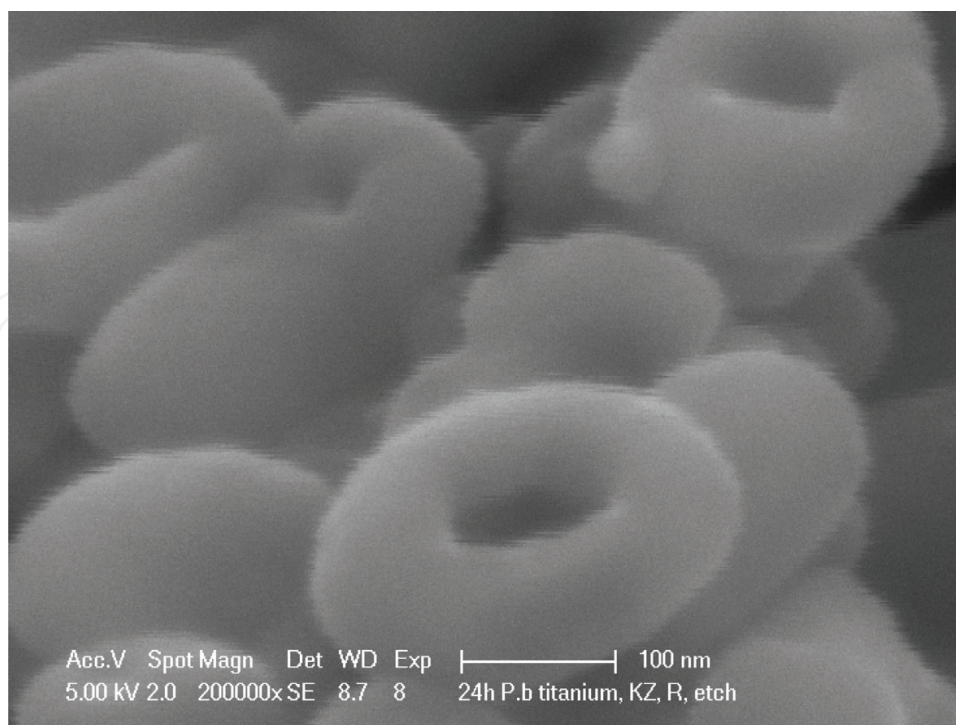


Figure 7. SEM images of the groups of molecules pack together to make these structures.

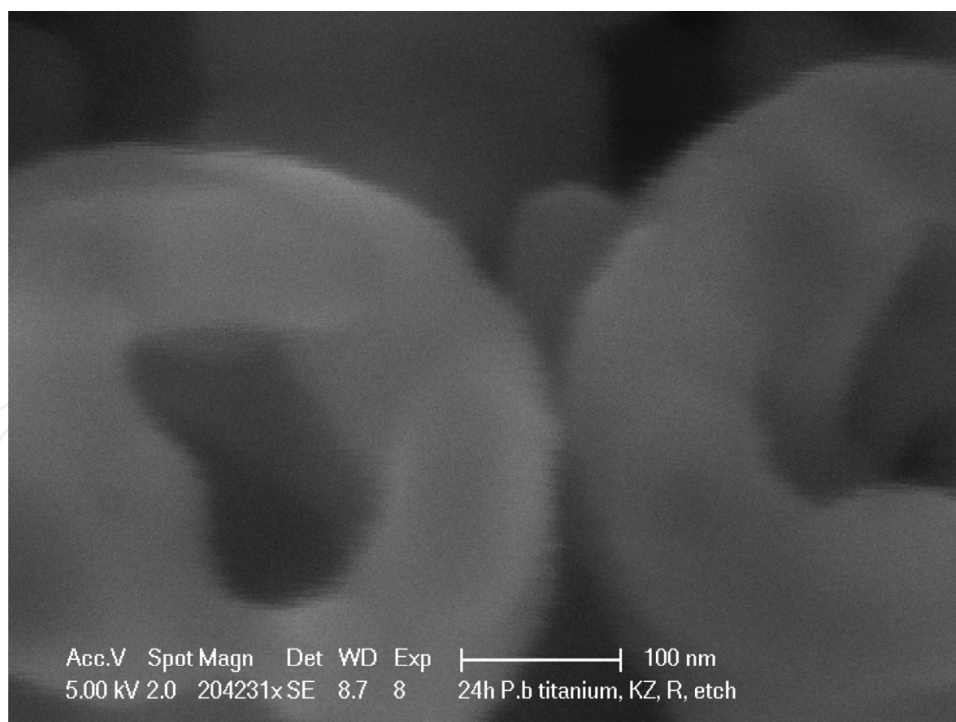


Figure 8. High magnification of SEM images of the groups of molecules packed together to make these structures.

The reaction, beginning with the hydrolysis of the HMDS molecule at the start, is summarized in the reaction table. The transformation of the reaction chain into the HMDSO molecule, of the step-by-step HMDS molecule, is followed by the formation of other siloxane structures from the HMDSO molecule [20]. It is understood that the polymeric structure

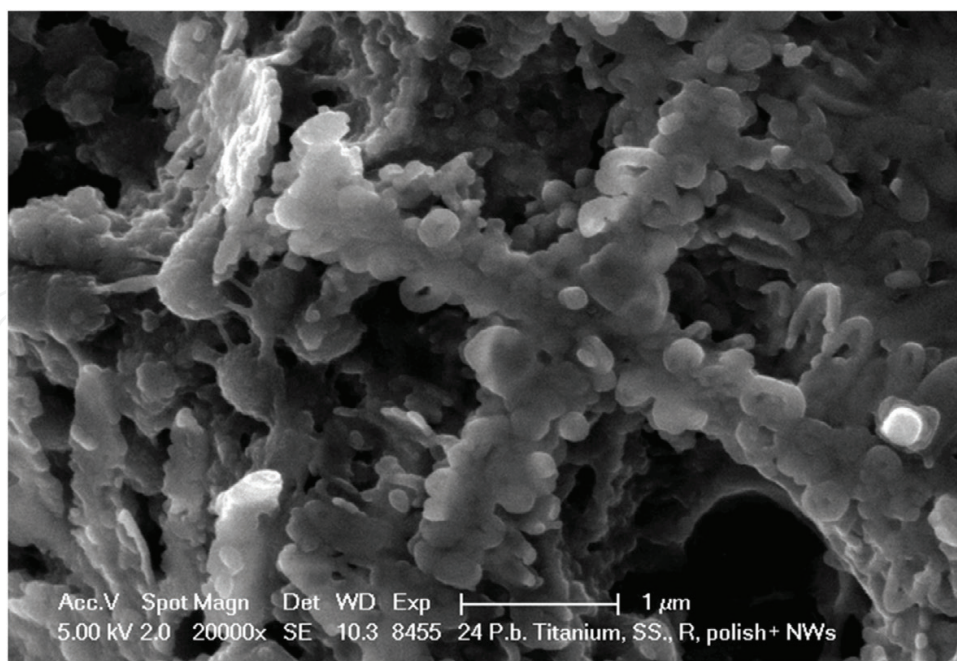


Figure 9. SEM images of the cross-linked linear siloxane polymers.

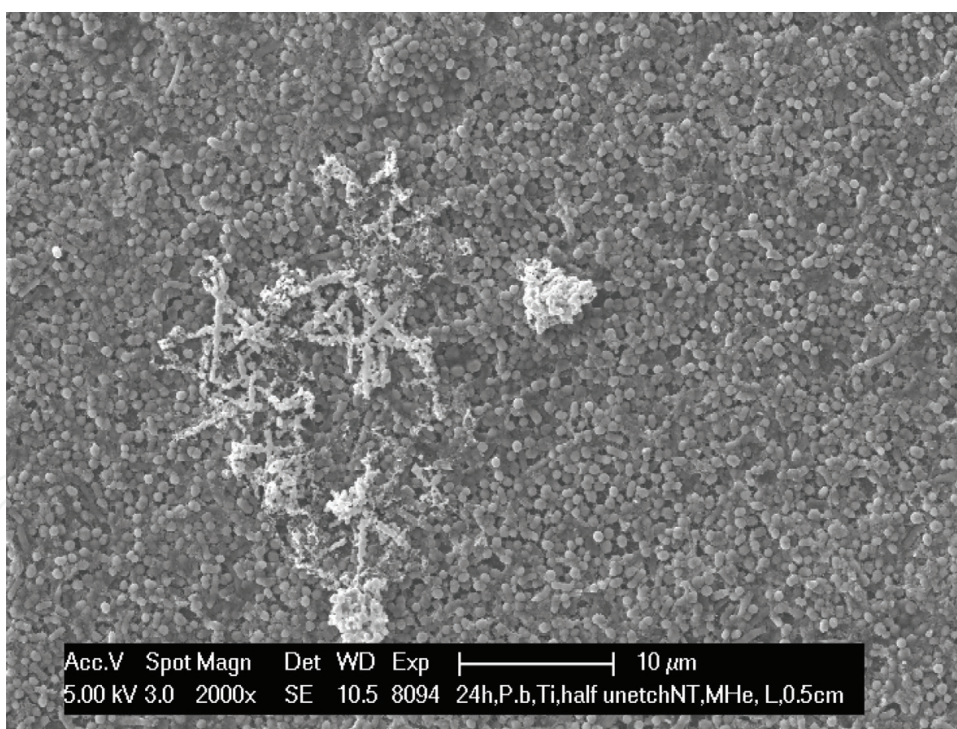


Figure 10. SEM image of adherent properties of siloxanes on biofilm surface.

has a lamellar appearance, polysiloxanes [21], and a circular structural form. In this work, the images obtained after the coincidence provided a visual display of a chemical reaction. Therefore, it is once again revealed that electron microscopy displays structures with a high magnification power of approximately 100 nm in size.

In this study, during examination of the biological structure on dental implants by electron microscopy, residues were noted on the surface. When considering what this compound may be, it is understood that the electron microscope is the HMDS used in the sample preparation stages and its related properties. Otherwise, the surface containing silicone is free of contaminants.

As a result of closely examining the structures, the states of the HMDS molecule used to provide the fixation on the surface were altered when hydrolysis occurred. It is understood, according to the information in the literature [22], that the molecule resulting from hydrolysis was the HMDSO molecule. Thus, imaging of HMDSO molecules was provided. There exists no similar information in prior studies.

The HMDSO molecule resulting from the hydrolysis of HMDS was observed in various photographs that had been converted to other siloxanes. The structures of the images were predicted from the chemical structure formulas belonging to the silicon structure. It is possible to calculate the number of Si—O bonds [23] in these molecular groups. This study reflected that the reactions of molecules entering the imaging boundaries of electron microscopy can be observed at various stages. Thus, chemical variations can also be visualized by electron microscopy, utilizing simulation studies.

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