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Hollow polysiloxane nanostructures based on pressure-induced film expansion

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Superhydrophobicity has gained extensive interest in academia and industry. One of the most facile ways of creating superhydrophobic surfaces is the surface-initiated synthesis of 1D polysiloxane nanostructures known as silicone nanofilaments. However, physicochemical details of their synthesis process remain a puzzle, and studies so far have fallen short in explaining the ways in which the 3D film growth transforms into 1D objects. From the observation of hollow cylindrical polysiloxane nanostructures, this study proposes a growth model based on pressure-induced uniaxial elongation of a partially cross-linked polysiloxane film. The pressure build-up is caused by gaseous by-products of hydrolysis and condensation reactions. The presented model aims to promote the understanding of the growth processes, and could thus facilitate the design of robust superhydrophobic coatings onto various surfaces. Furthermore, it is envisioned that novel applications utilizing the tubular nature of the nanostructures could emerge.

1. Introduction

Superhydrophobic surfaces comprise a class of materials characterized by extreme water repellency, a low roll-off angle and self-cleaning ability.^{1–5} These ultimate properties are achieved by combining roughness with a low-energy surface.^{1–3,6–9} The composite Cassie–Baxter wetting state¹⁰ is connected to superhydrophobicity through high contact angles and low roll-off angles. Industrial applications concerning superhydrophobicity are currently only slightly behind the academic state-of-the-art, which makes the field interesting from the point of view of basic research as well as applications, provided the structures are able to cope with both chemical and mechanical wear and tear.¹¹

An interesting approach using 1D nanostructures, denoted as silicone nanofilaments (SNFs), has shown excellent properties as well as resilience toward chemical and also mechanical wear.^{12,13} In addition, SNFs have been shown to retain the Cassie– Baxter wetting state even when subjected under pressure.⁹ In 2006–2007, three groups independently reported on the first successful synthesis of the 1D polysiloxane nanostructures^{14–16} and later more studies emerged to deepen the understanding of the process parameters,^{12,13,17–25} and recently, also larger tubular polysiloxane structures were introduced.²⁶

A few growth models for the SNFs have been proposed until this day.^{18–20,24,27,28} However, these models are challenged by our observation of hollow polysiloxane nanostructures. Gao and McCarthy²⁷ were the first to propose a growth mechanism for SNFs, which they synthesized in solution phase from a trimethylchlorosilane/tetrachlorosilane (TMCS/TCS) azeotrope. In their model, TCS molecules cross-linked and formed 3D structures, yet occasionally TMCS molecules terminated the growth. Finally, the lateral expansion was fully blocked and growth continued in one direction. Rollings and Veinot¹⁸ systematically expanded their original study¹⁶ using the atmospheric gas-phase process and introduced a growth model hypothesis. They reasoned

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that the hydrolyzed molecules could not bond to the surface with all three reactive sites, which left one or two hydroxyls available for cross-linking. In the growth phase, they stated that when two molecules cross-linked, they had to orient themselves so that there was adequate space for the unreactive sites. They further stated that due to the orientation, the remaining hydroxyl directed away from the substrate, which created a preferential direction for the growth. Khoo and Tseng¹⁹ synthesized SNFs in solution phase on glass and thermally grown SiO, using the solutionphase process. The study suggested a growth mechanism based on initial island growth followed by 'self-assembly' type of ordering due to the amphiphilic nature of hydrolyzed precursor molecules. Chen et al.20 used solution-phase synthesis and determined by differential thermal analysis that the end-product consisted of CH₃SiO_{1.12}(OH)_{0.76}, which indicated that *ca*. three quarters of the end-product polysiloxanes were not cross-linked. The study envisioned that a single CH₃SiO_{1.5} molecule bound with three CH₃SiO(OH) molecules to form secondary building units, which then in turn polymerized into linear structures. The linear structures formed further 1D aggregates.

This study presents the first experimental evidence that SNFs occasionally exhibit a hollow core. On the basis of this finding, the authors developed a physicochemical model for the growth process of hollow SNFs, which are denoted here as h-SNFs. The developed model especially aims to explain the phase during which the deposited film translates into the nanofilaments. The presented nanostructures are synthesized similarly to previously reported solid SNFs,¹²⁻²⁵ and under scanning electron microscope (SEM), they appear exactly similar, yet detailed transmission electron microscope (TEM) analysis reveals them to exhibit a hollow core. The h-SNFs also differ from the previously reported polysiloxane nanotubes²⁶ in that h-SNFs are topographically similar to solid SNFs, while the nanotubes exhibit a different morphology. Our model is based on (a) chemical condensation reactions occurring inside a partially cross-linked polysiloxane film, which release gaseous by-products, and (b) concomitant physical effects, which enable uniaxial elongation. It is conceivable that all SNFs grow through the proposed hollow-core process, but eventually collapse into a solid tube after loss of pressure in the gas-filled core. Finally, the study applies the model to describe the creation of distinct polysiloxane macrostructures, which demonstrates that its logic is scalable across length scales.

2. Experimental and simulations

h-SNF synthesis was carried out in an in-house built vacuum gas-phase reaction apparatus using a process similar to described previously.^{9,16,18,29} Deposition-grade methyltrichlorosilane (MTCS) was acquired from Sigma-Aldrich (St. Louis, MO, USA) and used as received. It was stored and used exclusively in a dry nitrogen atmosphere. Purified water was provided by a Millipore Milli-Q system (Millipore, Billerica, MA, USA). The synthesis

apparatus (a glass reaction vessel with lid, VWR International (Radnor, PA, USA), total volume *ca.* 5·7 liter) was connected to a combined vacuum/nitrogen gas line, which allowed evacuation and flushing. The vacuum was created with an Adixen Pascal 2010 C2 rotary vane pump (Pfeiffer Vacuum, Asslar, Germany), and the purity of the purging nitrogen exceeded 99.5%. An analog pressure gauge measured the vacuum level inside the reactor, and it was used to ensure that no leaks occurred during the synthesis process. Water and MTCS were introduced from separate lines, which were kept as short as possible. All tubings were composed of either PTFE or silicone, which were found to sufficiently resist the reactants and the by-products. Vacuum and nitrogen gas lines were stainless steel, and the vacuum level reached was on the order of 1 mbar.

Hundred-millimeter diameter silicon (100) test grade wafers (Universitywafer, South Boston, USA) were typically cut into four *ca.* 2000 mm² pieces. Substrates were ultrasonicated in an alkaline detergent (Deconex 11 Universal, Borer Chemie, Switzerland) for 15 min followed by copious rinsing with deionized water (18·2 $M\Omega cm^{-1}$, Milli-Q by Millipore, USA) and dried in a stream of nitrogen (purity 99·5%). Further activation was performed by oxygen plasma cleaning (Gatan Solarus Model 950, O₂/H₂ plasma, radiofrequency power of 60W) for 15 min to increase the surface hydroxyl coverage. This method for the cleaning was chosen because of its simplicity and non-hazardous nature.

Cleaned and activated substrates were promptly (within a few minutes) transferred into the reactor chamber, which was subsequently evacuated. The reactions were run at room temperature (ca. 20-23°C). After ca. 30 min of evacuation, the desired volume of deionized water (Milli-Q) was pipetted into a test tube connected to the reactor and the inlet valve was opened. To facilitate the evaporation of water, heating (with a hot air blower) was applied onto the test tube, and after all water had evaporated, the inlet valve was closed. The reactor was let to equilibrate typically for 15 min before proceeding. Operating in a nitrogen glove box, MTCS (deposition grade, Sigma-Aldrich) was sealed into a PTFE container with a valve and then transferred and connected to the reactor. Opening the inlet valve allowed the MTCS to readily evaporate and migrate into the reactor. The inlet valve was left open until the end of the reaction process. At the end of the reaction, nitrogen gas was streamed through the reactor for ca. 30 min to remove all by-products and potential unreacted chemicals.

Scanning electron microscopy was performed on Zeiss Sigma VP (Carl Zeiss Microscopy Ltd, Cambridge, UK) and JEOL JSM-7500FA SEMs (JEOL Ltd, Tokyo, Japan). For high-resolution imaging, a thin layer of gold/palladium was sputtered onto the surface (Emitech K100X). An FEI Tecnai 12 Bio Twin TEM (Hillsboro, OR, USA) was used for imaging the cores of the filaments. Operating voltage was 120 kV, and imaging was

performed under slight underfocus to increase phase contrast and to minimize imaging artifacts. A single-use razor blade was used to cleave the h-SNFs from a silicon surface. Thereafter, a small amount of ethanol was used to disperse the filaments and to deposit them directly on carbon film support grids. Ion-milled cross-section samples were prepared by gluing sample wafers into a stack with epoxy; ultrasonic-cutting a *ca.* 3-mm diameter cylinder from the stack; cutting the stack into *ca.* 100-µm slices using a diamond blade; prethinning using SiC wet abrasion paper; thinning and polishing using a dimple grinder (Gatan, Pleasanton, CA, USA) and finally ion milling (Gatan PIPS) in cryoconditions until sufficiently thin.

Finite-element method simulations were performed with the Elmer software.³⁰ A 2D profile of a thick-walled cylinder with a spherical cap in both ends was used to define the geometry, and the simulation was performed with an axisymmetric coordinate system, to effectively simulate a solid of revolution. A linear elastic model was used. The ratio between outer and inner radii was $r_o/r_i = 3$, and the length of the cylinder (without cap) was $h = 10r_i$. Normal stress on the inner boundary was set to a fixed value, and on the outer boundary, it was set to zero ($p_o = 0$). For reference, a thinner-walled cylinder was simulated with a larger r_i ; $r_o/r_i = 6/5$. Units in the simulation were arbitrary, because only the distribution of stresses was of interest, not absolute values.

3. Results and discussion

Gas-phase synthesis using MTCS and water onto hydroxylated surfaces has previously been reported to lead to solid SNFs. However, this study found out that synthesis under certain conditions lead to structures that exhibited hollow interiors. For clarity, these structures are denoted as h-SNFs to distinguish them from solid SNFs in this text. Transmission electron micrographs of the hollow structures are shown in Figure 1(a)-1(c). Two distinct preparation methods were used to rule out sample preparation artifacts from the micrographs. In the first method, samples were embedded in epoxy and ion milled. In the second method, the h-SNFs were mechanically cleaved from a silicon surface using a razor blade. With both methods, hollow structures were found from the micrographs. It is worth noting that the hollow structures could not always be observed and that several samples exhibited both solid and hollow structures, yet except for the interior, the appearance of both types of structures was similar. A cross-sectional profile over a single h-SNF reveals the hollow core most clearly and also shows that the diameter of the h-SNF is comparable to the diameter of SNFs. The diameter of the structures is only a fraction of the hollow polysiloxane structures reported previously,²⁶ wherein the structure diameters were in excess of 60 nm.

The control of surface-adsorbed water appears an important factor in the synthesis process. When water vapor is released into the reaction chamber, it adopts an equilibrium with the solid interfaces, resulting in a layer of adsorbed water even when the relative humidity is below 100%. Estimates from separate adsorption studies^{31–33} suggest that a few monolayers are adsorbed and the number of layers increases with relative humidity³² and with the hydrophilicity of the surface.³³ Yoshida *et al.*³¹ have estimated that two monolayers of surface-adsorbed water result in the highest silylation coverage using vinyltrimethoxysilane. In conclusion, water is expected to adsorb onto the surface in the amount of a few monolayers while the majority of the water resides in the vapor phase.

The reaction precursor molecules (MTCS) can hydrolyze in the presence of water to form methyltriolsilane (h-MTCS) species through the reaction $H_3CSiCl_3 + 3H_2O \rightarrow H_3CSi(OH)_3 + 3HCl.$ Thus, the reaction consumes water and releases hydrochloric acid. In the reactor, the precursor molecules are primarily in the gaseous form due to their vapor pressure. The MTCS molecules can migrate onto the surface water layer on the substrate and hydrolyze to form a continuous organosilane film, as seen in Figure 2(a), where the reactor conditions have been such that no h-SNFs have formed. Once such a film has formed, the unreacted Si-Cl bonds continue to hydrolyze, and the hydrolyzed species start to cross-link to form oxygen bridges between the organosilanes, $2H_3CSiR_{\mu}(OH)_{3-\mu} \rightarrow$ $H_3CSiR_n(OH)_{2_n} - O - (OH)_{2_n} R_nSiCH_3 + H_2O$. Both the hydrolysis and condensation reactions release gaseous by-products. Individual gas molecules can become dissolved into the matrix; yet, the unfavorable interaction between the surrounding film and the gas molecules can be reduced by the formation of gas-filled cavities inside the film. SEM micrographs from the initial stage of growth (see Figure 2(b)) exhibit roughness features whose generation can be explained by the formation of the gas-filled cavities. Such cavities inside the film are also seen in the cross-section TEM micrographs (see Figure 1(b)). Figure 2 also shows that the h-SNFs originate from these roughness features, which further supports that they act as 'seeds' for the growth.

3.1 Uniaxial elongation of the cavities

In the following, this study presents a model, which allows uniaxial elongation of cylindrical structures instead of anisotropic growth, such as formation of a film or spherical structures, which would be otherwise expected. First, assume a gas-filled cavity inside a film and, for simplicity, require that it exhibits a cylindrical shape. Then note that pressure is generated inside the cavity is due to chemical processes, which release gaseous by-products, such as hydrochloric acid and water. Next, a mechanical model is defined for the newly formed material, which undergoes a transition from a weakly crosslinked plastic state to a highly cross-linked elastic film. Furthermore, most of the deposition of new material is expected to occur to the dangling hydroxyl groups, which reduce in number as the film crosslinks. Finally, a stable axial growth mode is made possible.

The reasoning begins by considering the stresses inside a cylinder cavity with height *H*, inner radius r_0 , outer radius r_0 , inner pressure



Figure 1. (a, b) Cross-sectional transmission electron micrographs of the h-SNFs: (a) Color added for emphasis. The cross-sectional cut of the sample shows the silicon substrate (blue), the h-SNFs (yellow) and the embedding epoxy (red). The thickness of the h-SNF layer is a few hundred nanometers. There is a layer covering all of the substrate and the nanostructures have grown from the layer; (b) a higher magnification shows a lighter interior in all of the h-SNFs indicating a hollow structure. Also, some voids can be observed in the layer







beneath the structures (marked with an arrow). An inset taken from the micrograph and a grayscale analysis indicates a h-SNF diameter of 20-5 nm and a hollow interior; (c) h-SNFs cleaved from silicon surface exhibiting hollow cores; (d, e) representative SEM micrographs from h-SNFs synthesized onto silicon substrate; (f) an SNF structure, which exhibits a 'pearl-necklace'-type section (marked with arrow). h-SNFs, hollow silicone nanofilaments; SEM, scanning electron microscope; SNFs, silicone nanofilaments

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Figure 2. Formation of pregrowth film and SEM micrographs from syntheses resulting in different morphologies due to varying reaction conditions: (a) Gaseous reactants interact with the surface water layer on the substrate to form a film as seen on the SEM micrograph; (b) gaseous reaction by-products from hydrolysis and condensation reactions migrate preferentially into defects to form cavities. These correspond with the protrusions on the micrograph; (c) the cavity

enlarges as more gas is generated. At the same time, the film crosslinks and forms a more elastic structure; (d) long cylindrical structures form due to pressure build-up as explained in the text. Cross-linking proceeds upwards from the surface. Note that only the tip of the structure is expected to exhibit reduced amount of cross-linking, and therefore, the tip undergoes elongation by plastic deformation. SEM, scanning electron microscope



Figure 3. A thick-walled cylinder with a spherical cap. Inner and outer radii are indicated, as well as inner and outer pressure and axial and tangential stress components

 p_i and outside pressure p_o (see Figure 3). First, we present equations governing the tangential and axial stresses, σ_0 and σ_z , inside the cylinder wall. The latter can be derived from a simple force-balance consideration, yet the former needs a more complicated formulation. A derivation for the stresses in a thick-walled cylindrical pressure vessel is found in numerous text books, and assuming an isotropic, fully elastic material, which obeys Hooke's law, leads to the wellknown Lamé equations³⁴:

1.
$$\sigma_{\rm r} = \alpha - \frac{\beta}{r^2}$$

2.
$$\sigma_{\theta} = \alpha + \frac{\beta}{r^2}$$

The radial stress at the inside wall matches the inner pressure, and equivalently, on the outside wall, it matches the outside pressure. These boundary conditions give the values for α and β .

3.
$$\sigma_{r}[r]|_{r=r_{i}} = \alpha - \frac{\beta}{r_{i}^{2}} = -p_{i}$$
4.
$$\sigma_{r}[r]|_{r=r_{o}} = \alpha - \frac{\beta}{r_{o}^{2}} = -p_{o}$$

which yields the following equations for the tangential stress:

5.
$$\sigma_{\theta}[r] = \frac{p_{i}r_{i}^{2}}{r_{o}^{2} - r_{i}^{2}} \left[1 + \frac{r_{o}^{2}}{r^{2}}\right] - \frac{p_{o}r_{o}^{2}}{r_{o}^{2} - r_{i}^{2}} \left[1 + \frac{r_{i}^{2}}{r^{2}}\right]$$

To compare the different stresses, the equation can be simplified by assuming that outside pressure is negligibly small, $p_0 \approx 0$, which eliminates the second term. Therefore, the highest stress lies on the inner wall, $r = r_i$ and equals to

6.
$$\sigma_{\theta}^{\max} = \frac{p_{i}r_{i}^{2}}{r_{o}^{2} - r_{i}^{2}} \left[1 + \frac{r_{o}^{2}}{r_{i}^{2}}\right]$$

where, the term r_o^2/r_i^2 is always greater than unity and increases with increasing wall thickness.

The axial stress is derived by considering the situation depicted in Figure 3. A force $F_z = p_i \pi r_i^2 - p_o \pi r_o^2$ due to inner and outer pressures acts on the cross-section of the walls, which have an area of $A = \pi \left[r_o^2 - r_i^2 \right]$. Again, assume that the outside pressure is negligible and write:

7.
$$\sigma_{z} = \frac{p_{i}r_{i}^{2}}{r_{o}^{2} - r_{i}^{2}}$$

which is always less than half of the maximum tangential stress.

Unfortunately, the stresses in the tip of the hollow filament cannot be derived analytically in a straightforward way. To obtain the complete linear elastic solution, finite-element method simulations were carried out. Figure 4(a) shows the simulated von Mises stress distribution in the filament cross-section. Von Mises stress, σ_v , is used to quantify stress intensity, because it is a scalar quantity that is commonly used in yield criteria.

8.
$$\sigma_{v}^{2} = \frac{1}{2} \begin{bmatrix} \left\{ \sigma_{rr} - \sigma_{\theta\theta} \right\}^{2} + \left\{ \sigma_{\theta\theta} - \sigma_{zz} \right\}^{2} + \left\{ \sigma_{rr} - \sigma_{zz} \right\}^{2} \\ + 6 \left\{ \sigma_{r\theta} + \sigma_{\theta z} + \sigma_{rz} \right\} \end{bmatrix}$$

Figure 4(c) shows that the stress on the inner surface is relatively uniform, with only slightly lower values inside the spherical cap. For comparison, a simulation was performed also with a much thinner-walled geometry (Figure 4(b)), and the results show that thin walls cause the stresses to concentrate on the inside of the cylinder walls much more. This highlights that thick walls are more favorable for axial growth than thin walls (where yielding of cylinder side walls would be expected to lead to radial growth), in agreement with experimental data where predominantly thickwalled h-SNFs are observed.

Now, consider a film of organosilane that has deposited onto a solid substrate. There are two primary chemical processes proceeding in the film. First, the organosilane hydrolyzes into a silanol form, which releases hydrochloric acid (gas) into the film. Second, the silanols cross-link to form a network of polysiloxane, which in turn releases water (gas). These reaction by-products are expected to migrate into the cavities inside the



Figure 4. Von Mises stress distribution in h-SNFs, calculated with a linear elastic finite-element model: (a) The distribution of von Mises stresses in the cross-section of a h-SNF; (b) a h-SNF with much thinner walls for reference. The stress distribution is significantly different with more stress in the cylinder walls; (c) the von Mises stress along the inner

boundary of h-SNF (corresponding to the inner boundaries shown in (a) and (b) where stresses are concentrated). For a thick-walled filament, the von Mises stress does not vary significantly between the cylinder and the cap, in contrast to a thin-walled case where stresses in the cap are low. h-SNFs, hollow silicone nanofilaments

film, which then begin to expand as more gases are generated. At first, the film is mostly liquid-like and thus able to easily expand. However, as the number of cross-links increases, the pressure required to expand the cavity also increases. To model this system, this study considers a viscoelastic material exhibiting a yield stress, σ_y , which is a monotonically increasing function of the cross-links (see Figure 5(a)-5(b)). The fraction of cross-links is further a function of the time available to form cross-links. Therefore, the material at a certain height, H, has had less time to form cross-links than the material closer to the substrate. The yield stress is thus a function of the height along the cylinder axis. Furthermore, in the model the film deposition begins from the surface, yet continues primarily onto the top of the cylinder. The incoming MTCS molecules are expected to primarily bond with the dangling hydroxyls, which exist in the highest numbers where there is the least amount of cross-links, that is, near the cap of the cylinder.

The derivation presented earlier introduced the stresses that act on a thick cylindrical pressure vessel and noted that the highest one is the tangential stress. As the pressure inside the cylinder is constant throughout its height and the yield stress decreases with increasing height, the point where the structure is most likely to yield is located where the cylinder cap begins. As the cylinder wall yields, the inner volume increases, which reduces the pressure. If the pressure generation is extremely rapid (i.e. $dp/dt >> d\sigma_y(h)/dt$ in the deformation), a hollow spherical structure would be expected. In the other extreme, where the pressure generation is slow (i.e. $dp/dt << d\sigma_y(h)/dt$), the yield stress at height *h* increases faster than the stress caused by the inner pressure. Therefore, the yield height moves away from the surface. If the yield point moves fast, the whole structure could freeze until the pressure reaches such a value that the film ruptures. However, if the yield point movement speed is only slightly faster than the increase of pressure, a stable axial growth mode for elongated cylindrical structures would be made possible.

The presented growth model is argumented through a series of simple chemical and physical phenomena. None of the previously proposed models is able to describe the growth of hollow nanostructures and therefore do not apply to h-SNFs. Current model can also describe conditions where the growth of h-SNFs fails. It is often observed that when there is insufficient water, SNF structures do not form, yet a rough layer, such as seen in Figure 2(a), is evident.^{18,21} In this situation, the concentration of water is low, which limits the reaction rate of hydrolysis reactions. Therefore, cross-linking proceeds relatively faster in the film, which then becomes overly elastic to allow for pressure-induced elongation. The model also predicts that the number density of the h-SNFs is solely dependent on the number of cavities formed in the initial stage.

Our growth model leads to the formation of hollow nanostructures. However, the occurrence of solid SNFs can be explained by a collapse of the initially hollow cores as a result of loss of pressure, perhaps due to gas escaping though a rupture in the sidewall. Also, an increase in the ambient pressure after the growth has terminated might have a similar effect. The collapse



Figure 5. Strain behavior of expanding cylinders: (a) idealized stress–strain curves for idealized viscoelastic materials, which exhibit irreversible plastic yield at σ_{y} ; (b) the number of cross-links in the material is expected to increase the elasticity of the material, which causes the yield stress to increase; (c) a hollow cylinder, such as seen in the figure, forms from the substrate up, which indicates that the

could be further driven by a reduction in interfacial energy with decreasing diameter of the core. Yet, it is possible that no cavity is even required, if dissolved gases (or any other mechanism) give rise to sufficient internal stresses in the structure that could lead to the kind of yielding described on our model. The fact that hollow and solid SNFs have been found to coexist suggests that the proposed growth process could be used to explain both, as it would seem unlikely for them to have completely separate growth mechanisms. From a wettability point of view, the hollow and solid SNFs are equivalent, as wetting is a surface phenomenon that is not affected by the internal structure of the filament. Furthermore, the presented data were gathered from gas-phase synthesis, yet liquid-phase syntheses could analogously be described by taking into account hydrostatic pressure and slower diffusion in the denser medium. In fact, this study notes that a viable growth model for SNFs should be



material near the surface has had more time to cross-link; (d) the yield stress is a function of the height along the cylinder axis. A certain inner pressure, Δp , corresponds with a yield stress, σ_{y} , at a certain height, which leads to plastic yield occurring primarily near the tip of the structure

universal and not dependent on the chemistries of the precursor molecules. Our model does indeed satisfy the requirement in the sense, that the chemical reactions could be changed to similar gas-producing precursors without affecting the principles of the model.

On several occasions researchers have reported on SNFs, which exhibit 'pearl-necklace'-type morphologies.^{19,21} These morphologies are typically observed at highly concentrated conditions. One could apply our model to explain their formation by noting that at concentrated conditions the reactions are expected to occur faster due to increased probability of interaction between the moieties. Therefore, the chemical reactions would be faster, which could lead to situation where $dp/dt \gg d\sigma_y(h)/dt$ indicating rapid isotropic expansion near the tip of the structure. These processes could follow each other in a manner in which



Figure 6. Growth of polysiloxane macrostructures: (a) Drops of MTCS are submerged into a bath of water; (b) a solid polymerized shell forms around the drop; (c) pressure inside the drop increases due to creation of gaseous reaction by-products and finally the shell bursts. A new shell is rapidly formed around the expunged MTCS; (d)

spherical structures are subsequently formed and then crosslinked. Figure 1(f) displays a structure that appears to exhibit a solid SNF structure, yet at a certain point it transforms into a 'pearl-necklace'-type structure. Furthermore, the highest contact angles reported from SNF structures are from those synthesized in a solution.^{15,25} First of all, the reactants are expected to exhibit a slower mobility due to the higher viscosity of the matrix medium, which limits the reactivity at the surface. Second, the outside pressure is considerably higher due to both atmospheric pressure and hydrostatic pressures. Therefore, a higher inner pressure is required to reach the stresses needed for yielding behavior, which could lead to a more controlled formation of the structures, since the reactions are slower.

3.2 Polysiloxane macrostructures

Finally, the model is applied to describe the formation of a polysiloxane structure at macroscale. When MTCS is pipetted drop-wise into a bath of distilled water, a structure, denoted here as polysiloxane macrostructures, emerges (see Figure 6 and Supplementary Video (http://youtu.be/1thVYIfwe4E)). As a drop of MTCS is submerged into water, the molecules at the surface go through rapid hydrolysis and cross-linking processes, leading to a polymerized shell around the drop, which becomes cloudy in appearance. The drop submerges to the bottom of the container, and after a few seconds, it bursts from the top releasing liquid MTCS into water. The released MTCS again polymerizes, and the process is repeated until the reactants are consumed. It is notable, that this process actually leads to hollow elongated shells, which exhibit a surprisingly similar morphology to h-SNFs albeit on a different length scale. In the process, the

sequential bursts result in linear growth of the shells; (e) snapshots from a video of the process show that the resulting structures exhibit a striking resemblance to h-SNFs and SNFs. h-SNFs, hollow silicone nanofilaments; MTCS, methyltrichlorosilane; SNFs, silicone nanofilaments

pressure inside the polymerized shell increases due to generation of gases in the chemical reactions (seen as formation of bubbles inside the structure), which then in turn causes a rupture of the film at the top of the sphere. The second rupture occurs again at the topmost sphere, since it is the one that has had the least time to cross-link. If the polymerized shell was able to withstand the pressure inside, there would be no rupture and no formation of the structures. This study foresees that similar processes are dominant in both the generation of polysiloxane macrostructures and h-SNFs.

4. Conclusions

This study demonstrated that SNFs, which have previously been exclusively considered as nanofibers with a uniform solid core, were observed to occasionally exhibit a hollow interior, and they could be described as close-capped nanotubes, which are denoted as h-SNFs. A growth model was developed, which proposes that the growth of the h-SNFs occurs as a local film deformation process, where pressure pockets are formed into a partially cross-linked polysiloxane film due to released gaseous by-products of the hydrolysis and condensation reactions of the organosilanes. The proposed mechanism described in this study advances the understanding of the synthesis process and could finally lead to improved protocols for the creation of superhydrophobic surfaces. The observed hollow core of the h-SNFs could even allow new functionalities for the h-SNFs. The application of the model to describe a formation process of macroscopic structures demonstrates that the model is valid across multiple length scales.

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