Hydrosilane-Modified Poly(2-Hydroxyethyl Methacrylate) Brush as a Nanoadhesive for Efficient Silicone Bonding

Stefan Urth Nielsen †,‡, Mark Holm Olsen,§ Mikkel Skorkjær Kongsfelt,§ Steen Uttrup Pedersen,†* and Kim Daasbjerg †

†Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark
‡RadiSurf ApS, Arresøvej SB, 8240 Risskov, Denmark
§Teknologisk Institut ApS, Gregersensvej 6, 2630 Taastrup, Denmark

ABSTRACT: Leaching of chemicals from adhesion promoters is, in particular, problematic for the food, water, pharmaceutical, and MedTech industries where any chemical contamination is unacceptable. A solution to this issue is to employ covalently attached nanoscale polymer brushes as adhesive layers for plastics. One of the industrially most relevant adhesion targets in that respect is poly(dimethylsiloxane) (PDMS), being used for many high-end applications such as catheters and breast implants. In this work, we have synthesized a novel surface-immobilized poly(2-hydroxyethyl methacrylate)-based brush adhesive containing reactive hydrosilane groups that can bond directly to PDMS. Two different medical grades of addition-cured PDMS were molded on top of titanium substrates already coated with the polymer brush. Titanium plates were used for the chemical analysis, and titanium rods were used for adhesion testing. Adhesion testing revealed a high adhesive force, in which cohesive failure was observed in the bulk PDMS. The necessity of the hydrosilane group in the polymer brush adhesive layer was demonstrated in comparative studies using similar brushes lacking this functionality.

INTRODUCTION

Adhesion of plastics to metals, ceramics, glass, and other polymers using glues is often problematic due to leaching of chemicals from glues over time. Nanoscale polymer chains end-tethered to a surface, so-called polymer brushes, have attracted much attention in the last two decades due to the strong mode of attachment, usually covalent, to the surface, the nanometer scale, and the possibility to tune the chemical features. Polymer brushes can provide a surface with properties such as wetting, adhesion, biocompatibility, antifouling, and corrosion resistance. Hence, designing polymer brushes with new chemical structures has the potential to bring new surface properties to materials.

The use of polymer brushes as nanoscale adhesive layers has been addressed from both academic and industrial points of view. In particular, the adhesion of plastic promoted by polymer brushes has had a strong focus. In one such study, a 43-nm-thick polymer brush layer of poly(methyl methacrylate) (PMMA) was used as the adhesive layer for bonding to bulk PMMA. It was shown that the adhesion was sufficiently strong to yield cohesive failure in the bulk PMMA. Nanoentanglement was suggested to be the nature of adhesion between the PMMA polymer brush chains and the polymer chains of the bulk PMMA. This means that polymer brush adhesion requires tailor-made brushes that are chemically compatible with the plastic in question. On top of this, chemical bonds can be established in the entangled polymer matrix by introducing specific reactive chemical groups in the brush part.

The potential industrial applications of polymer brushes are immense, considering the low material consumption (<100-nm-thick adhesive layers), the high stability of the surface anchoring points providing a long shelf life, and the avoidance of the chemicals usually added to induce covalent bond formation. In particular, the absence of hazardous chemicals is germane for the food, water, pharmaceutical, and MedTech industries to diminish as much as possible the risk of chemicals leaching to the surroundings over time. For such reasons, further development of polymer brush systems with the aim of matching them up chemically with relevant plastic materials is crucial.

In this work, we report the design and testing of a novel polymer brush layer for adhesion to poly(dimethylsiloxane) (PDMS). PDMS is used extensively by the MedTech industry, e.g., as catheters, medicine pumps, and percutaneous implants. By introducing hydrosilane groups in the polymer brush structure based on poly(2-hydroxyethyl methacrylate) (PHEMA) and by exploiting their ability to react during the Pt-catalyzed curing process of the PDMS, it becomes possible to match the polymer brush layer to the PDMS surface.

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to establish covalent bonding between the brush and the PDMS. Adhesion testing is performed for two medical grades of PDMS to show that the failure, once induced, is fully cohesive. Finally, it is shown that the hydrosilane group is pertinent for the successful outcome of this process since adhesion becomes significantly weaker upon replacing Si–H with a Si–Me group.

RESULTS AND DISCUSSION

Synthesis of Functional Polymer Brushes. Scheme 1 summarizes the synthesis protocol for designing polymer brushes having the appropriate chemical properties to make them compatible with a PDMS bulk polymer. The steps involved in the synthesis of the functional polymer brushes are the following (see Experimental Section): (1) silane grafting onto the surface using (3-aminopropyl)trimethoxysilane (APTMS), followed by annealing to promote cross-linking, to yield TiAPTMS; (2) the polymerization initiator, Tiinitiator, is obtained by reacting TiAPTMS with α-bromoisobutyryl bromide (BiBB); (3) the TiPHEMA polymer brushes with their reactive hydroxyl groups are fabricated using the protocol for activators regenerated by electron transfer for atom transfer radical polymerization (ARGET ATRP) in a protic polar solvent system; and (4) TiDMS and TiTMS with their pendant dimethylsilane or trimethylsilane functionalities are obtained by reacting TiPHEMA with the pertinent chlorosilanes.

The hydrosilane group in TiDMS is selected because of its ability to react with the vinyl group in the PDMS during the curing process. In this manner, an interfacial cross-bonding network can be established to strengthen the adhesion. In contrast, the TMS-terminated polymer brushes in TiTMS, although being similar in the overall chemical structure, are disclosed from being involved in this type of reactions. Depending on the ability of the brushes to mix with the PDMS polymer, nanoentanglement may occur with the expectation that the TiDMS and TiTMS samples would entangle equally well with PDMS.

Table 1 shows the thicknesses and the atomic composition (atom %) for the Ti samples obtained at the various synthesis steps (Scheme 1). For Tiblank, the ratio of Ti (21.2 atom %) and O (45.1 atom %) is close to 1:2 as expected for a TiO2 surface. This is accompanied by the presence of a substantial amount of adventitious C (27.6 atom %) and some N (3.5 atom %), the latter, most likely, originating from the physical vapor deposition fabrication process of the Ti substrates. The TiAPTMS sample contains a slightly higher N content (3.8 atom %), which can be attributed to the introduction of the amine group. In addition, Si (1.9 atom %) is observed in accordance with expectations. The value of $d = 1.1 \pm 0.4$ nm is consistent

![Scheme 1. Steps Involved in the Synthesis of Polymer Brush Structures](image-url)

1. Silane grafting using APTMS, (2) synthesis of the radical initiator using BiBB, (3) ARGET ATRP of 2-hydroxyethyl methacrylate (HEMA), and (4) introduction of two different kinds of silyl groups.

| sample      | $d$, nm | C 1s, atom % | O 1s, atom % | N 1s, atom % | Si 2s, atom % | Ti 2p, atom % | Br 3p, atom % |
|-------------|---------|--------------|--------------|--------------|--------------|--------------|--------------|
| Tiblank     | 0.0 ± 0.0 | 27.6 ± 2.2   | 45.1 ± 1.2   | 3.5 ± 0.1    | 21.2 ± 1.0   |              |              |
| TiAPTMS     | 1.1 ± 0.4 | 26.0 ± 1.4   | 45.4 ± 0.9   | 3.8 ± 0.1    | 19.0 ± 0.2   | 20.2 ± 0.4   |              |
| Tiinitiator | 0.9 ± 0.4 | 29.3 ± 4.5   | 43.8 ± 2.7   | 3.6 ± 0.6    | 3.9 ± 0.6    | 16.6 ± 1.7   | 0.7 ± 0.1    |
| TiPHEMA     | 52 ± 6    | 69.4 ± 0.3   | 30.6 ± 0.3   |              |              |              |              |
| TiDMS       | 63 ± 7    | 68.5 ± 0.5   | 25.0 ± 2.0   | 6.5 ± 2.5    |              |              |              |
| TiTMS       | 65 ± 4    | 70.1 ± 1.0   | 24.9 ± 1.9   | 4.9 ± 1.9    |              |              |              |

For Tiblank, TiAPTMS, Tiinitiator, and TiPHEMA, the amount of other elements (i.e., Na, Ca, Co, and Zn) detected is <3 atom %. For TiDMS and TiTMS, the amount of these other elements is <0.5 atom %.
with 1–3 layers of APTMS, considering that the molecular length of ATPMS is ∼0.5 nm (determined from a MM2 molecular dynamics energy minimization using the Chem3D software with the following parameters: step interval, 2 fs; frame interval, 10 fs; heating/cooling rate, 1,000 kcal atom$^{-1}$ ps$^{-1}$; and target temperature, 300 K). Substantial amounts of Ti, O, and C are still detected to bear witness of the low thickness of the APTMS coating.

Going to $T_{\text{initiator}}$, the prominent features are 0.7 atom % of Br and the increase in C content by 3.3 atom %, which verify the successful introduction of Br from the reaction with BiBB. The increase in the content of Si from 1.9 to 3.9 atom % is expected and may originate from glassware contaminants. The film thickness ($d = 0.9 ± 0.4$ nm) is within the uncertainty of the $T_{\text{APTMS}}$ sample thickness, which is expected considering the small size of the added initiator group. After the polymerization of HEMA using ARGET ATRP, the corresponding $T_{\text{HEMA}}$ samples show a large increase in the film thickness ($d = 52 ± 6$ nm), in line with the growth of polymer brushes. Furthermore, C and O from the PHEMA part are the only ones seen, arriving in, by and large, the expected 2:1 ratio. Ti, N, and Si are no longer detectable because the XPS probing depth is only ∼10 nm.

Upon reaction with chlorotrimethylsilane, $T_{\text{PHEMA}}$ is converted into $T_{\text{DMS}}$ as evidenced from the presence of 6.5 atom % Si. For a full conversion, the Si/O ratio should theoretically be 1:3, while the experimental value is closer to 1:4. This indicates that ∼75% of the pendant hydroxyl groups in the polymer brush have reacted, which also is reflected in the significant thickness increase by 11 nm to now $d = 63 ± 7$ nm. In comparison, the corresponding conversion using chlorotrimethylsilane to give $T_{\text{TMS}}$ provides 4.9 atom % Si (∼60% functionalization) and a thickness increase by 13 nm to $d = 65 ± 4$ nm. The larger thickness increase is expected for $T_{\text{TMS}}$ considering the presence of an extra methyl group compared to that of $T_{\text{DMS}}$, although the high uncertainties associated with the measurements make it difficult to use the results in a more quantitative manner. In summary, the XPS and ellipsometry data confirm the steps in the synthesis protocol.

**Adhesion Tests.** Figures 1 and 2 show the maximum adhesive force and percentage of cohesive failure obtained for the $T_{\text{blank}}$, $T_{\text{DMS}}$, and $T_{\text{TMS}}$ samples molded with two different medical grades of PDMS, i.e., MED-4420 and MED-6215 (see the Experimental Section). We chose not to normalize the measured adhesive force with the area, although the contact surface area between the rod and the PDMS was known (∼3 cm$^2$). Such numbers would not be representative of the actual tensile strength due to the geometry of the setup, where a combination of adhesion, shear, and tear strengths comes into play. Measurement of the tensile strength is often done by a classical peel test, but soft PDMS substrates are known to be notoriously difficult to perform this kind of test, and given that the purpose here is merely to compare the adhesive properties we choose not to do so. The percentage of cohesive failure was evaluated visually by estimating the fraction of the Ti surface still covered with remains of PDMS after failure. A sample molded with the commercially available PDMS primer MED-161 (denoted $T_{\text{MED1-161}}$) served as a reference.

For $T_{\text{blank}}$ with both MED-4420 and MED-6215, the adhesive force is low (<80 N) and no cohesive failure is observed at all. In contrast, both the commercially available primer MED1-161 and the $T_{\text{DMS}}$ show 100% cohesive failure with, by and large, the same maximum adhesive force. At 100% cohesive failure, the strength of the PDMS alone determines the maximum adhesive force required for failure. It is worth noting that the adhesive force measured for MED-4420 (∼250 N) is almost twice that for the softer MED-6215 (∼130 N).

In the case of the $T_{\text{TMS}}$ samples, the percentage of cohesive failure is significantly lower (∼20%), while the adhesive force is higher than that for $T_{\text{blank}}$ but smaller than that for $T_{\text{MED1-161}}$ and $T_{\text{DMS}}$. To better understand these results, three adhesion components should be considered, i.e., physisorption (wetting), entanglement, and covalent bonding. The $T_{\text{blank}}$ sample can only provide adhesion by physisorption of the PDMS, while $T_{\text{TMS}}$ provides additional adhesion by entanglement of the TMS brushes with PDMS. This contributes to the improved strength in the latter case. Only $T_{\text{DMS}}$ allows all three components of adhesive forces, including the covalent bonding obtained during the curing reaction of PDMS (Scheme 2). This explains the remarkably enhancement in the strength of the interface for $T_{\text{DMS}}$.

**CONCLUSIONS**

In this study, we have introduced a novel PHEMA brush postmodified with a hydrosilane (i.e., DMS) moiety. We show that this system is able to promote strong adhesion to two different medical grades of addition-cured PDMS showing full cohesive failure. Replacing the hydrosilane hydrogen atom with a methyl group (i.e., TMS) results in a markedly lower adhesive force to PDMS with a significantly larger degree of adhesive failure. These results are explained by the ability of the DMS-modified PHEMA brushes to participate in the PDMS curing reactions, thus affording covalent bonding between the DMS brushes and the bulk PDMS. The fact that TMS-modified PHEMA brushes show a lower adhesive strength for Ti samples molded with MED-6215 showing the maximum adhesive force (blue) and the percentage of cohesive failure (red solid square).
than that of the DMS-based brushes but, nevertheless, a higher adhesion force than that of a blank sample without brushes suggests that both the modified polymer brushes experience nanoentanglement with PDMS. Importantly, this study shows that a nm-thin DMS-derived PHEMA brush system yields the adhesion of a size, similar to that accomplished with a 1–5-μm-thick commercial primer. We believe that such polymeric adhesive systems will have a promising future in the MedTech and similar industries having strict requirements to evade leaking of chemical agents.

**EXPERIMENTAL SECTION**

**Materials.** All chemicals were purchased from Sigma-Aldrich, unless otherwise stated. Acetone, dichloromethane (DCM), methanol (MeOH), isopropanol, acetonitrile (MeCN), diethyl ether, and pentane were all high-performance liquid chromatography-grade and purchased from Th. Geyer. 2-Hydroxyethyl methacrylate (HEMA, 97%) was purified by passing it through a column of Al₂O₃ to remove the inhibitor. CuCl₂·2H₂O (>99%), (+)-sodium L-ascorbate (NaAsc, >98%), 2,2′-bipyridine (BiPy, >99%), triethylamine (TEA, >99%), α-bromoisobutyryl bromide (BiBB, 98%), 4-(dimethylamino)-pyridine (DMAP, >99%), chlorodimethylsilane (DMS-Cl, 98%), and chlorotrimethylsilane (TMS-Cl, >98%) were used as received. (3-Aminopropyl)trimethoxysilane (APTMS, 97%) was obtained from FluoroChem. Cylindrical rods (L = 50 mm, d = 5 mm) of Ti–6Al–4V were supplied by Elos MedTech Pinol A/S. Ti plates (TiO₂ on SiO₂ wafer; 1 cm × 1 cm) were produced by the Danish Technological Institute using physical vapor deposition. The two medical grades of PDMS (MED-6216 and MED-4420) and the PDMS primer (MED1-161) were purchased from NuSil.

**X-ray Photoelectron Spectroscopy (XPS).** XPS analysis on the plates was performed with a Kratos Axis Ultra-DLD instrument equipped with an Al Kα X-ray source at 150 W. The pressure in the chamber was kept below 5 × 10⁻⁹ mbar during measurements. Survey scans were obtained with a pass energy of 160 eV from 0 to 1400 eV and accumulated for two scans. High-resolution spectra were recorded using a 20 eV pass energy and by accumulating four scans. CasaXPS software was used for data analysis, where C 1s = 285.0 eV was set as calibration for the binding energy. All peaks were integrated using a Shirley background.

**Ellipsometry.** The thicknesses of the dry-state surface layers on the plates were measured using a rotating analyzer ellipsometer (Dre, Germany). The samples were measured at an angle of incident at 75°. Parameters of the bare (Δ₀, Ψ₀) and modified (Δₘ, Ψₘ) substrates were measured at ambient temperature in air, where Δ is the phase shift and tan Ψ is the amplitude ratio of reflection. The complex part of the reflective index of the bare substrate was calculated from the Δ₀ and Ψ₀ values. A three-layer optical model with the substrate with its complex refractive index, the surface layers with their refractive index and thickness, and the surrounding air was used to get the overall coefficients for in-plane (Rᵣ) and out-of-plane (Rᵣ) polarized lights. The real and imaginary parts of the refractive index of each substrate were obtained using clean substrates prior to surface modification. The refractive index of the

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**Figure 3.** (A) Sample used for the adhesion studies, (B) schematic illustration of the locking posture, (C) load sample that is ready for adhesion testing, and finally, the apparatus setup (D) before and (E) after testing.
organic surface layers was set at constant values (1.55 and 0 for
the real and imaginary parts, respectively). The thickness and
standard deviation reported originate from minimum three
spots measured on each sample.

**Adhesion Testing of PDMS-Molded Samples.** An AG-10 apparatus from Shimadzu KK was used for adhesion testing,
where the Ti rods were pulled upward (2 mm min⁻¹) while
holding the PDMS in place with a fixture (Figure 3). The force
applied was measured as a function of the distance traveled by
the rod. As the rod is pulled upward, the PDMS is under both
elastic strain and compression until either an adhesive or a
cohesive breakage occurs. The degree of cohesive and adhesive
failure was subsequently evaluated visually by looking at the
amount of PDMS that remains on the surface of the Ti rod
after failure. We report the adhesive force for the maximum
force calculated as the mean of at least three tests. The contact
surface area between the rod and the PDMS is the same for all
samples (∼3 cm²).

**Molding of PDMS onto Ti Rods.** MED-4420- and MED-
6215-type PDMS were molded in a PTFE mold with the Ti
rod positioned in the middle of the mold. Both types consisted
of two components that should be hand-mixed in the ratio 1:1
for MED-4420 and 10:1 for MED-6215 for 5 min before it was
vacuum-treated for 10 min to remove entrapped air bubbles
and then poured into the mold. The sample was cured at 165
°C for 20 min and left in the mold to cool down to room
temperature.

**Synthesis Protocol for Sample Preparation.** Scheme 1
summarizes the synthesis protocol employed for producing
polymer brushes on the Ti plates/rods with the individual
steps as listed as follows.

**Silane Grafting on Ti Samples.** Ti items (denoted TiBlatak)
were sonicated for 10 min in deionized water, then in
acetone and, finally, in pentane. Each item was placed in 12 mL
of solution taken from a standard solution of APTMS (1.05
mL) in MeOH (300 mL). After heating to 60 °C, the samples
were left to react for 3 h without stirring. The samples
(denoted TiAPTMS) were then washed with MeOH and
annealed at 120 °C for 1 h.

**Synthesis of the Initiator.** A solution of DCM (240 mL),
TEA (16.5 mL), and BiBB (14.7 mL) was prepared and
distributed into several test tubes (10 mL), each containing
one TiAPTMS sample. The samples were left at 0 °C on a
shaking table (80 rpm) for 3 h. After the reaction, the samples
(denoted TiInitiator) were sonicated for 10 min in DCM and
acetone, respectively.

**Activators Regenerated by Electron Transfer for Atom
Transfer Radical Polymerization (ARGET ATRP)
of the HEMA Monomer to Produce Brushes.** A solution of
deionized water (40 mL), MeOH (40 mL), and HEMA (12.3
mL) in a 100 mL chemical reactor was purged with argon for
15 min and then mixed with CuCl₂·2H₂O (64.0 mg), BiPy
(117.5 mg), and NaAsc (79.1 mg). The solution was cooled to
0 °C and purged with argon for additional 15 min. The TiInitiator
samples hanging from a lid were introduced to the solution and
polymerized under high shear stirring and continuous argon
purging for 4 h. After the polymerization, the samples were
sonicated in acetone for 10 min. A distinct surface layer of
PHEMA was visible on the samples (denoted TiHEMA).

**Reaction of Polymer Brushes with DMS-CI.** The
TiHEMA samples were submerged in a solution consisting of
dry DCM (90 mL), DMAP (24.8 mg), DMS-CI (1.02 mL),
and TEA (1.125 mL) in an argon-purged 100 mL chemical
reactor. The samples were left overnight under stirring at 0 °C.
After the reaction, the samples (denoted TiTMS) were
sonicated 10 min in acetone followed by further flushing in
acetone.

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