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# Non-stick properties for dental restorative instruments by thin film coatings

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## Non-stick coatings for restorative instruments

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3

#### 4 **Abstract**

5 The non-stick properties of thin film coatings on dental restorative instruments were  
6 investigated by static contact angle measurement using dental filler resin as well as by  
7 scanning electron microscopy of amount of sticking dental restorative material. Furthermore,  
8 using a customized dipping measurement setup, non-stick properties were evaluated by  
9 measuring force-by-time when instrument was pulled out of restorative material. Minor  
10 improvements in non-stick properties were obtained with commercial Diamond-Like Carbon  
11 and commercial Polytetrafluoroethylene-based coatings. Major improvements were obtained  
12 with an in-house fabricated superhydrophobic coating prepared by multistep process  
13 consisting of surface microstructuring by etching in HF:H<sub>2</sub>O<sub>2</sub>, 7 nm Atomic Layer Deposition  
14 coating of aluminium oxide and titanium oxide, and a self-assembled monolayer of  
15 fluorinated organosilicon. Superhydrophobic coatings provide a possible future solution to  
16 prevent unwanted sticking of composite restorative material to dental instruments.

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18 **Keywords:** adhesion; non-stick; restorative composite material; thin film coating; superhydrophobic

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Filling materials used in dental restorative treatment should adhere well to human tooth substance to minimize complications of the treatment (1, 2). A large number of academics as well as commercial companies have focused their interest – and product development work – on designing dental restorative materials with two apparently opposite objectives. In dental restorations produced using the direct technique, the ideal dental filling material has a low viscosity. Such materials flow readily into all areas desired, providing maximal contact area of restorative material to the tooth surface for optimal adherence. At the same time, the material should stay put for the dentist to be able to shape details of surface contours of the restoration to mimic the original contours of the tooth. This serves the purpose of re-establishing the function and occlusal balance of the dentition, and the recreation of an acceptable aesthetic appearance of the tooth.

A large amount of research has focused on maximizing the adhesion of dental restorative materials to tooth substance, on investigating the long-term durability of the fillings, and on comparing different filling material in these respects (1-6). Much less effort has been devoted to investigation of the adhesion of dental restorative material to the instruments used when filling the cavity and modelling the surface contours of the filling. Reported major cause of eventual failure of dental composite fillings is void formation in material processing during treatment (7). Indeed, sticking of restorative material to instruments used in clinical work can compromise the adaptation of the material to the tooth substance prior to polymerization. The approaches taken to alleviate this problem include, among others, adjustment of the adhesive resin chemistry (4, 8), use of multi-step adhesives (9, 10), protease inhibitors (8, 11) and collagen cross-linkers (8, 12), with some products already available on the market.

One possible solution to prevent the sticking of the restorative material to instruments upon pull-out from the cavity is the use of non-stick coatings. Low surface-energy coatings have been researched and are available for a wide variety of applications ranging from consumer

products to microelectronics (13-20). Among the available coatings, polytetrafluoroethylene (PTFE) based coatings are common in consumer products such as cooking utensils (14), though their mediocre wear resistance limits their use. Doped Diamond Like Carbon (DLC) thin film coatings (19, 21) have attracted recent attention, and are commercially available. Recent research has shown it possible to obtain superhydrophobicity by structuring of the surface alone (22-26). In order to obtain repellence not only to water, but also to non-polar liquids, adoption of fluorinated and perfluorinated materials has become well-established (27), and various fluorination processes are generally incorporated in the fabrication of superomniphobic surfaces (28-31).

Despite the extensive research on and even wide scale adoption of fluorinated low surface-energy non-stick coatings, they have not been previously explored for reducing sticking of restorative materials to steel dental instruments. This study investigates commercial non-stick coatings and an in-house fabricated non-stick thin film coating for reducing the sticking of restorative material to restorative instruments.

## **Materials and methods**

### **Materials used**

Dental instrument blades and disks made from martensitic stainless steel commonly used in dental instruments were used as substrates. Both sample types were manufactured by LM-Instruments, Parainen, Finland. Apart from shafts being manufactured straight, the instruments were otherwise identical to those used in actual clinical dental restorative procedures. The width of the cylinder-like tip was 2.5 mm, with the calotte at the tip of the cylinder having a radius of 1.5 mm. The length of the instrument blade was 49.0 mm and the surface roughness value of the tool ( $R_a$ ) approximately 400 nm. Steel disks had a diameter of

10.0 mm and thickness of 5.0 mm. Their surface roughness was 50 nm root-mean-square (RMS).

The instruments and disks were coated with three different types of coatings: i) a commercially available BALINIT C DLC (Me-C:H – metal doped amorphous hydrogenated) non-stick thin film coating deposited by Physical Vapor Deposition (PVD), purchased from Oerlikon Balzers (Halmstad, Sweden); ii) a commercial PTFE-based coating with reinforcing materials, purchased from Alu-Releco (Riihimäki, Finland), and iii) a superhydrophobic surface subjected to microstructuring by etching, followed by 7 nm Atomic Layer Deposition (ALD) of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, and a self-assembled monolayer (SAM) of fluorinated organosilicon. This in-house fabricated thin film coating is hereafter referred as “the superhydrophobic coating”.

The total number of available non-coated samples and samples with commercial coating was 10 disks and 20 instruments – three samples were chosen for each measurement set randomly from the samples available. The total number of samples with the superhydrophobic coating was three disks and three instruments – all three samples were used in each measurement set. After each measurement set, the samples were ultrasonically cleaned first in acetone and then in ethanol for two min, followed by dry blowing with hot air.

For investigating the non-stick properties of these coatings, everX Posterior (GC, Tokyo, Japan) dental restorative material was used. EverX Posterior is a short fibre-reinforced resin composite designed especially for large cavities in posterior teeth. The details on composition and preparation process of the restorative material are described in GAROUSHI *et al.* (32). This material mimics the natural behaviour of dentine tooth substructure in terms of mechanics. In dental treatments, it is used when dentine structure is lost due to caries and needs to be replaced with composite material. Especially in high-stress areas in the tooth, this material has a better fracture toughness than other composite fillings (33). While possessing excellent

mechanical properties and good adhesion to tooth substance, this dental filling material has been found to adversely adhere to the instrument blade in clinical work. The material is applied into the tooth cavity preparation directly with instruments. If the material sticks unnecessarily to the instrument, there is a risk that it does not adapt precisely to the cavity walls, thus leaving unwanted voids (air bubbles).

### **Static contact angle measurements with dental filler resin**

Static contact angle measurements with dental filler resin were conducted using a KSV CAM 200 Tensiometer (KSV Instruments, Helsinki, Finland). Prior to the measurements, the coated steel disks ( $n = 3$ ) were ultrasonically cleaned first in acetone and then in ethanol for two min, followed by dry blowing with hot air. Droplets of approximately 10  $\mu$ l of everX resin without reinforcing glass fibres were carefully manually placed on the steel disks, and an automated camera was set to record the image of the droplet at 30 s intervals for a total time period of 10 min. Contact angle values for each sample were averaged from the contact angles measured during the last five minutes of the measurement session. Standard deviation was used as a measurement error.

The durability of all the samples was evaluated by autoclaving durability testing, where three of each sample type went through 30 autoclaving cycles in STATIM 2000S N-type autoclave (SciCan, Toronto, ON, Canada) – one autoclaving cycle consisted of 3.5 min in 134 °C temperature at a pressure of 2 bar. The contact angle measurements were repeated on these samples.

In addition, the effect of wear and surface contamination (residues filling the surface structures) on the phobicity of the superhydrophobic coating was evaluated by the following procedure: i) three disks were worn by cotton fabric Webril handi-pads (Fiberweb, CITY, STATE, USA), using High Temperature AntonPaar THT Tribometer (AntonPaar, CITY,

Austria) on ball-on-disc configuration. The cotton fabric was positioned on top of 6 mm diameter AIS 316 steel counterface balls. Each sample was worn with 10 N load, 0.05 m/s linear speed, for a total of 100 wear cycles, in a controlled environmental conditions of room temperature 23 °C and humidity of 50 %, ii) approximately 10 µl of everX resin without reinforcing glass fibres were deposited on the disks, and were left exposed to sunlight for 5 d, and iii) the disks were cleaned with 2 h ultrasonication in heated (40 °C) acetone, followed by 2 min ultrasonication in ethanol, then followed by rinsing with distilled water, and finally by dry-blowing with nitrogen. The contact angle measurements were repeated on the three disks after these procedures.

The described procedure was repeated for commercial coated and non-coated steel disks to confirm there was no unexpected change in their performance. Only one disk per sample type was used for these confirmation tests.

### **Customized dipping measurement**

In order to better simulate tooth cavity preparation during dental restorative treatment, a customized dipping measurement was developed to evaluate the unwanted sticking of dental restorative material to the dental instruments when the tool is pulled out of restorative material. The setup utilized controlled translation stage movement and force transducer measurements, with a setup similar to what has been demonstrated for characterization of frictional behaviour of biomimetic structures (34, 35).

Fig. 1 shows a photograph of the setup. A linear translation stage is mounted on a metal frame, and the force transducer is mounted on the translation stage. An aluminium adapter is used to connect the dental instrument blade to the actuator rod of the force transducer. The motorized translation stage is used to repeatedly dip the instrument into an aluminium cup filled with restorative material, and thereafter to pull it out. The movement of the stage is

controlled by stage motor driver and the force transducer signal is amplified by strain gauge amplifier before it is processed by a data acquisition (DAQ) device. The voltage signal obtained by DAQ device is plotted, processed and saved using LabVIEW 2013 software (National Instruments, Austin, TX, USA), while the movement sequence of the translation stage is controlled by Thorlabs APT User –software (Thorlabs, Newton, NJ, USA).

The metal frame, the adapter for instrument blade placement and the cup containing restorative material were manufactured in Aalto University workshop. Other components in the setup are commercially available scientific instruments. The test setup was positioned in a room illuminated only with red photography lamp to avoid polymerization of the restorative material.

Before the test series, the voltage-to-force conversion ratio of the force transducer was calibrated with three measurement points using different masses hanged from the actuator rod. Fresh restorative material was dispensed into the aluminium cup, and the zero level of the material in the cup was estimated by manual stage movement with 0.1 mm steps, using the force transducer signal to confirm contact into restorative material. Before the main measurements, three dummy test dip sets were done to minimize the effect of the restorative material thixotropy.

Before the measurements, all the samples were ultrasonically cleaned with two min in acetone and then in ethanol, followed by dry blowing with hot air. The measurements were conducted on two different days, with fresh restorative material used for both measurement sets. Three of each instrument type were used on both measurements. For commercial coated and non-coated instruments, the total amount of used samples was six. Only three samples with the superhydrophobic coating with the specific parameters used in this investigation were fabricated – these samples were used on both measurement sets. The instrument blade was dipped 1.0 mm into the restorative material, held inside the restorative material for 1.0 s,

and pulled out with a speed of 1.0 mm/s and an acceleration of 2.0 mm/s<sup>2</sup>. The instrument was pulled approximately five mm above the surface. This dip procedure was repeated five times for every instrument.

An example of the voltage-time data obtained by a single dipping is shown in Fig. 2. Approximately at 13 s, the instrument blade hits the surface of the restorative material. A force resists the movement, resulting in a voltage valley at approximately 15 s. After 1 s delay time in the restorative material, the pull-out of the blade is started. Adhesion between the instrument surface and the restorative material resists this movement, and keeps increasing until the adhesion between the instrument surface and the restorative material breaks, resulting in a voltage peak at approximately 17 s.

To evaluate the non-stick properties of the thin film coatings, three evaluation parameters were adopted: *pull-out force*, *follow-up distance* and *sticking area*. *Pull-out force* was calculated from the voltage peak value using voltage-to-force conversion ratio obtained in calibration. *Follow-up distance* was calculated from the time between voltage peak and voltage valley, using the known and controlled dipping depth, pull-out speed, delay time and acceleration. Sticking area was determined with a different test series. This testing procedure was otherwise identical to that used for determination of *pull-out force* and *follow-up distance*, except the dipping depth was increased to 1.5 mm, the number of dips was increased to ten in order to obtain a larger amount of sticking mass on the surfaces, and total number of measured samples was three per sample type instead of six. After the dipping procedure, the restorative material on the instrument was polymerized by FlashSoft dental curing light (CMS Dental, Copenhagen Denmark). These samples were SEM-imagined with Hitachi TM-1000 (Hitachi, Tokyo, Japan) using a magnification of 100 X. Backscattering imaging was used, as it allows a distinct contrast based on the atomic number (Z) of the atoms. The amount of sticking restorative material was evaluated by calculating the area fraction of adhered

restorative material to the total instrument area from a top view image. ImageJ (Version 1.51 h; US National Institutes of Health, Bethesda, MD, USA) image processing software was used to adjust the image contrast and calculate the area fraction. Standard deviation was used as measurement error in all the measurements.

To investigate the durability of the superhydrophobic coating in more detail, instrument blades with the superhydrophobic coating were autoclaved using the same procedure as with steel disks, and the dipping measurements were repeated with the autoclaved samples. A reference set of non-coated instrument blades ( $n = 3$ ) was run along this test series to confirm there was no unexpected variation.

In addition to the tests described, a video recording was used to demonstrate the superior performance of the superhydrophobic coating. This video material is available as supplementary information online (Video 1).

## **Fabrication of the superhydrophobic coating**

Chemical etching of samples was conducted at room temperature in a HF:H<sub>2</sub>O<sub>2</sub>(1:1) solution for 5 min followed by distilled water rinsing and drying. 5 nm Al<sub>2</sub>O<sub>3</sub> + 2 nm TiO<sub>2</sub> ALD thin film coating was deposited on etched steel using a Beneq TFS-500 reactor (Beneq, Espoo, Finland). For Al<sub>2</sub>O<sub>3</sub>, trimethylaluminum (TMA) was used as a metal precursor and water as a precursor for oxidation. Nitrogen was used as a carrier gas and to purge reaction gases from the reactor during each reaction half cycle. 250 ms precursor pulses and 1 s purge pulses (the same for both precursors) were used. The deposition temperature was 120 °C. A 2 nm layer of TiO<sub>2</sub> was deposited using the same ALD system, with TiCl<sub>4</sub> and water as the two precursors. For this, 250 ms precursor pulses and 250 ms purge pulses (the same for both precursors) were used. The deposition temperature was 300 °C. The pressure in the reactor was kept at about 4 Torr for both depositions. Finally, on top of the TiO<sub>2</sub>, an organosilicon

self-assembled monolayer (SAM) was deposited. This process used 1h-1h-2h-2h-perfluorodecyltrichlorosilane 97% from Sigma Aldrich (Helsinki, Finland) as a precursor in a mildly elevated temperature (65°C) in a sealed glass petri dish for 2 h.

The fabrication with the parameters reported here was done for three disks and three instruments. Additional samples were used at the start of the investigation to optimize the coating. Both these additional samples and samples used in the investigation were visually examined for corrosion after three months storage in ambient conditions.

Superhydrophobicity of the thin film coating was confirmed by advancing and receding water contact angle measurements and sliding angle measurements using a Biolin Scientific Theta optical goniometer (Biolin Scientific, Espoo, Finland). In addition, the water droplet sliding angles were measured with an in-house built tilting stage using a water droplet size of 10  $\mu$ l.

## **Results**

### **The superhydrophobic coating surface**

The water advancing contact angle was 168° and the receding contact angle was 156° for the superhydrophobic coating. The receding contact angle showed slip stick behaviour, indicating heterogeneity of the surface. The sliding angle of 10 $\mu$ l water droplets was 10.2°  $\pm$  8.6°.

Fig. 3 shows the structure of a steel disk surface after etching. The surface roughness (RMS) of the sample was 340  $\pm$  170 nm (mean  $\pm$  SD) after the organosilicon deposition. After the wear procedure, the surface roughness (RMS) was 310  $\pm$  250 nm (mean  $\pm$  SD).

### **Static contact angle measurements with dental filler resin**

Fig. 4 shows example photographs of static contact angles. In Fig. 4A, the restorative material resin droplet has spread out on a non-coated steel disk and the contact angle is approximately

42°. Fig 4B shows that using the superhydrophobic coating results in contact angles clearly above 90° – the surface is thus phobic towards the dental restorative resin.

The results of contact angle measurements are shown in Table 1. With commercial non-stick DLC thin film coating, the contact angles were actually less than with non-coated. A PTFE based coating increased the contact angles noticeably, from about 40° to about 70°. Subjecting these coatings to autoclaving reduced, however, the contact angles to 50°. With the superhydrophobic coating, the contact angles were clearly above 90°, even after autoclaving, as autoclaving reduced the contact angles from 128° to 113°.

After wear and surface contamination (residues filling surface structuring) procedure, the contact angles of the superhydrophobic coating (n = 3) were reduced to  $67^\circ \pm 5^\circ$  (mean  $\pm$  SD). The performance of DLC thin film coating, PTFE based coating, and non-coated remained unchanged (n = 1).

### **Customized dipping measurements**

Results from customized dipping measurements are shown in Table 2. The results correspond well with static contact angle measurements. DLC thin film coating gives no improvement on the measured non-stick properties, while minor improvement is obtained with PTFE based coating. The superhydrophobic coating results in major improvement, especially in reduction of *follow-up distances*, even after autoclaving.

The differences in follow-up distance are also clearly observed in video as supplementary information online (Video 1). Variation analysis of dip measurements and effect of dip depth is available as supplementary information online (Appendix 1).

### **Amount of sticking material**

Examples of SEM-images after the dipping procedure are shown in Fig. 5. For instruments with no coating (Fig. 5A), DLC thin film coating (Fig. 5B) or PTFE based coating (Fig. 5C), a noticeable area is covered by the dental restorative material. For the superhydrophobic coating (Figs. 5D, E), only a very minor area is covered. As the image contrast is based on relative atomic numbers of different materials, the restorative material appears as dark for non-coated (Fig. 5A) and the superhydrophobic coated (Figs. 5D,E) samples, but bright for DLC coated (Fig. 5B) and PTFE based coated (Fig. 5C) samples. The uneven surface structure in samples with the superhydrophobic coating is due to the microstructure obtained by etching, as shown more clearly in Fig. 3.

Results for the *sticking area* are shown in Table 3. A smaller amount of dental restorative material adhered on DLC coated than on PTFE based coated instruments, which is opposite to the contact angle results and dipping results. The variation for the DLC thin film coating was also noticeably smaller. The superhydrophobic coating performed vastly better than the other coatings – the difference was here even more prominent than with other evaluation methods. The amount of adhered material increased after 30 autoclaving cycles, with the covered area fraction increasing from less than two percent to about ten percent (Table 3).

## Discussion

Non-stick coatings offer a possible solution to prevent sticking of restorative material to dental instruments upon pull-out from the cavity. Although the commercial DLC thin film coating actually reduced the contact angles measured and showed no improvement of *pull-out force* and *follow-up distance*, it reduced the *sticking area* of restorative material. For the PTFE based commercial coating, the contact angles were noticeably increased, but for other evaluation parameters, the improvements were either minor (*follow-up distance*) or negligible (*pull-out force* and *sticking area*).

One possible explanation for the different results with DLC and PTFE based coating relates to the coefficient of friction (CoF) of the coatings. DLC coatings are known to allow for a very low CoF due to formation of an a-C:H (amorphous carbon hydrogenated) transfer layer (36). In investigations aiming to improve the anti-sticking behaviour of micro-moulds, it has been shown that reduction of both adhesion force and friction force by surface coatings have a major effect on the required demoulding energy (37). SAHA *et al.* (21) showed that doped DLC coatings dramatically improve the performance of silicon moulds.

The superhydrophobic coating yielded clearly superior performance by all measurement methods. In addition to providing the largest static contact angles, the coating reduced the *pull-out force* by about 45 %, the *follow-up distance* by about 60 %, and the amount of sticking restorative material by about 90 %. It is known that water droplets on top of superhydrophobic surfaces adopt the Cassie-Baxter state (38), which is a composite state where the liquid only contacts a small fraction of the solid surface and mostly sits on an airbed. This is due to the low surface energy coating and geometrically re-entrant surface features creating a capillary pressure that prevents the liquid from penetrating into the asperities of the surface (23). Since there can be no adhesion onto the air part of the composite surface, the overall adhesion of liquids on such surfaces is limited to the solid fraction. While the Cassie-Baxter model was originally developed to explain the lack of adhesion of simple liquids, the same mechanism also applies to complex liquids, such as dental restorative materials. The restorative material only contacts a small fraction of the superhydrophobic surface, and this smaller contact area leads to reduced adhesion, lower *pull-out forces*, smaller *follow-up distances* and reduced *sticking area*.

The steel surface on the superhydrophobic coating was shown to have a multilevel hierarchy, both on micron and submicron scale. LI *et al.* (39) investigated similar stainless steel and reported HF etching proceeding along the grain boundaries, and postulated that this

results in formation of iron and chromium fluorides, based on X-ray photoelectron spectroscopy measurements. Re-deposition of these fluorides was thought to result in multilevel structure both in micron and submicron scale. This postulate was based on previous research by GALVEZ *et al.* showing that precipitation of iron and chromium fluorides occurs in HF based etching used in steel pickling when the etch bath becomes supersaturated by metal fluoride (40). In the investigations by LI *et al.* it was reported that five-minute etching was sufficient for superhydrophobicity on AIS 304 stainless steel, with longer etch times only resulting in minor changes in contact angles (39).

The role of the 7 nm thick ALD coating for the performance of the superhydrophobic coating is twofold: i) it re-passivates the etched stainless-steel surface, as the etching steps removes the protective chromium oxide layer from surface, as reported by LI *et al.* (39), and ii) it sets surface chemistry to a state known suitable for SAM deposition. The bonding of the self-assembled organosilicon molecules is improved, as ALD TiO<sub>2</sub> has more available hydroxyl groups for the adsorption of silanes (41, 42). As the self-saturating surface reactions of ALD allow conformal and uniform deposition on 3D morphologies (43, 44), the chemical bonding can be expected to be solely between ALD and SAM organosilicon. The final superhydrophobic surface is CF<sub>3</sub> terminated surface chemistry on top of micro- and nanotopography shown in Fig. 3.

In this investigation, the superhydrophobicity obtained with hierarchical structuring was shown reasonably durable when exposed to autoclaving. While the contact angles were reduced from 128° to 113° and the amount of sticking restorative material was increased from two to ten percent area fraction, the *follow-up distances* were unaffected. The small reduction in performance is most probably due to the covalent bonding of the SAM molecules breaking due to the high temperature and pressurized steam employed in autoclaving. Steam autoclaving has been reported to have only a minor effect on hexadecyltrichlorosilane (45)

and perfluorodecyltrichlorosilane (31) SAMs. FLEITH *et al.* investigated CH<sub>3</sub>-terminated SAMs and reported a decrease of water contact angle from 107° to 102° by steam autoclaving at 121 °C for 2 h (45) – a total autoclaving time close to that applied in this investigation.

Routine handling of the same three samples with the superhydrophobic coating and repeating measurements on them was observed to have minor effect on the measured non-stick parameters. Surface wear by cotton fabric was also observed to have only minor effect on the surface structure of the superhydrophobic coating. Superhydrophobic surfaces, similar to those studied here, which combine microstructuring or nanostructuring of the surface with fluorination, have been shown for silicon (microelectronics) (24, 46), cast iron (47), steel (39, 48, 49) and various other metals (49, 50). Microstructuring for hierarchical roughness allows for mechanically more durable superphobic surfaces compared to those obtained by just adjusting surface chemistry (25, 26). It has been shown that hierarchically structured polydimethylsiloxane with an ALD TiO<sub>2</sub> coating retains its superhydrophobicity after abrasion, water jetting, UV exposure and annealing in 300 °C (51).

Surface contamination by particles and accumulation of impurities have been identified as a major challenge for structured superhydrophobic surfaces (25). Accumulation of restorative material resin residues was observed to be detrimental for the performance of the superhydrophobic coating in this work – the residues caused a larger reduction in contact angles than autoclaving. During the course of this investigation, the cleanability of the structured surface of the superhydrophobic coating was observed to be noticeably worse than with the commercial coatings. From clinical point of view, this imposes a strict requirement for proper and non-delayed cleaning of instruments after use. Nevertheless, it should be noted that even after wear procedure and surface contamination, the contact angles on the superhydrophobic coating were still higher than with commercial coatings. One possible measure to counteract this loss of performance could be self-cleaning of the surfaces by the

photocatalytic effect of TiO<sub>2</sub> to induce decomposition of contaminants (22, 51, 52). The photocatalytic effect is generally induced by UV light, but light in the visible spectrum range has also been reported sufficiently effective for practical applications (22).

The loss of corrosion resistance by HF etching due to removal of passivating chromium layer (39) is another concern for the performance of these kind of superhydrophobic coatings. Unlike LI *et al.* (39), who observed corrosion already at ambient conditions, we observed no corrosion even after autoclaving of the samples used in the main tests. However, after three months of storage in ambient conditions, some rust was noticed on the backside of steel disks with etch time of 15 min instead of 5 min that were used at the start of the investigation to optimize the coating process. The ALD coating on the back of the disk is thinner due to backside being in physical contact with the ALD chamber, reducing the amount of ALD precursor gases available. Based on our observations, we can conclude with reasonable certainty that the ALD coating re-passivates the surface, restoring the corrosion resistance. The use of ALD Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> for corrosion protection of steel has been reported in recent investigations (53).

Compared to many other structuring methods for superhydrophobicity found in the literature, wet etching is inexpensive, simple and easily adapted to different materials. The ALD layer repassivates the stainless-steel surface, and allows for a stronger and more durable bonding of SAMs; when compared to stainless steel, it has more available hydroxyl groups for the adsorption of silanes (41, 42). Self-assembled monolayers of fluorinated organosilicon allow phobicity towards non-polar liquids without affecting the submicron scale dimensions of the etched surface.

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## **Conflicts of Interest**

Toni Luoto is an employee of LM-Instruments (Parainen, Finland) and works in product development. All other authors certify that they have no potential proprietary, financial, or

other personal interest of any nature or kind in any product, service, or company that is present in this article.

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## Supporting Information

Additional Supporting Information may be found in the online version of this article:

**Video 1:** Comparison of restorative instrument blade without coating to blade with the superhydrophobic coating. The speed in the video is 2x to the real speed used. Millimeter scale paper is used as background. Restorative material is seen to stick more prominently and follow a greater distance upon pull-out for the non-coated instrument. This video was recorded using the same equipment as in the main measurements in this investigation.

**Appendix 1:** Variation analysis on customized dipping measurement and effect of dip depth.

### List of Figure captions

**Figure 1:** Customized measurement setup for evaluating the non-stick properties of coated dental instruments. Coated instrument is repeatedly dipped into restorative material and pulled out. The adhesion force by time is measured by a force transducer.

**Figure 2:** Voltage-by-time curve obtained by a single dip and pull-out in customized measurement setup.

**Figure 3:** SEM-image of the superhydrophobic sample surface after etching; (A) topside view; (B) tilted view. Image was taken by Zeiss Supra 40 (Carl Zeiss Microscopy, Jena, Germany).

**Figure 4:** Dental restorative material resin droplet on (A) non-coated steel disk and (B) steel disk with the superhydrophobic coating after 10 min.

**Figure 5:** SEM-images of tool surfaces after dipping procedure: (A) non-coated, dark area is restorative material, B) DLC coated, light area is restorative material, (C) PTFE based

coated, light area is restorative material, (D) the superhydrophobic coating, dark area is restorative material, (E) the superhydrophobic coating, after autoclaving.