Journal of
Materials Chemistry A

ROYAL SOCIETY
OF CHEMISTRY

PAPER

Cite this: DOI: 10.1039/c3ta15017h

Development of sol–gel processed semi-transparent and self-cleaning superhydrophobic coatings†

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Received 4th December 2013
Accepted 20th January 2014

DOI: 10.1039/c3ta15017h

www.rsc.org/MaterialsA

Optically transparent, mechanically durable, and self-cleaning superhydrophobic coatings are greatly awaited for applications in daily life. An attempt has been made to develop sol–gel processed semi-transparent, durable and self-cleaning superhydrophobic coatings on glass using a silica–PMMA composite. A water drop acquires a near spherical shape on the coating exhibiting a water contact angle of ~159° and immediately rolled off under small disturbance. A 10 μl water drop could individually collect around 10 mg of dirt particles along the way whilst rolling off the coating surface. The superhydrophobicity of the coatings remained intact under the impact of a water jet. A water jet hits the superhydrophobic coating and was repelled straightaway off the surface, without leaving any trace of water. These coatings showed both strong superhydrophobicity and superoleophilicity. We observed an improvement in mechanical stability, as well as optical transparency of the coatings in the visible range (R#3, Issue#1) after low loadings of PMMA polymer (2 vol%) in silica. The prepared coatings maintained excellent superhydrophobicity even after 6 months storage under normal conditions in air.

1. Introduction

'Perfect mimicry' is always impossible in both the arts and sciences. Excellent self-cleaning superhydrophobic surfaces exhibiting a high water contact angle (≥150°) and low roll off angle (≤10°) have been developed by mimicking the surface micro/nanostructure and chemical composition of lotus leaves.[1] However, perfect mimicry of the extent of surface non-wettability, lifelong durability, self-healing of the surface micro/nanostructure and chemical composition after mechanical damage, and superior self-cleaning properties of lotus leaves on artificial superhydrophobic surfaces is a tough mission for the scientists working in this challenging research field. In order to use superhydrophobic coatings in applications in daily life, the demands of both a high optical transparency and mechanical durability for the superhydrophobic coatings should be provided. To combine both high optical transmission as well as mechanical durability in superhydrophobic coatings is the main challenge because to develop superhydrophobic surfaces, surface roughness is one of the most important parameters, in conjunction with low surface energy which modifies the interaction of the liquid with solid.[2–4] On such rough superhydrophobic surfaces, the interfacial contact area between the solid and liquid is very low and water drops roll over the surface effortlessly, collecting the dust particles along the way and leaving no water trace behind. However this high surface roughness is again the main obstacle between transparency and durability of the superhydrophobic coating. A highly rough surface can be semi-transparent or opaque due to the extent of light scattering and also the rough surfaces are brittle, which can easily be damaged by little applied force.[5] For this reason, it is difficult to utilize highly rough superhydrophobic surfaces in daily life applications. The light scattering from the surface can be extensively reduced only when the scale of surface roughness is smaller than the wavelength of light. The surface with a roughness value less than 400 nm can be highly transparent towards visible light (R#3, Issue#1). Subtracting the durability and transparency value from the superhydrophobic coatings will always give a lower value of the coating. Such surfaces can be applied only where the transparency is a secondary interest, for a short time duration and in the damage-free areas.

Today superhydrophobic surface research is moving towards more practical concerns. Transparent and durable superhydrophobic coatings can be applied to outdoor road convex mirrors, traffic indicators, side mirrors, indicators and front windshields of automobiles, window and door glasses of the buildings, and also on various metals for anti-corrosive applications.[6–11] Polymers with excellent film-forming properties, natural hydrophobicity, remarkable optical transparency,

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ta15017h

toughness and flexibility are the material of choice for the design and development of transparent and durable superhydrophobic surfaces.[12] The addition of polymer even at low loadings in the inorganic phase can improve the overall properties of the composite coating, especially the mechanical durability and optical transparency of the coatings. Recently, Park *et al.*[13] developed transparent superhydrophobic films by modifying silica nanoparticles with hydrophobic polydimethylsiloxane (PDMS) layers using a thermal evaporation process and dispersing and pressing them on the adhesive surface. Xu *et al.*[14] described the synthesis of raspberry-like SiO_2/polystyrene (PS) particles by introducing methacryloxypropyltrimethoxysilane (MPS)-functionalized SiO_2 particles into the radiation mini-emulsion polymerization of styrene. The films prepared from these raspberry-like SiO_2/PS particles exhibited a high water contact angle, however, and showed a large contact angle hysteresis and strong adhesion to water. Du *et al.*[15] prepared time-saving superhydrophobic porous polymer coatings on a variety of substrates using the anionic polymerization accompanied by the phase separation of poly(2-octyl cyanoacrylate) upon treatment with a water–ethanol mixture. However, the coatings were white in color and showed weak mechanical stability due to the highly porous microstructure of the polymer. In our present work, we observed that the superhydrophobic coating prepared from a small quantity of Poly(methylmethacrylate) (PMMA) polymer in sol–gel processed silica sol exhibited better optical transparency and scratch resistance. Although the optical transparency was improved, the mechanical durability of the coatings was decreased by further raising the quantity of PMMA in the silica network. An easy and straightforward method to develop semi-transparent, durable and self-cleaning superhydrophobic coatings has been proposed in this paper.

Now-a-days, superhydrophobic surface research is moving towards more practical concerns. Transparent and durable superhydrophobic coatings can be applied on outdoor road convex mirrors, traffic indicators, side mirrors, indicators and front windshields of automobiles, window and door glasses of buildings, and also on various metals for anti-corrosive applications.[6–11] Polymers, with their excellent film-forming properties, natural hydrophobicity, remarkable optical transparency,

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2. Experimental

2.1. Materials

Methyltrimethoxysilane (MTMS, 98%), poly(-methylmethacrylate) (PMMA, $M_w \sim 120\,000$), and *N*,*N*-dimethylformamide (DMF, ≥99.9%) were purchased from Sigma Aldrich, USA. Ethanol (99.9%), ammonia solution (28%) and Oil Red O (154-02072) were obtained from Wako Pure Chemical Industries Ltd, Japan. Methylene Blue (M0501) was purchased from Tokyo Kasei Kogyo Co. Ltd, Japan. Glass micro slides (Matsunami, S1127) were obtained from Glass Ind. Ltd, Japan.

2.2. Preparation of the superhydrophobic coatings

At first, 2 ml of doubly distilled water and 1 ml of ammonia solution was added to 20 ml of ethanol under constant stirring. After 1 hour of stirring, 2 ml of MTMS was added drop-wise into it and the mixture was stirred for another 3 hours. Meanwhile, a 10 mg ml^{-1} of PMMA solution in DMF was prepared. 2, 4 and 6 vol% of PMMA in the above prepared silica sol were prepared and kept stirring overnight. The pre-cleaned glass substrates were dip-coated with a dipping rate of 5 mm s^{-1} and withdrawal rate of 2 mm s^{-1}. The deposition time was varied from 1, 15, 30 and 45 minutes. The coating on the glass substrates was performed on only one side by placing adhesive tape on the other side, which was removed after the coating. All of the above experiments were carried out at room temperature (~25 °C). Finally, the dip-coated substrates were dried at room temperature for 1 hour and annealed at 250 °C overnight with a ramping rate of 2 °C min^{-1}.

2.3. Characterization techniques

The surface microstructure of the coatings was analyzed by Field Emission Scanning Electron Microscope (JEOL, JSM-7600F). The surface chemical analysis of the coatings was performed by Energy Dispersive X-ray (EDX) (JEOL, EX-64235 ACSW) using the sample area of ~100 μm^2. The chemical compositions of the coatings were studied by Fourier transform infrared spectroscopy (FT-IR, JASCO, FT/IR-6100). The surface topography and roughness of the prepared coatings were analyzed by laser microscopy (KEYENCE, VK-X200 series). The surface roughness of the coatings were measured at 50 × 50 μm^2 planar in non-contact mode. The surface roughness of each of the coatings was measured for at least six different positions and the average was reported as the final value. The optical transmission of the coatings was measured by a UV-VIS spectrophotometer (JASCO, V-670). The optical photographs and videos were recorded using a Canon Digital Camera (G 15 series). The water contact angles were measured over five different positions on the samples and an average value was adopted as a final value using a contact angle meter (KYOWA, model DM-301). The scratch resistance of the coatings was tested by using a Scratch tester (Nano-Layer Scratch Tester, CSR-2000). The maximum force required to scratch/remove the coating material from the glass substrate was checked on at least 10 different positions on the coatings and an average value was reported as the final force value.

3. Results and discussion

3.1. Surface microstructure of the coatings

Among all the coating compositions, the coatings prepared with 2 vol% of PMMA in silica exhibited the highest water contact angle for 30 min of deposition time. Fig. 1 depicts the SEM images of the coatings prepared with different deposition times of 1 to 45 min from 2 vol% of PMMA in silica. The coating prepared from 1 min deposition time showed weak coverage of the coating material over the surface. The coating is not uniform and the porous structure was not well interconnected (Fig. 1a). This deposition time is not sufficient to achieve a superhydrophobic surface. For the deposition time of 15 min, the coating started to grow over the substrate area with a porous domain-like structure over the surface and some large sized voids between the surfaces (Fig. 1b). This morphology could not trap the air and even the air present in these big voids could be easily replaced by water during water contact angle measurements and the water drop acquires the Wenzel state.[16] After 30 min of deposition, the coating showed a porous interconnected solid layer with micrometer scaled voids present in between the structure (Fig. 1c). The presence of such micrometer scaled voids could easily trap the air and water could sit on the layer of air in the Cassie–Baxter state.[17] Further increase in the deposition time to 45 min shows that the voids and rough structure developed at 30 min of deposition time is filled out after a prolonged deposition time (Fig. 1d) and it could act as a relatively smooth surface, as compared to the surface prepared from 30 min deposition time.

The surface morphology of the coatings prepared from 30 min of deposition time from all the coating compositions from 0, 2, 4 and 6 vol% of PMMA in silica are shown in Fig. 2. Fig. 2a shows a dense and porous surface morphology with a few micro-cracks over the surface of the silica coating (0 vol% PMMA in silica). A coating prepared with 2 vol% of PMMA in silica sol shows a rough, porous, interconnected solid layer structure with many voids (Fig. 2b). These voids and the rough structure seem to be covered and filled by the addition of more PMMA content in the coating structure, resulting in a relatively smoother and porous surface morphology (Fig. 2c and d).

The 3-D laser microscope images of all the coating compositions are shown in Fig. S1 and S2† (ESI). The coatings prepared from 2 vol% of PMMA in silica with 1, 15 and 30 min deposition time showed an increase in the surface roughness values from 166, 201, and 376 nm, respectively, whereas, the 45 min deposited coatings showed a decrease in the surface roughness of 185 nm, confirming the rough microstructure filling after a prolonged deposition time. The coatings prepared from 0, 2, 4 and 6 vol% of PMMA in silica with 30 min of deposition time showed a slow decrease in the surface roughness of 318, 376, 345 and 310 nm, respectively, confirming the rough microstructure filling by smooth PMMA polymer.

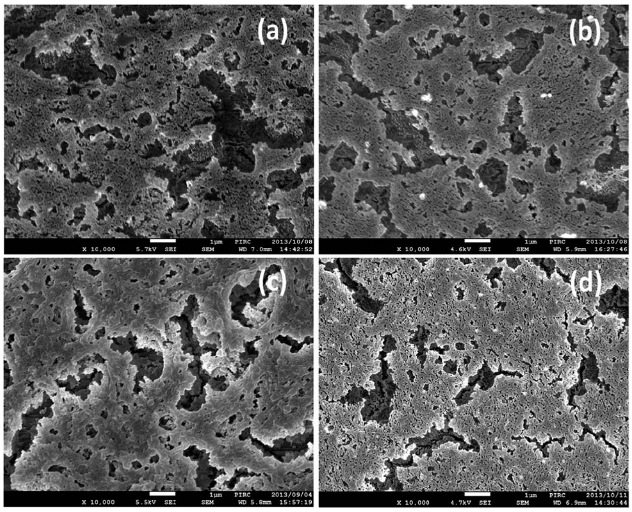

Fig. 1 SEM images of the coatings prepared from 2 vol% of PMMA in silica at deposition times of (a) 1, (b) 15, (c) 30, and (d) 45 min.

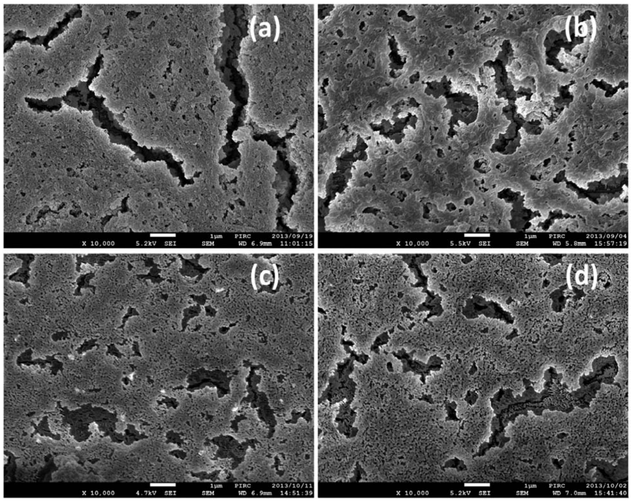

Fig. 2 SEM images of the coatings prepared with a 30 min deposition time from (a) 0, (b) 2, (c) 4, and (d) 6 vol% of PMMA in silica.

3.2. FT-IR And EDX studies

The FT-IR spectra of the MTMS, PMMA and MTMS–PMMA composites are shown in Fig. S3† (ESI). In the FT-IR spectra of MTMS, the two associate absorption peaks arise from the Si–O–Si groups at 1032 and 1131 cm^{-1} that are in cyclic and linear molecular sub-structures.[18] The absorption band observed at 782 cm^{-1} is attributed to the Si–C bond, whereas the peaks observed at around 1270 and 1411 cm^{-1} can be assigned to the bending of C–H bonds and 2969 cm^{-1} can be assigned to the stretching of the C–H bonds.[19] The peak observed at around 1640 cm^{-1} and the broad absorption band at around 3450 cm^{-1} are due to the presence of hydroxyl groups.[20] The FT-IR spectra of the PMMA shows the C–O–C stretching vibration, confirmed by the absorption bands arising between 1150 and 1250 cm^{-1}. The absorption bands observed near 843, 976 and 1065 cm^{-1} are attributed to the specific absorption vibration of PMMA. The α-methyl group vibrations could be assigned to the two absorption bands observed at 754 and 1386 cm^{-1}. The existence of the acrylate carboxyl group was confirmed by the absorption band observed at 1725 cm^{-1}. The absorption band near 1442 cm^{-1} confirms the bending vibration of the C–H bonds of the methyl group. The two bands at 2997 and 2952 cm^{-1} can be attributed to the C–H bond stretching vibrations of the $-CH_3$ and $-CH_2-$ groups, respectively.[21] In the FT-IR spectra of 2 vol% PMMA in silica, the absorption peaks related to both MTMS and PMMA are clearly observed confirming the formation of the silica–PMMA composite. The surface chemical analysis of the superhydrophobic coating prepared from 2 vol% PMMA in silica by EDX shown in Fig. S4† (ESI) confirms that the surface contains the elements silicon, oxygen and carbon.

3.3. Wetting and optical properties of the coatings

The surface wettability of the coatings was evaluated by the water contact angle measurements (Fig. 3). All the coatings showed a gradual increase in the water contact angles with increasing the deposition time up to 30 min, whereas the water contact angles of all the coatings decreased, respectively, above the deposition time of 30 min. The coatings prepared with the deposition time of 30 min time showed the highest water contact angles for each coating composition. A pure silica coating exhibited a water contact angle of ~149°, nearly in a superhydrophobic state. This is due to the MTMS precursor used in the sol–gel process having one non-hydrolysable methyl group and three other methoxy groups getting hydrolyzed and forming the porous network structure. However, the water contact angle decreases slowly (~146°) above the 30 min deposition time due to the pore filling by silica itself. The coatings prepared from 2 vol% of PMMA in silica exhibited the highest water contact angle of ~159° among all the PMMA–silica coatings. With an increase in the PMMA amount in silica, the water contact angle decreases. This decrease in water contact angle with the increase in the amount of PMMA might be due to the rough structure created by silica particles, which could be reduced by the soft polymer. As the PMMA amount in the silica increases, the optical transmission of the coating in the visible range (R#3, Issue#1) is also enhanced (Fig. 4). This might be due to the coverage of rough scattering centers for light by the soft polymer.

In the sol–gel process, an optimum time is required to grow the rough structure on the substrate. At lower deposition times, the coating was not grown evenly and homogeneously on the substrate, and still shows a higher water contact angle around 140°. These lower deposition times are not enough to achieve a superhydrophobic surface. It is observed that for all compositions, 30 minutes deposition time is optimum to create a rough microstructure, whereas, a prolonged deposition may fill the rough microstructure and may act as a relatively smooth surface. However, as the PMMA is intrinsically hydrophobic in nature, the water contact angle could not decrease below 140° for all the coating compositions. Here, we observed two types of wettability switching, one is from the Wenzel to Cassie–Baxter state from 1 to 30 minutes of deposition time, which might be due to the formation of rough microstructures and again from the Cassie–Baxter to Wenzel state, above the deposition time of 30 minutes (~45 minutes), which might be due to the filling of the rough microstructures by polymer, which can act as a comparatively smooth surface.

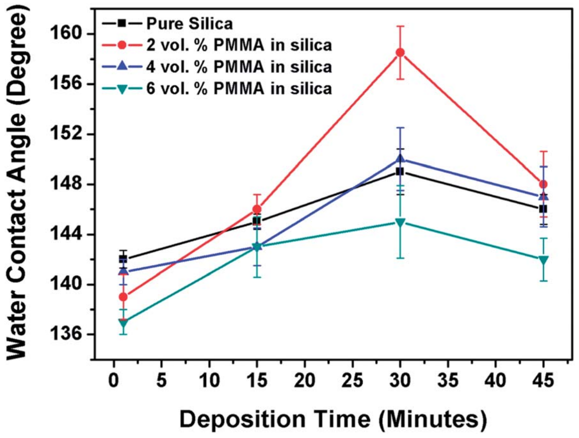

Fig. 3 Water contact angles of the coatings prepared from 0, 2, 4 and 6 vol% of PMMA in silica at deposition times of 1, 15, 30, and 45 min.

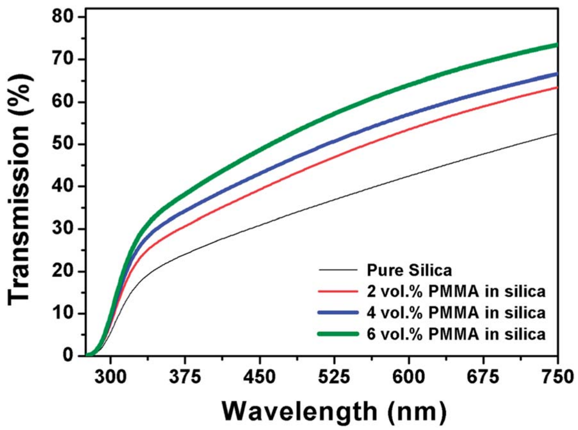

Fig. 4 Optical transmission spectra of the coatings prepared from 0, 2, 4 and 6 vol% of PMMA in silica at the deposition time of 30 min.

Fig. 5(a) shows the optical images of 10 μl water drops on semi-transparent superhydrophobic coating prepared from 2 vol% of PMMA in silica at a deposition time of 30 min. Some of the water drops were colored blue using methylene blue for better optical clarity of the drops. The 10 μl water drops acquire an almost spherical shape and roll off the surface under small disturbances. The drops maintained their spherical shape for a long time of almost 1 hour. Due to the water evaporation effect, the water drop volume decreases after staying constant for long time. During constant water evaporation (after 1 hour), the contact line of water drop reduces and water might intrude slowly inside the rough microstructure, which results in sticky water drops on the coating surface, which may not fall down or roll off even after tilting for 90° or holding upside down. The porous surface microstructure prepared from the hydrophobic materials usually shows superhydrophobic behavior, whereas these surfaces can be easily wetted by non-polar liquids due to the large internal volumes which provide a high surface for interaction.[5] The hexane was colored red by Oil Red O and 10 μl of hexane was dropped on the coating surface, which immediately (in fractions of a second) spreads on the surface Fig. 5(b) with a hexane contact angle of almost 0°. So the prepared coatings showed both superhydrophobic and superoleophilic behavior.

We placed a big volume of water drops (~2 ml) on the superhydrophobic coatings. Initially, at around 10 μl volume of water drops, they acquire a ball-like spherical shape, but the continuous addition of water makes this water drop look like an elliptical shape (Fig. 6a). This big volume of water drops hardly stays on the coating surface. In Fig. 6b, the blue colored water spreads completely on the non-coated glass substrate (right part of the substrate), whereas the water drop acquires an elliptical shape on the coating surface. This transformation of spherical shape at a low volume to an elliptical shape at a high volume of the water drops is simply due to the effect of gravity. As shown in Fig. 6c, the superhydrophobic coating was placed in the middle of a glass petri dish and blue colored water was slowly poured in the petri dish. The water acquires all the volume in the petri dish, but could not easily pass on the top of the superhydrophobic coating. The water acquires a height of nearly 5 mm around the boundaries of the superhydrophobic coating forming an air column. This state was maintained overnight. We placed a water drop in the middle of the superhydrophobic coating after many attempts, which involved rolling off and mixing in with the blue colored water. This confirms that the superhydrophobic surface strongly repels water and always remains dry.

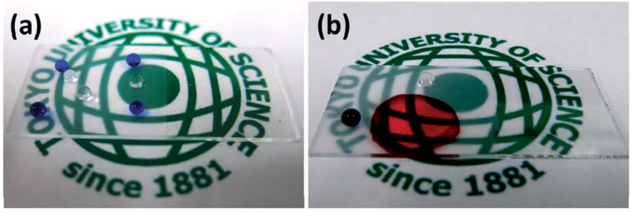

Fig. 5 Images of the semi-transparent superhydrophobic coatings prepared from 2 vol% of PMMA in silica at a deposition time of 30 min, (a) spherical water drops and (b) the superoleophilic behavior of the coating.

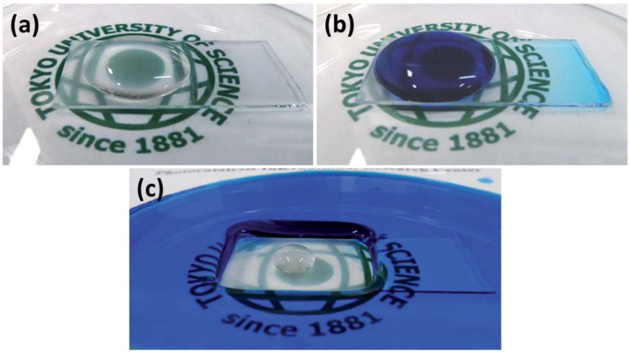

Fig. 6 Images of the semitransparent superhydrophobic coatings prepared from 2 vol% of PMMA in silica at a deposition time of 30 min, (a and b) big volume water drops and (c) the formation of an air-column on the superhydrophobic surface.

3.4. Self-cleaning behavior

Lotus leaves always stay dirt-free due to their self-cleaning behavior. Water drops roll off lotus leaves at small tilt angles collecting dirt particles along the way. To confirm the self-cleaning ability of the superhydrophobic coatings, we spread about 50 mg of Oil Red O powder as dirt particles on the coating. As shown in Fig. 7, the three water drops of 10 μl of volume were placed on the coating and slowly rolled back and forth over the surface in order to collect the dirt particles. These three water drops could collect almost 40 mg of dirt particles. The water drops were fully covered by the dirt particles and there is no space to collect the extra remaining dirt particles. The dirt particles remained attached to the water drops without detaching to the surface. In the detailed self-cleaning experiment, we put five water drops of 10 μl volume, which cleaned the coating surface totally and no dirt particles were observed as being left behind on the surface. As we rolled the water drops over the surface, dirt particles were easily adsorbed on the water drops, efficiently detaching from the coating surface. In this

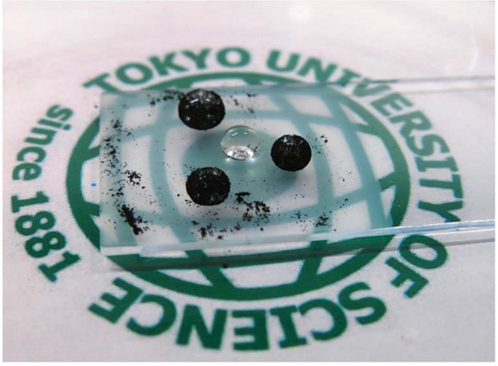

Fig. 7 The self-cleaning behavior of the superhydrophobic coatings prepared from 2 vol% of PMMA in silica at a deposition time of 30 min.

case, each water drop collects at least 10 mg of dirt particles from the superhydrophobic surface. The water drops surrounded by dirt particles showed no change in spherical shape.

3.5. Stability of the coating under the impact of a water jet

The stability of the self-cleaning superhydrophobic coating, especially the surface microstructure under the impact of a water jet is of critical interest. For many superhydrophobic coatings, their micro/nanostructure, as well as surface wettability, is disturbed/distracted under the impact of a water jet and/or drop impact test.[22–24] The air trapped in the rough micro/nanostructures of superhydrophobic coatings can be squeezed out by the impact of a water jet. In our study, a 25 ml syringe was completely filled by the blue colored water and a jet of water was produced under normal force (Fig. 8). This water jet was kept 2–3 cm above the sample surface by making an angle of nearly 45° and directed over all of the coating surface for almost 1 minute (with a syringe pressing rate of $\sim$1 mm s^{-1}). We observed no surface damage, which was confirmed by water contact angle measurements, showing no change in surface wettability. A short video clip of the water jet impact on the superhydrophobic coating is shown in the ESI.† The water jet hits the coating surface and is immediately repelled off by forming an angle. If the surface microstructure is weak, then the impacted water jet may disturb/damage the coating and water may be accumulated over the surface instead of being repelled off. These water jet experiments were repeated again and again for the duration of 1 minute and no damage was observed over the coating, which shows the stability of the surface microstructure. We also checked the SEM image after the water jet impact treatment as shown in Fig. S5† (ESI), which showed no substantial change in surface morphology and also the surface roughness values remained unchanged.

3.6. Scratch resistance property of the coating

The durability of the coatings under mechanical force was studied using a scratch tester which is shown in Fig. S6† (ESI). The pure silica coating showed poor mechanical stability and coating material was removed by applying a force of $\sim$1.1 mN. Whereas, a small loading of PMMA in silica showed better durability against mechanical force. A coating prepared from 2 vol% of PMMA in silica showed improved scratch resistance and the coating material was removed at an applied force of $\sim$2.8 mN, which is more than two times compared to the pure silica coating. However, the further loading of PMMA in silica reduces the mechanical stability and the force required to scratch the 4 and 6 vol% of PMMA in silica coating to 1.9 and 1.6 mN, respectively. The polymer rich surfaces can be easily scratched. The decrease in mechanical stability with the increase in polymer concentration may be due to the minimization of the surface roughness of the coating by a soft polymer, which can be easily scratched away from the surface. So the optimum material should be obtained between the inorganic silica phase and polymer to get improved mechanical stability of the coating, which in our case was the coating prepared from 2 vol% of PMMA in silica. The wettability, as well as durability of these superhydrophobic coatings, is intact under normal circumstances in air for a period of more than 6 months.

Fig. 8 Water jet impact study on the superhydrophobic coatings prepared from 2 vol% of PMMA in silica at a deposition time of 30 min.

4. Conclusions

The semi-transparent and self-cleaning superhydrophobic coatings have been successfully prepared. The coatings showed improved hydrophobicity, scratch resistance and optical transparency under a small loading of PMMA polymer in silica. The water drop acquired a spherical shape on the superhydrophobic coating with a contact angle as high as 159°, which immediately rolled off easily under small disruption. The hexane drops were immediately spread out on the surface showing strong superoleophilic behavior. The dirt particles accumulated on the surface were easily cleaned away by the action of rolling water drops. The wettability, as well as surface microstructure, was not affected under the impact of water jet. These coatings could find potential applications in optical industries.

Acknowledgements

This research work is supported by the Japan Society for the Promotion of Science (JSPS) Postdoctoral Fellowship Program for Foreign Researchers (ID: P13067).

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