On-site applicable flat anti-adhesion coatings

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Abstract

Anti-adhesion surfaces capable of repelling various liquids would have broad technological implications. However, the on-site application of such surfaces has been limited by the need for complex processes and extra equipment. Here we have created a solvent-free mixture containing miscible silicon precursors, which can be readily sprayed, dipped, or painted onto virtually any substrate to prepare flat anti-adhesion coatings. By embedding the lubricating silicon segments on surfaces via the novel synergetic reactions that spontaneously occur at room temperature, we can fabricate coatings that are readily applicable on-site to cover large objects, and which offer excellent repellency against various liquids (water, hydrocarbons, crude oil, and oily-ink) as well as viscoelastic and sticky adhesives. These coatings are transparent, flexible, and durable. We believe these coatings can be utilized in many commercial and residential situations to address a wide range of undesirable interfacial adhesion issues such as smudge, drag, and blockage.

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A novel large-area and flat anti-adhesion coating can be formed spontaneously at room temperature, thus it can be readily applied on-site via industrially-viable spray-, dip-, or paint-coating techniques to cover large objects, and which offer excellent repellency against various liquids and sticky adhesives.

Abstract

Anti-adhesion surfaces capable of repelling various liquids would have broad technological implications. However, the on-site application of such surfaces has been limited by the need for complex processes and extra equipment. Here we have created a solvent-free mixture containing miscible silicon precursors, which can be readily sprayed, dipped, or painted onto virtually any substrate to prepare flat anti-adhesion coatings. By embedding the lubricating silicon segments on surfaces via the novel synergetic reactions that spontaneously occur at room temperature, we can fabricate coatings that are readily applicable on-site to cover large objects, and which offer excellent repellency against various liquids (water, hydrocarbons, crude oil, and oily-ink) as well as viscoelastic and sticky adhesives. These coatings are transparent, flexible, and durable. We believe these coatings can be utilized in many commercial and residential situations to address a wide range of undesirable interfacial adhesion issues such as smudge, drag, and blockage.

Keywords: anti-adhesion coatings, on-site applicable coatings, solvent-free coatings, liquid repellency, self-cleaning

Introduction

Undesirable interfacial adhesion causes numerous technical issues that can impact various fields. A wide range of advanced anti-adhesion materials capable of repelling both water and oils have been developed to address these challenges, and they are described as anti-adhesion,[1] non-stick,[2]self-cleaning,[3] antifouling,[4]anti-smudge,[5] anti-graffiti,[6]superwettability,[7] superoleophobic,[8]superamphiphobic,[9] or slippery liquid-infused porous surfaces (SLIPS).[10] The common purpose of these materials is to minimize the interfacial wetting behavior and intermolecular forces between liquids and solid surfaces, which is achieved via the construction of micro/nanomorphologies or the manipulation of low-surface-energy molecules.

Micro/nanoscale roughened textures and re-entrant curvatures, which are generally regarded as lotus bioinspired structures, can enhance the liquid repellency of amphiphobic materials and render them superam-

phiphobic due to the presence of air pockets, exhibiting contact angles (CAs) greater than 150° and sliding angles (SAs) below 10°.[11,12] Despite decades of intense research in this area, the applicability of these intricate micro/nanoscale surfaces has often been limited by their poor wear resistance, opacity, and the need for complex manufacturing processes.[13,14]

Flat surfaces comprised of molecules with weak intermolecular forces, including hydrogen bonds, electrostatic interactions, and van der Waals interactions, can also exhibit anti-adhesion performance, such as the repellency against water and cooking oil that is exhibited by polytetrafluoroethylene (PTFE, Teflon). It is noteworthy that the dynamics or rotation mobility of liquid molecules would greatly enhance the anti-adhesion performance. For example, the anti-adhesion function of solid Teflon would fail during contact with objects that exhibit strong multivalent hydrogen bonding such as crude oil, blood, and 2-amino-4-hydroxy-6-methylpyrimidine (UPy) modified hydrogels.[1,15] In contrast, anti-adhesion behavior against these objects could be achieved by using a perfluorinated polyether (PFPE) lubricating film (with CAs of less than 120° and SAs below 10°).[10] Unfortunately, it is a challenge to convert lubricating molecules into materials or incorporate them onto surfaces. The use of chemically modified monolayers,[16,17] slippery liquid-infused porous surfaces (SLIPS),[4,18] heating or UV-triggered polymer matrices,[19,20] have been reported to achieve this so far, but these strategies plagued with the requirement of complex processes and extra equipment that restrict their on-site application onto structures with large surface areas.

Herein, we report a novel large-area and flat anti-adhesion coating with a lubricating surface that can be formed spontaneously at room temperature, thus it could be readily applied on-site via industrially-viable spray-, dip-, or paint-coating techniques onto various objects. The silicon-based and solvent-free precursor system also offers various attractive features, such as low cost, environmental friendliness, and biocompatibility, thus further enhancing the applicability of these anti-adhesion coatings.

Experimental Section

Materials

Hydroxyl-terminated poly(dimethylsiloxane) (HO-PDMS-OH, ˜60 mPa·s) was purchased from Wacker Chemie AG. (3-Aminopropyl)triethoxysilane (APTES), 3-glycidoxypropyltrimethoxysilane (GPTMS), dibutyltin dilaurate (DBTB), ethanol, diiodomethane, and hexadecane were provided by Shanghai Macklin Biochemical Co., Ltd. Light crude oil samples with a viscosity of ˜300 cP were provided by PetroChina. Hydrochloric acid (HCl), sodium chloride (NaCl), and sodium hydroxide (NaOH) were procured from Tianjin Damao Chemical Reagent Factory and were of analytical reagent grade. Peanut oil and pump oil were purchased from local stores.

Preparation of the coatings

APTES (0.580 g), GPTMS (0.620 g), HO-PDMS-OH (1.800 g), and dibutyltin dilaurate (DBTL, 0.010 g) were thoroughly mixed in a sealed container via stirring at 300 rpm for 24 h. This stirring treatment was performed in order to enhance the homogeneity of the coating. The precursors could be applied onto various kinds of substrates via spray-, dip-, or paint-coating techniques, and the coatings were spontaneously formed at room temperature over a period of 7 days.

Characterization of the coatings

The molecular weight of HO-PDMS-OH was characterized by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS, AB SCIEX, MALDI-TOF 5800). Fourier-transform infrared (FTIR, Bruker Optics, Spectrum 100) spectra were recorded with a Tensor-27 spectrometer in order to monitor the synergetic reactions, and KBr was used as the sample matrix. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, K-Alpha) was employed to analyze the elemental compositions of the coating. The morphology and the energy-dispersive X-ray spectroscopy (EDX) mapping of the coating were characterized with a scanning electron microscope (SEM, Zeiss, Sigma300). The morphology and roughness of the coating were investigated via atomic force microscopy (AFM, Bruker, Multimode 8). Meanwhile,

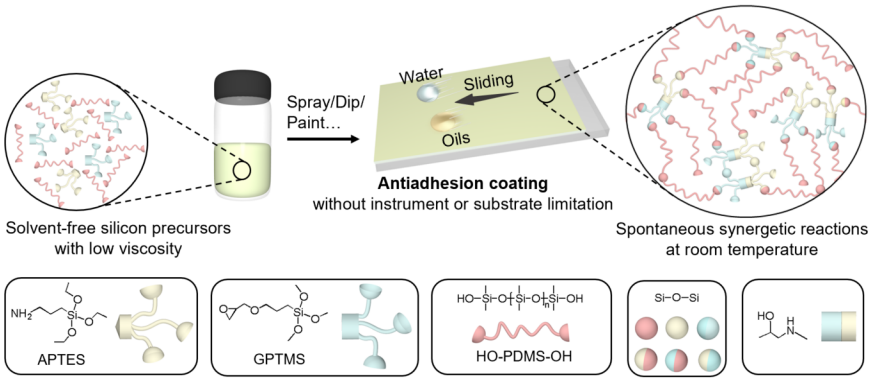
differential scanning calorimetry (DSC, PerkinElmer, DSC8000) measurements were performed under a nitrogen atmosphere at heating and cooling rates of 10 K/min. The optical transmittance of the coating was measured using a UV-visible spectrometer (Perkin Elmer, Lambda 950) with air employed as a reference. Pencil hardness tests were performed using a VF2378 pencil hardness tester (Thermimport Quality Control, Netherlands).

An abrasion test system (Chuangheng, A20-339) with a piece of cotton fabric as the abrasion material was used for the abrasion tests, and a weight of 500 g was placed above the fabric to enhance the abrasion force.

The contact angles (CAs), sliding angles (SAs), and hysteresis angles ([?]$\vartheta = \vartheta_A - \vartheta_R$) were measured using a contact angle measuring instrument (Shengding, JC2000A). The droplet volume employed for the CA measurements was 2 μL, and that used for the SA measurements was 20 μL. Theϑ_A and ϑ_R were measured by injecting the test liquids into or withdrawing from the droplets resting on the coatings until they advanced or receded. The shear strength and tensile strength were evaluated using a universal tester at a rate of 300 mm/min (Dongguan Lixian, HZ-1007E).

The size of the 3M® Scotch adhesive tape employed for the shear strength test was 4 cm × 2 cm, while the size of the 3M® Scotch double-sided mounting tape used for the tensile strength test was 2 cm × 2 cm. A roller with a weight of 2 kg was passed over these tape samples twice to ensure that they were in full contact with the coatings and various uncoated substrates, and the strengths were measured 20 min after this treatment.

Results and Discussion



Scheme 1. Design and fabrication of the on-site applicable flat anti-adhesion coating.

Scheme 1 illustrates the preparation of the coating and its multi-crosslinked networks that are generated via the synergetic reactions including ring-opening, co-hydrolysis, and polycondensation reactions. The selection of the silicon precursors including 60 wt% lubricating molecules of silanol- terminated polydimethylsiloxane (HO-PDMS-OH, molecular weight of ˜260 g/mol), and the remaining 40 wt% was comprised of γ-aminopropyltriethoxysilane (APTES), and 3-glycidoxypropyltrimethoxysilane (GPTMS) at an equimolar ratio, as determined by the equimolar reaction between the amino and the epoxy groups. The low molecular weights of the precursors provide the mixture with a low viscosity, exhibiting both fluidity and substrate wettability, thus allowing solvent-free processing and convenient application onto various substrates. Subsequently, the desirable coating properties can be obtained by simply waiting for 7 days to allow the spontaneous synergetic reactions to occur. The precursor and resultant coating were characterized by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS, Fig. S1), Fourier-transform infrared spectroscopy (FTIR, Fig. S2), X-ray photoelectron spectroscopy (XPS, Fig. S3), and energy-dispersive X-ray spectroscopy (EDX, Fig. S4).

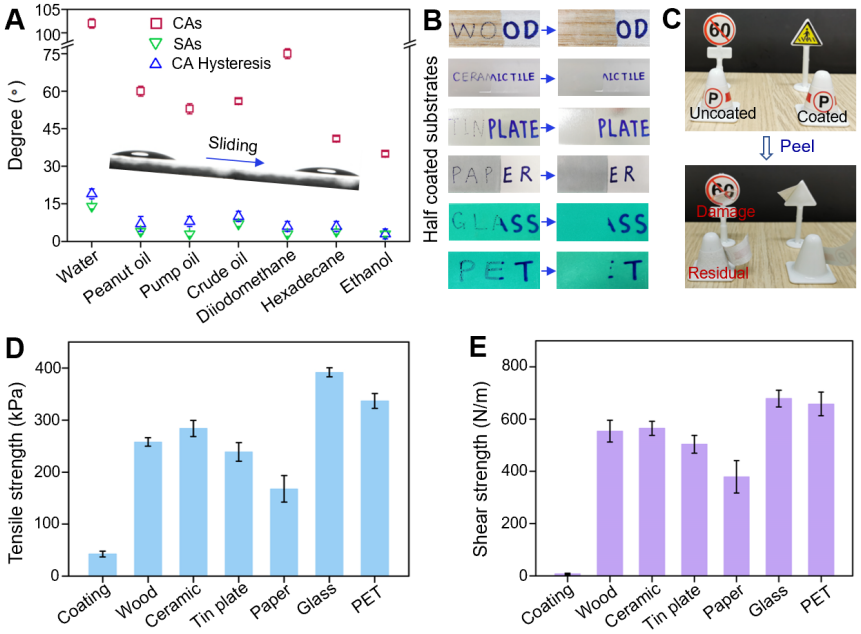


Figure 1. (A) CAs, SAs, and CA hysteresis of various test liquids on the coatings. The inset image demonstrates the sliding behaviour of hexadecane. (B) Anti-adhesion performance against oil-based ink exhibited by the coatings on various substrates. (C) The tapes could be readily removed from the coating surfaces, while were damaged and left residuals for the uncoated substrates. (D,E) The tensile strength and shear strength between the adhesives and the coating as well as various uncoated substrates.

To evaluate the anti-adhesion properties of the coating, liquids with various surface tensions such as water, diiodomethane, hexadecane, and ethanol (72.8, 50.8, 27.5, and 22.1 mN/m, respectively at 20 °C), as well as oils with different viscosities such as cooking oil, pump oil, and crude oil (˜80, 200, and 300 cP, respectively at 20 °C) were used for the CAs, SAs, and CA hysteresis measurements. As shown in Fig. 1A, the coating displayed low SAs and CA hysteresis toward all of these test liquids. These simple and complex liquids could be repelled and readily slid off the tilted coating surfaces without leaving any residues. When the HO-PDMS-OH was covalently linked into the network to generate a lubricating segment, it no longer exhibited a liquid state at the macroscopic level. Meanwhile, the glass transition temperature of the coating as determined via differential scanning calorimetry (DSC) experiments was ˜ -35 °C, implying that the polymer chains with abundant lubricating segments could be stretched and rotated readily at room temperature and provide the desired liquid-like interfacial anti-adhesion behavior (Fig. S5).

Moreover, the oil-based ink traces of Sharpie markers readily contracted on a diverse range of coated substrates (Fig. 1B), including hard, thermosensitive, and flexible materials such as glass, metal, wood, paper, and polyethylene terephthalate (PET). The shrunken ink traces could be readily wiped away with dry tissues. In contrast, it was difficult to remove the ink from the uncoated regions of the substrates. Noteworthy, the coating was found to exhibit low adhesion against viscoelastic and sticky adhesives. The adhesive tapes could be readily removed from the coating surfaces, and thus ensure the cleanability of substrates as well as the recyclability of adhesives and advertisement papers (Fig. 1C). Pieces of 3M Scotch® double-sided mounting tape and adhesive tape were applied onto the coating and various uncoated substrates to evaluate the tensile strength and shear strength (Fig S6).[21] As shown in Fig. 1D and E, these tapes could be removed from the coatings with the tensile strength of ˜42 kPa and negligible shear strength, and the values were far lower than those estimated for the uncoated substrates.

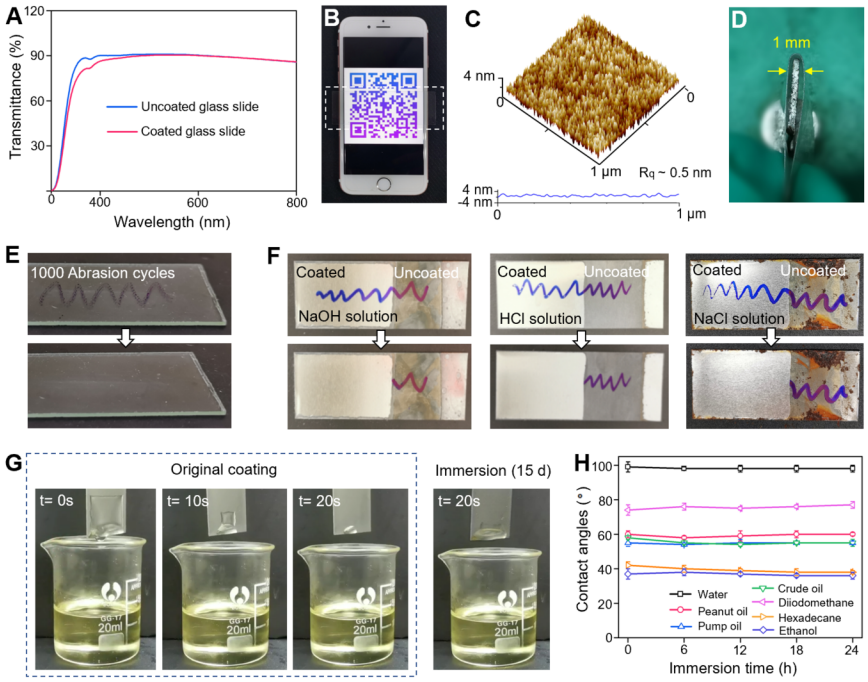


Figure 2. (A) The coated glass exhibited an optical transmission close to that of its uncoated counterpart. (B) Photograph of a smartphone screen covered by the coated glass in the middle region that is outlined by white dashed lines. (C) AFM image of the coating surface. (D) Photograph of the minimum bending radius measurement of the coated PET. (E) The coating maintained its anti-adhesion performance against oil-based ink after it had been subjected to 1000 abrasion cycles. (F) Antiadhesion performance against oil-based ink after the coatings had been immersed into NaOH (pH = 14), HCl (pH = 0), and NaCl solutions (10 wt%) for 7 h, 16 h, and 15 d, respectively. (G) The sliding behaviour of cooking oil before and after the coating had been immersed in this oil for 15 d. (H) The CAs of various liquids exhibited negligible changes after the coatings had been immersed in these liquids for various lengths of time.

The coating also possesses excellent transparency, flexibility, and durability. The optical transmission of uncoated and coated glass slides exhibited negligible differences in the visible light range (400-750 nm, Fig. 2A). The glass slide bearing the transparent coating did not obscure the screen (Fig. 2B), indicating its potential applicability for electronic displays or devices. This optical clarity could be attributed to the flatness of the coating surface, thanks to the excellent miscibility of the silicon precursors and the lack of solvent volatilization disturbance in this solvent-free system. The atomic force microscopy (AFM, Fig. 2C) image indicated that the root-mean-square surface roughness was only ˜ 0.5 nm, while the SEM (Fig. S4) image revealed that the coating possessed a featureless surface with no evidence of structures or roughness above the micrometer scale. A minimum bending radius of less than 1 mm was reached for the coated PET (Fig. 2D). This excellent flexibility and foldability would expand a diverse range of coating applications, including the coating of soft pipelines, as well as flexible materials or devices for prosthetics and advanced robotics. The coating possessed a hardness rating of HB according to the ASTM D3363 protocol, and the oil-based ink could still be completely removed from the coating even after it had been subjected to 1000 abrasion cycles with cotton fabric under a load of 500 g (Fig. 2E). The coatings maintained their long-term anti-adhesion performances even after they had been immersed in basic, acidic, salt solutions, and oil (Fig. 2F and G). The negligible chemical change of the coating surface after the immersion in different liquids for various lengths of time has been confirmed via CA measurements (Fig. 2H) and XPS (Fig. S7). With the high crosslinking density that is induced by the low molecular weight of processors, the migration of interfacial segments as well as the chemical reconstruction at the interfaces of the coating and ambient liquids

would be restrained.

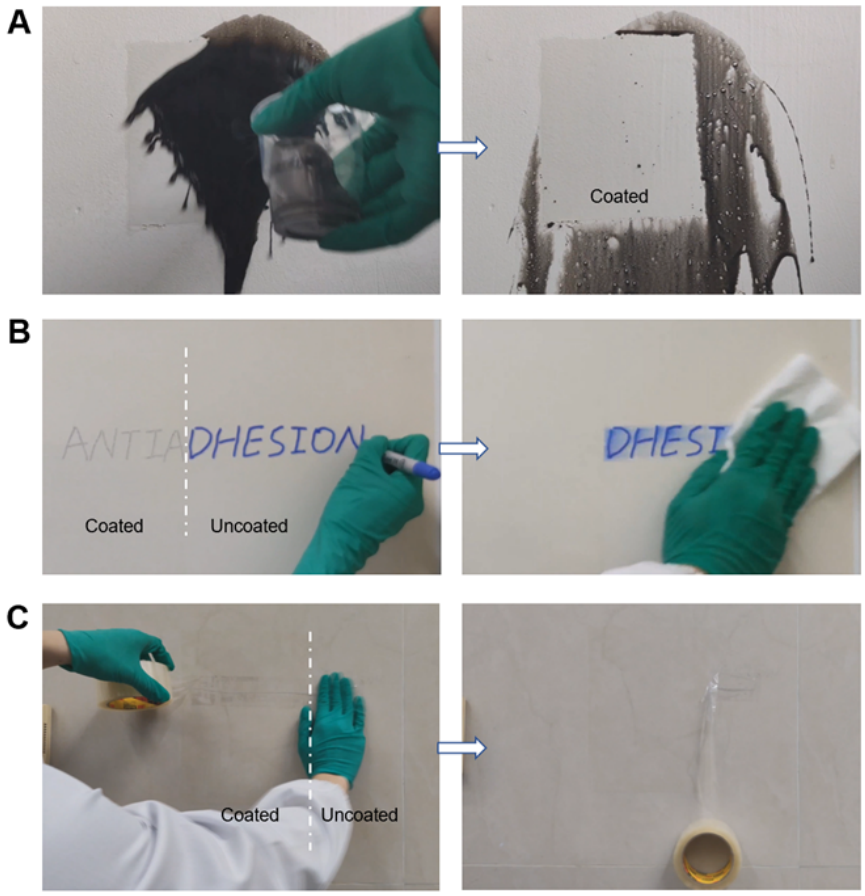


Figure 3. (A, Movie S1) Coated and uncoated sections of a wall that are exposed to dyed water. (B, Movie S2) The oil-based ink traces on the coated section of the wall readily contracted and they could be easily wiped away with dry tissues. (C, Movie S3) 3M tape readily fell from the coated section of the wall by the action of its own weight, while strongly adhering to the uncoated section of the wall.

Finally, in order to evaluate the on-site use of the coating on large-area substrates, we applied our coatings on different building walls (lime and ceramic tile walls) and exposed them to splashes of water, graffiti, and adhesive tapes. As anticipated, outstanding self-cleaning and anti-graffiti performance was achieved, and the tapes could be readily removed from the coated walls (Fig. 3A-C, Movies Si-S3).

Conclusion

In summary, we report a facile one-step strategy to fabricate universal large-area and flat anti-adhesion coatings that can readily be applied on-site onto various substrates, without requiring special curing condition or equipment. The coating generated from the novel spontaneous synergetic reactions exhibits outstanding anti-adhesion performance against a diverse range of liquids and adhesives. In addition, this coating possesses desirable transparency, flexibility, and durability. Considering the affordability, environmental friendliness, and biocompatibility of this solvent-free coating strategy, we believe that this coating will have a wide range of applications, including the elimination of fouling or contamination on large surfaces such as building walls, bridges, fuel lines, ships, aircraft, trains, or other vehicles, as well as onto polymer or textile materials with poor temperature-resistance.

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