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Transparent Omniphobic Coating with Glass-Like Wear Resistance and Polymer-Like Bendability

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Abstract. Transparent omniphobic or anti-smudge coatings with glass-like wear resistance and polymer-like bendability have many potential applications but no reports of such materials exist. Reported herein is a molecular composite possessing these properties. The composite is prepared via the photo-initiated ring-opening polymerization of the epoxide rings of glycidyloxypropyl polyhedral silsesquioxane (GPOSS). While the desired hardness is rendered by the silica core of GPOSS, the flexibility is imparted by the glycidyloxypropyl network. Further, oil and water repellency is achieved without adversely affecting the other properties by incorporating into the coating a low-surface-tension liquid lubricant poly(dimethyl siloxane). On the final coating, various organic solvents and water readily and cleanly glide, while complex fluids such as ink and paint facilely contract. These properties are retained after an initially flat coating sample is rolled into a U-shape 500 times or is abraded with steel wool. While the reported coating has various applications, the insight gained from this research will facilitate the design of other analogous materials.

Materials that are both wear-resistant and bendable are rare because hard inorganic materials are normally brittle and flexible polymer materials typically lack wear resistance.^[1] If such materials are also transparent, they can fulfil many applications. For example, a polymer possessing these properties is said to be a key invention that led to the touchscreen for the Samsung Galaxy Fold smartphones.^[2] We report herein the development of a transparent polymer/inorganic hybrid coating that has a pencil hardness exceeding 9H and is simultaneously so flexible that a rectangularly-shaped sample of this composite on a poly(ethylene terephthalate) (PET) substrate can be rolled into a tube. We further report the endowment of omniphobic or anti-smudge properties to the coating so that it repels water- and oil-borne contaminants, while complex liquids such as ink and paint readily contract on its surface.^[3-4]

We note that naturally-occurring hard and tough (not brittle) materials are mostly made of inorganic/organic nanocomposites. For example, nacre and human teeth are nanocomposites of proteins and minerals.^[5] They possess Young's moduli E , a measure of a material's resistance to elongation, close to those of the inorganic components because the inorganic nanophases bear most of the tensile loads.^[6] The composites are tough because the protein glues absorb much of the impact energy and cracks formed there do not readily propagate from one organic nanophase to another due to the intervening strong inorganic nanophase.^[6]

Studies of non-transparent metal alloys have revealed that the key criteria for hard and flexible alloys include not only high hardnesses H , resistance to penetration by an indenter, but also hardness-to-Young's modulus (H/E) ratios exceeding 10%.^[7-9] In addition, they have $w_e = w_w/w_p > 60\%$,^[7-8] where w_p is the work done on a material by an indenter when it is pressed into that material and w_w is work done on the indenter by the material when the indenter is withdrawn from it. A high w_e value is important because it suggests the material's ability to undergo reversible

deformation. Instead of confronting an indenter head-on, resulting in catastrophic failure, such a material deforms under an indenter and stores the work done by the indenter as elastic energy. The latter is then mostly recovered once the indenter is removed from a depressed site. Upon the further fulfilment of a high H/E value, the material would resist destructive piercing due to its high H value and deform laterally under a pressing indenter due to its low E value.^[10]

Scheme 1. Structures of: a) ladder-like siloxane used by Bae and coworkers,^[9] b) GPOSS used in this study, c) the triphenylsulfonium salts, and d) PDMS-NH₂. Frame e) shows the process used to prepare the targeted coating.

The first synthetic inorganic/organic molecular composite that meets the above criteria has been recently reported.^[9] The composite is transparent and flexible and possesses a pencil hardness exceeding 9H. The precursor to the composite was a siloxane consisting of a ladder-like silica core and 3,4-epoxycyclohexyl ethyl groups that were attached to the Si atoms (Scheme 1a). The composite was prepared via the ring-opening polymerization of the siloxane's epoxide groups using photogenerated cations.^[11] Despite its superior properties, the preparation of the composite was somewhat complex. The complete polymerization of the epoxide groups, which was essential for the targeted wear resistance, required first a photolysis step and subsequent exposure to air for 2 h at 85 °C at a relative humidity of 85%.^[9]

We obtained a hard flexible transparent coating from octa(3-glycidyloxypropyl) polyhedral oligomeric silsesquioxanes (GPOSS) (Scheme 1b).^[12] GPOSS was chosen because it was structurally similar to the afore-mentioned ladder-like siloxane. While the nanocaged silica core was predicted to provide the hardness to the final coating, the 3-glycidyloxypropyl groups were anticipated to undergo cationic ring-opening polymerization^[11] and provide the desired flexibility. Moreover, GPOSS was commercially available.^[13] Our further hypothesis was that the crosslinking of the epoxide rings in GPOSS should be more facile than those in the ladder-like siloxane, firstly due to the reduced steric hindrance of the epoxide groups and secondly due to the flexibility of the ether and methylene linkages between the silica core and epoxide rings of GPOSS.

Although there have been publications on the crosslinking of GPOSS,^[14-15] the mechanical properties of crosslinked GPOSS have not been reported. Further, previous work on GPOSS and other functional POSS compounds has focused on their use as nanofillers to enhance the rigidity, wear resistance, glass transition temperature, anti-oxidation properties, and flammability resistance of polymers.^[16-18] We did not find reports on mechanical properties of crosslinked neat POSS.

To prepare a crosslinked neat GPOSS coating, GPOSS and the photo-initiator (Scheme 1c) were mixed in butanone at a mass ratio of 100/2.5 and subsequently cast onto a glass substrate. After solvent evaporation, the coating was irradiated for more than 5 min (typically for 10 min) with a focused beam from a 500-W Hg lamp after passing through a 274 nm cut-off filter. As will be discussed later, this treatment alone was sufficient to consume most of the epoxide rings. Thus, the photo-initiated cationic polymerization of GPOSS was facile as hypothesized and did not require subsequent exposure of the photolyzed coating to hot humid air.

The first experiment aimed at assessing the hardness of the GPOSS coating involved tracing a 9H pencil across it via the standard ASTM D3363 protocol (Supplementary Information or SI). Figure 1a shows a photo of such a coating after the test. No visual damage was detected. Thus, this coating had a hardness exceeding 9H, the highest pencil hardness rating. Figure 1b shows a photograph of a polyurethane (PU) coating after it had been scratched with a 3H pencil following the same protocol. This coating was prepared from crosslinking a mixture of a triisocyanate, an oligomethacrylate polyol (P1), and a graft (g) copolymer P1-g-PDMS (consisting of P1 bearing one poly(dimethyl siloxane) (PDMS) side-chain).^[19] Here, the PDMS molecular weight was 5.0 kDa and its content in the final coating was 6.0% (m/m). The 3H pencil left two visible lines on this sample, indicating that this coating had a hardness below 3H. In fact, this coating had a hardness of 2H, characteristic of that for many polymer materials. Therefore, the GPOSS coating was harder than the PU coating by at least 7 pencil hardness ranks.

Further insights into the wear resistance were gained by subjecting the two coatings to nano-indentation tests. It involved monitoring the variations in the force acting on a diamond tip with a well-defined shape as the tip was pressed into a coating, held at the maximum force, and then withdrawn from the coating. Figure 1c shows such force loading, holding, and releasing curves for the GPOSS and PU coatings, respectively. At an equal loading force, the tip penetrated deeper into the softer PU coating. A quantitative analysis of the data via the Oliver-Pharr method^[20] revealed that for the GPOSS coating $H = 0.70$ GPa, $E = 3.3$ GPa, $H/E = 21\%$, and $w_e = 79\%$, while $H = 0.20$ GPa, $E = 4.8$ GPa, $H/E = 4.2\%$, and $w_e = 28\%$ for the PU coating. The GPOSS coating had an H value that was 3.5 times greater than that of the PU coating. Further, the GPOSS coating had much higher H/E and w_e values. Thus, only the GPOSS coating met the criteria for high wear resistance.^[8]

Figure 1. Wear resistance of a PU coating, the crosslinked GPOSS coating, and the NP-GLIDE GPOSS coating. Photographs a) and b) show the GPOSS and PU coatings after scratching with 9H and 3H pencils, respectively. Frame c) shows data obtained from the nanoindentation experiments. A photograph of the steel wool wear test apparatus is shown in d). Frames e) and f) compare SEM images of the NP-GLIDE GPOSS and PU coatings after they were abraded with steel wool for 20 and 2 times, respectively.

The facile photocuring of GPOSS and the superior mechanical properties of the GPOSS coating prompted us to endow anti-smudge properties to it. Previously, anti-smudge coatings were prepared via the lotus-leaf approach,^[21-29] the pitcher plant approach,^[30-31] monolayer grafting,^[32-34] and the preparation of an NP-GLIDE coating that contained in its matrix **nanopools** of a **grafted lubricating ingredient** for **de-wetting enablement**.^[3-4, 35-37] In the lotus-leaf approach, low-surface-tension rough coatings are produced to allow air to be trapped between protrusions under a test liquid. Such coatings feature high liquid contact angles and low droplet sliding angles, but they normally lack optical clarity and wear resistance.^[23] Meanwhile, the void spaces in a rough coating are over-filled in the pitcher plant approach with a lubricant and an immiscible test liquid readily slides on the lubricant due to a low friction coefficient between the two liquids.^[30-31] Unfortunately, this approach may suffer from lubricant loss with coating usage. In the third approach, a monolayer of a low surface-tension liquid polymer is grafted onto a smooth solid surface to convert

it into a liquid-like low-friction one, facilitating test liquid sliding and contraction.^[32-33] In the NP-GLIDE coating approach, a low-surface-tension liquid such as PDMS is incorporated into a coating formulation as a graft copolymer that consists of a reactive coating precursor bearing one or more PDMS side chains.^[3-4] The use of a graft copolymer prevents the macrophase separation of PDMS from the coating matrix and enables PDMS dispersion as nanopools. Since the diameters of these pools are much smaller than the wavelength of light, the high optical clarity of the base coating is retained. Further, the spontaneous enrichment of the PDMS chains on the surface during coating formation provides a low-surface-tension and low-friction liquid-like PDMS monolayer (Scheme 1e). In this study, the NP-GLIDE coating approach was used to prepare a highly transparent anti-smudge coating by incorporating GPOSS-*g*-PDMS, GPOSS coupled with a PDMS chain, into the GPOSS base coating.

To prepare GPOSS-*g*-PDMS, PDMS_{2k}-NH₂ (Scheme 1d) and GPOSS were heated at 110 °C in butyl acetate for 1.5 h at a molar ratio of 3.5/100. Here the subscript 2k denotes a number-average molar mass (M_n) of 2.0 kDa for PDMS-NH₂. GPOSS-*g*-PDMS_{2k} was used because coatings containing GPOSS-*g*-PDMS_{1k} did not have sufficient anti-smudge properties and PDMS-NH₂ of a higher molecular weight was not commercially available. For GPOSS-*g*-PDMS_{2k} preparation, a low PDMS_{2k}-NH₂/GPOSS molar ratio was used to avoid the attachment of two or more PDMS chains to one GPOSS molecule. The grafting of two or more PDMS_{2k} chains onto one GPOSS molecule might shield the residual glycidyl groups, inhibiting their reaction with other GPOSS molecules. Moreover, the number of the reactive epoxide rings per GPOSS molecule would be reduced. Both factors would weaken the bonding between GPOSS-*g*-PDMS and the other GPOSS molecules. While the use of the large GPOSS/PDMS_{2k}-NH₂ molar ratio yielded a mixture of GPOSS and GPOSS-*g*-PDMS_{2k}, this situation was not a concern because the amount

of GPOSS-*g*-PDMS_{2k} required for superior anti-smudge properties was low and GPOSS would be added into a pure GPOSS-*g*-PDMS_{2k} sample, if the latter could be synthesized, for coating preparation anyhow. Lastly, the reaction temperature and duration were optimized to minimize epoxide ring opening by hydroxyl groups that were generated from epoxide ring opening by the amine group of PDMS-NH₂.

¹H NMR spectroscopy and size exclusion chromatography (SEC) were used to confirm the occurrence of the targeted reaction. Figure 2a compares the ¹H NMR spectra of GPOSS and the reacted mixture of GPOSS and GPOSS-*g*-PDMS after the unreacted PDMS_{2k}-NH₂ was removed via precipitation in acetonitrile, a good solvent only for GPOSS (SI). While no noticeable changes were detected in the other peaks due to the low molar ratio of GPOSS-*g*-PDMS_{2k} in the final GPOSS and GPOSS-*g*-PDMS_{2k} mixture, the presence of the new PDMS peak at 0.09 ppm confirmed the synthesis of GPOSS-*g*-PDMS_{2k}. A quantitative analysis yielded a PDMS weight fraction of 4.2% in the mixture.

Figure 2. (a) ¹H NMR spectra and (b) SEC traces confirming the synthesis of GPOSS-*g*-PDMS and (c) FTIR spectra confirming the curing of the anti-smudge coating.

Figure 2b compares size exclusion chromatography (SEC) traces for PDMS_{2k}-NH₂, GPOSS, and the reacted mixture of PDMS_{2k}-NH₂ and GPOSS after the removal of unreacted PDMS_{2k}-NH₂. The SEC trace of the GPOSS sample had two peaks and was broad because the GPOSS sample

was not pure $[\text{RSiO}_{1.5}]_8$ but contained $[\text{RSiO}_{1.5}]_{10}$ and $[\text{RSiO}_{1.5}]_{12}$, which were caged species containing 10 and 12 silicon atoms, respectively. The $\text{PDMS}_{2k}\text{-NH}_2$ peak was negative due to its lower refractive index than that of the eluent chloroform containing 2.5 vol% triethylamine. The formation of GPOSS-g-PDMS_{2k} was deduced from an increased shoulder intensity on the higher molecular weight (or shorter retention time) side of the SEC trace for the final reacted mixture.

An NP-GLIDE precursor was prepared by mixing pristine GPOSS, the prepared GPOSS and GPOSS-g-PDMS mixture, and the photoinitiator (Scheme 1c) in acetonitrile and propylene carbonate, which were good solvents for GPOSS and the photoinitiator but poor solvents for PDMS. In such solvents, GPOSS-g-PDMS formed micelles and the solution mixture scattered light, exhibiting a bluish tint as seen in Scheme 1e1. The isolation of PDMS in the cores of the micelles was shown to play an important role at least during the early stages of coating formation because it ensured the compatibility of the different components and the formation of smooth coatings.^[3-4] Precursor films were formed by first casting the solution onto a substrate and allowing the solvent to evaporate, and the final coating was obtained after these precursor films were photolyzed (Scheme 1e, 1 $\rightarrow$ 2). In the final coating, the mass fraction of PDMS and initiator were 2.0% and 2.4%, respectively, to ensure that the coating possessed sufficient anti-smudge properties and wear resistance and was facile in crosslinking. We note that increasing the PDMS mass fraction improved the anti-smudge performance at the cost of the wear resistance.

Figure 2c compares FTIR spectra of a coating film before and after photolysis for 5 and 10 min, respectively. While the characteristic peak at 915 cm^{-1} for the epoxy groups disappeared, the C-O-C stretching peak of ethers at 1100 cm^{-1} emerged after 5 min of irradiation. The intensities of these peaks did not change further when the irradiation time was extended to 10 min. Therefore, the cationic ring-opening polymerization was complete within 5 min and was indeed facile.

However, the tested coating samples were still photolyzed for 10 min to ensure proper curing. Further, an O-H stretching peak at 3426 cm^{-1} emerged after coating curing and the hydroxyl groups were probably formed during the cationic ring-opening polymerization of the epoxides due to chain growth via the activated monomer mechanism.^[9]

The incorporation of 2.0% (m/m) of PDMS did not weaken the wear resistance of the coating. Figure 1c also displays force-loading, -holding, and -removing curves, which were obtained from a nano-indentation experiment, for the NP-GLIDE GPOSS coating. The curves for the GPOSS and NP-GLIDE GPOSS coatings were essentially identical. In another experiment, the NP-GLIDE GPOSS coating was abraded 20 times with steel wool at an average pressure of 13.0 kPa using an apparatus shown in Figure 1d and Figure S1. No scratches were visible in the SEM image of this coating (Figure 1e). On the other hand, wearing tracks were clearly visible on the control PU or NP-GLIDE PU coating mentioned above after it was abraded for only 2 times or one cycle involving moving the steel wool once forward and once backward (Figure 1f). Thus, the new NP-GLIDE GPOSS coating was much more wear-resistant than the NP-GLIDE PU coating.

We note that the calculated pressure of 13.0 kPa was probably much lower than the actual pressure experienced by the coating. The steel wool was unlikely to make a full contact with the coating as was assumed in the pressure calculation. Rather, only certain protruded regions of the wool contacted the coating and exerting much higher localized pressures.

Aside from its remarkable wear resistance, the NP-GLIDE GPOSS coating was highly flexible. When this coating was cast onto a PET film, the resultant film could be bent without damage into a tube shape or a shape possessing a U cross-section (Figure 3a).

Figure 3. (a) Flexibility and (b-e) anti-smudge properties of the NP-GLIDE GPOSS coating. While water was marked in (b) with a blue dye, hexadecane was marked in (c) with a red dye. Frame (d) shows red ink patches after the contraction of the original ink stroke and frame (f) shows snapshots of green paint immediately and 20 s after application of glass plates bearing and not bearing an NP-GLIDE GPOSS coating, respectively.

The PDMS-containing GPOSS coating also possessed other anticipated properties. First, PDMS enriched itself on the coating's surface as confirmed by an X-ray photoelectron spectroscopic (XPS) analysis (Table S1 in the SI). Moreover, PDMS was found by atomic force microscopy to segregate from the coating matrix and form pools that had diameters of < 15 nm (Figure S4 in the SI). Additionally, tests liquids with room-temperature surface tensions $\gamma > \sim 22$ mN cleanly and readily glided off the coating at low substrate tilting angles (Table S2 in the SI). For example, 5 μ L droplets of methanol ($\gamma = 22.7$ mN/m) and decane ($\gamma = 23.8$ mN/m) had sliding angles (SAs) of $8 \pm 1^\circ$ and $3 \pm 2^\circ$, respectively, on the coating. Lastly, the coating had superior

optical clarity in the visible region of the light spectrum. While Figure S2 shows that the transmittance of a 50- μm -thick coating was higher than 98% between 450 nm and 800 nm, Figure S3 shows that light transmittance at 500 nm was essentially unchanged from $99 \pm 1\%$ to $98 \pm 1\%$ as the coating thickness increased from 10 to 100 μm .

Figure 3 further exemplifies the anti-smudge performance of the NP-GLIDE GPOSS coating. A dyed blue water droplet and red hexadecane droplet were seen to cleanly glide down the coating in Figures 3b and 3c, respectively. Figure 3d shows ink puddles left from the contraction of a uniform ink trace that was initially applied with a red marker. This behavior was mirrored by that of a film of spray-paint in Figure 3e. Initially, the paint covered the entire coating surface. Due to the high repellency of the coating and facile movement of the paint on the liquid-like PDMS surface, the paint contracted over 20 s into disperse thick puddles or flowed off the coated glass plate, exposing uncovered regions.

The high wear resistance of the GPOSS base coating ensured that the NP-GLIDE GPOSS coating would possess robust anti-smudge properties. Table 1 lists the SAs and contact angles (CAs) of water and hexadecane droplets on the NP-GLIDE GPOSS and NP-GLIDE PU coatings after abrasion with steel wool for different durations at an average pressure of 13.0 kPa. After 200 abrasion runs or 100 abrasion cycles, the SA of hexadecane barely changed on the NP-GLIDE GPOSS coating. In contrast, hexadecane lost its ability to cleanly slide but left a streak on the NP-GLIDE PU coating after the coating was abraded only 20 times.

In the case of water, the droplet was pinned by the NP-GLIDE PU coating after it had been subjected to only 30 abrasion runs. In contrast, the NP-GLIDE GPOSS coating retained its water sliding capabilities after it was abraded 200 times.

Table 1. Changes of in the contact angles and sliding angles of water and hexadecane droplets on NP-GLIDE PU and GPOSS coatings as a function of the abrasion cycles with steel wool.

Abr. Runs	Water CA (°) ^a		Hexadecane CA (°) ^a		Water SA (°) ^b		Hexadecane SA (°) ^a	
	PU	GPOSS	PU	GPOSS	PU	GPOSS	PU	GPOSS
0	101 ± 1	99 ± 2	33 ± 1	30 ± 1	23 ± 1	28 ± 1	2 ± 1	10 ± 2
10	100 ± 1	98 ± 2	33 ± 1	32 ± 1	42 ± 2	30 ± 2	3 ± 1	10 ± 1
20	98 ± 1	96 ± 1	-	32 ± 1	46 ± 1	32 ± 2	spread	8 ± 2
30	-	94 ± 2	-	30 ± 1	pinned	32 ± 2	-	10 ± 1
100	-	85 ± 2	-	25 ± 2	-	36 ± 2	-	10 ± 2
200	-	78 ± 2	-	21 ± 2	-	45 ± 2	-	10 ± 2

^a: Measured using a droplet volume of 5 μ L. ^b: Measured using a droplet volume of 15 μ L.

The initial CAs were higher and the SA angles were lower on the NP-GLIDE PU coating than on the NP-GLIDE GPOSS coating because both the molecular weight and the mass fraction of the low-surface-tension PDMS polymer used in the PU coating were higher. At a higher molecular weight of 5.0 kDa and a higher bulk mass fraction of 6.0% (m/m) for PDMS, the surface of the PU coating should be better covered by PDMS. Despite this difference, the NP-GLIDE GPOSS coating possessed superior repellency against ink and paint.

We further tested the effect of coating flexing on its anti-smudge properties. A square section of the coating on a PET film was folded into a shape possessing a U cross-section and an end-to-end distance of ~ 0.8 cm (Figure 3a) and released. After this bending cycle was repeated 500 times, no noticeable degradation in ink contraction capabilities was observed (Figure S6). Thus, the anti-smudge properties were not affected by the bending of the coating.

In conclusion, we have demonstrated the high flexibility and wear resistance of a coating that was prepared from a commercial precursor GPOSS. The coating can be photocured in one step within 5 min. Through the incorporation of PDMS into the coating via the use of GPOSS-*g*-PDMS_{2k}, an NP-GLIDE coating was produced. At a thickness of 100 μ m, this coating had a transmittance of $98 \pm 1\%$ at 500 nm. Test liquids such as decane and methanol with surface

tensions higher than ~ 22 mN/m readily and cleanly glided off this coating at low substrate tilt angles. Meanwhile, complex liquids such as ink and paint readily contracted on this surface. The coating bore no wearing tracks observable by SEM after it was abraded with steel wool for 20 times at an average pressure of 13.0 kPa and this film retained its liquid sliding properties even after being abraded 200 times with steel wool. The anti-smudge properties were not affected after it was subjected to 500 cycles of a bending test involving folding a square coating on a PET substrate into a shape with a U cross section. Such wear resistance is unprecedented among prior examples of NP-GLIDE coatings. While the design principle may be extended for the development of coatings from other types of organic/inorganic nanoclusters,^[38] the current coating may already have practical applications.

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TOC Graphic and Description

A coating that is transparent, flexible, anti-smudge, and resistant to wear by steel wool has been developed. This coating is readily prepared by photolyzing a mixture of a commercial precursor glycidyloxypropyl polyhedral silsesquioxane (GPOSS) and GPOSS-*g*-PDMS (which denotes GPOSS bearing a poly(dimethyl siloxane) side chain) for 5 to 10 min

Keywords: Coating, omniphobicity, wear resistance, POSS, and ring-opening polymerization

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