Investigation of the Effects of Component Ratios on the Properties of Superhydrophobic Polyurethane/Fluorinated Acrylic Co-Polymer/SiO$_2$ Nanocomposite Coatings

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Abstract: In this work, polyurethane/fluorinated acrylic co-polymer/silicon dioxide (PU/FAP/SiO$_2$) hybrid superhydrophobic coatings were fabricated on glass substrates via a simple one-step coating process. The effects of each coating component on the coating properties were systematically investigated. The optimized coating exhibits a water contact angle (WCA) of 159° and a rolling angle of 3°. Meanwhile, the coating has an optical light transmittance of 88%, indicating the good transparency of the coating. Besides, the coating demonstrates an adequate level of abrasion resistance. After a total abrasion distance of 300 cm against a piece of 800 mesh sand paper, the sample still kept a water contact angle of about 110°, showing its high abrasion resistance. Therefore, the optimized coating has a great potential for practical application.

Keywords: superhydrophobic; nanocomposite; polyurethane; SiO$_2$; transparent

1. Introduction

Inspired by the unique water repelling nature of lotus leaves, superhydrophobic surfaces have been extensively explored for various potential applications, such as anti-fogging, anti-icing, anti-corrosion, oil/water separation, self-cleaning and anti-contamination, etc. [1–7]. Superhydrophobic surface has a water contact angle (WCA) higher than 150° and a water rolling angle less than 10°. In general, the superhydrophobic surfaces are fabricated by creating rough surface structures on low surface energy materials or utilizing low surface energy compounds to decorate materials with micro/nano-scale hierarchical rough surfaces [8–10]. To date, superhydrophobic surfaces on different substrates including glass, ceramics, metals, polymers, fabrics and etc., have been fabricated through various techniques, such as chemical etching, sol-gel, spraying, dip-coating, spin-coating, chemical vapor deposition and thermal oxidation [11–15]. Nevertheless, the superhydrophobic surfaces are vulnerable when working at high temperatures, in acid/alkali solutions, and under ultraviolet radiation and often of low abrasion resistance, which limits the practical applications of superhydrophobic coatings [16]. Therefore, it is extremely important to design and fabricate high performance superhydrophobic coatings with prolonging lifetime under various harsh working conditions.

It has been reported that polymers with low surface energy, such as polyacrylate (PA) [17,18], polystyrene (PS) [19,20], polyvinylidene fluoride (PVDF) [21,22], poly(dimethylsiloxanes) (PDMS) [23,24], epoxy [25,26], poly(methacrylic acid) (PMAA) [27,28], polyurethane (PU) [29–31], and have been used to fabricate superhydrophobic coatings. However, the water contact angle of these polymers is generally less than 120° on a homogeneous flat surfaces. The incorporation of inorganic nanoparticles, such as SiO$_2$ [32,33], TiO$_2$ [34,35] and ZnO [36,37], can increase the surface roughness of the hydrophobic coatings, therefore, their contact
angles, based on the Wenzel and Cassie-Baxter models, which show excellent water repellence and superhydrophobicity. For example, Satapathy et al. [38] prepared linear low density polyethylene (LLDPE)/SiO$_2$ superhydrophobic nanocomposite coatings by dip-coating technique. The porosity of the coatings was controlled by using phase separation method, the addition of non-solvent ethanol causes phase separation, in which a portion of LLDPE precipitates from the polymer matrix. With more non-solvent ethanol added into the system, more LLDPE precipitates from the polymer matrix, which increases the porosity of the coating. The coating’s WCA was 170° and the sliding angle was 3.8°. Besides, the coatings exhibit good thermal stability and durability as well. Radwan et al. [39] fabricated poly vinylidene fluoride (PVDF)/ZnO superhydrophobic composite coating on Al substrate. The coating shows a WCA of 155° and a WCA hysteresis of 4.5° with good corrosion protection property.

Among various polymers used to prepare superhydrophobic coatings, such as PA, PS, PVDF, PDMS, etc. Polyurethane is considered as one of the promising candidates due to its good optical transparency, stable weatherability and superior mechanical property.

Zheng et al. [31] prepared PMMA-fluorinated SiO$_2$ nanoparticle double layer composite coatings by a two-step spraying deposition method. Firstly, a layer of car refinishing paint was spray on the substrate, and the sample was dried at ambient temperature for 5 min. Subsequently, the PMMA-fluorinated SiO$_2$ nanocomposite coating was sprayed on the sample. Afterwards, the sample was dried at ambient temperature for 2 h to remove any ethanol and water. Although the coating exhibits superhydrophobicity and good abrasion resistance, the optical light transmittance of the composite coating is lower than 80%. In a report by Luo et al. [29], SiO$_2$ nanoparticle dispersion was firstly prepared by a sol-gel method using methyltrimethoxysilane as precursor and methanol as solvent in the presence of oxalic acid and NH$_4$OH as catalyst. Then a two-step dip-coating technique was employed to fabricate the PU/SiO$_2$ double layer composite coating by dipping glass slide in PU solution and SiO$_2$ nanoparticle dispersion. Excellent performance, with a WCA of 162° and a transmittance of 90%, was achieved. However, the process was complex and time consuming. Although significant progress has been made in fabrication of superhydrophobic coatings recently, problems including complex preparation process, harmful reagents used and poor transparency, abrasion resistance and hardness, which limit practical applications of superhydrophobic coatings, remain unsolved. Moreover, for composite coatings, understanding the effects of different components on the coating properties is important for the development of superhydrophobic composite coatings. However, few systematic studies in this field was reported. Moreover, it has been reported that such composite coatings can not only change the wettability of the surface, but also they can induce changes in other properties including thermal and electrical conductivity, which makes them candidates for various applications [40–42].

Herein, we report a facile, one-step dip-coating method to prepare polyurethane/silicon dioxide (PU/SiO$_2$) superhydrophobic coatings on glass substrates. The hybrid coatings exhibit superhydrophobic property with a WCA of about 159° and a rolling angle of less than 3°. In this work a convenient approach to create a mechanically robust and durable superhydrophobic coating with a proper abrasion resistance was developed. More importantly, the influences of the different coating constituents, including PU, ST-200 and SiO$_2$ nanoparticles on surface morphology, hydrophobicity and optical transmittance, were systematically studied.

2. Materials and Methods

2.1. Materials

FAP dispersion (Capstone™ ST-200) was purchased from Guangzhou Jianyi Chemical Import and Export Co., Ltd., Guangzhou, China. SiO$_2$ nanoparticles, AEROSIL R812s with a specific surface area of 195–245 m$^2$/g were obtained from Evonik Co., Ltd. Hanau, Germany. Solvent-based polyurethane resin (PU-166), serving as a binder and host for
the SiO$_2$ nanoparticles, was purchased from Anhui Sinograce Chemical Co., Ltd., Hefei, China. Butanone and toluene were supplied by Dongguan Jibao Petrochemical Co., Ltd., Dongguan, China. Adhesion promoter (BYK-4510) was received from Jiangmeng Dongyang Chemical Co. Ltd. Jiangmen, China. The glass substrates with a size of 90 mm × 90 mm × 2 mm were ordered from GULUO Glass Luoyang, China.

2.2. Coating Preparation

Certain amount of the R812s SiO$_2$ nanoparticles was first dispersed in a solvent mixture of butanone and toluene (with a volume ratio of 50:50) by ultrasonication for 30 min. Secondly, the Capstone™ ST-200 FAP and PU-166 polyurethane (PU) were added to the prepared SiO$_2$ nanoparticle suspension and mechanically stirred for 30 min. Afterwards, the adhesion promoter BYK-4510 was added and stirred mechanically for another 30 min to form a uniform coating solutions.

Before preparing the coating samples, glass substrates were cleaned in acetone, ethanol, and deionized water, respectively, for 10 min, and followed by drying in an oven at 80 °C for 30 min. The composite coatings were fabricated on the glass substrates via a dip coating method, in which the cleaned glass substrates were dipped in the coating solutions and drawn at a speed of 2 cm/s. Finally, the coated samples were cured at 100 °C for 1 h.

Three series of samples with varied contents of SiO$_2$ nanoparticles, PU, and ST-200, respectively, were prepared. The content of the adhesion promoter, BYK-4510, was set at 0.24 wt.% in the coating solution for all the samples. In order to investigate the effects of SiO$_2$ nanoparticle content on the coating properties, samples with different SiO$_2$ nanoparticle contents from 0 to 4 g with an increment of 1 g (denoted as sample R0 to R4, e.g., sample R4 was prepared using a solution containing 4 g of SiO$_2$ nanoparticles every 100 g solution) were prepared. For these samples, the PU was 5.0 wt.% while ST-200 was 2.5 wt.% in the coating solution. Similarly, coating samples with various PU contents from 0 to 10 g (denoted as sample P0 to P10, e.g., sample P5 was prepared using a solution containing 5 g of PU every 100 g solution) and different ST-200 contents from 0 to 10 g (denoted as samples S0 to S10, e.g., sample S5 was prepared using a solution containing 5 g of ST-200 every 100 g solution) were fabricated. For samples with varying PU loadings, SiO$_2$ nanoparticle was 2.0 wt.% while ST-200 was 2.5 wt.% in solution. For samples with different ST-200 contents, SiO$_2$ nanoparticle was 2.0 wt.% while PU was 5.0 wt.% in solution.

2.3. Characterization

The coating surface morphology was observed by Hitachi SU8000 Scanning Electron Microscopy (SEM) Hitachi High-Tech, Japan. Atomic force microscope (AFM, Oxford Instruments Cypher S) (Oxford Instruments, Abingdon, UK) was utilized to measure the surface roughness of the coating. Static and dynamic water contact angle (WCA) measurements were carried out using a JCY-2 contact angle measuring system (Shanghai Ruifang Instrument, Shanghai, China) by carefully applying water droplets (4 µL) onto sample surfaces. The average WCA was determined by measuring the same sample at three randomly chosen area. The coatings’ optical transmittance was tested by a haze meter (WGT-S) (Shanghai Shenguang Instrument, Shanghai, China).

The hardness of the coatings was measured by pencil test based on GB/T 6739 standard, which is conformed to ISO-15184. During the test, sample was placed on a hard and horizontal table surface. The pencil was hold against the coating surface at an angle of 45° and pushed forward for 10 mm at a speed of 1 mm/s. Initially, the pencil with the highest hardness was applied, afterwards, pencils with lower hardness were used in the test until the pencil did not cut through the coating nor scratched the coating surface. And the hardness of the coating was determined by the hardest pencil which did not cut through the coating during the test. The scale of hardness of the pencils ranges from 9B, the softest, to 9H, the hardest.
The adhesion of the coatings to substrates was evaluated by the cross-cut test based on GB/T 9286, which is conformed to ISO-2409. 20 mm long, 10 × 10 grid lines with 1 mm interspacing were cut by a razor blade on each sample. Then, a piece of 3M 600 tape was applied on the grid area and peeled off. The grid area was finally inspected and adhesion was rated according to the standard. The adhesion rates range from 0 to 5, in which rate 0 means 0% of the coating area is removed during the test.

The mechanical durability of the coatings was analyzed via an abrasion test. In the abrasion test, a load of 200 g was first put on the coating sample (3 cm × 3 cm), then, the coating sample was dragged on a piece of sandpaper (800 mesh) for 20 cm, which was defined as one abrasion cycle. WCA was measured after each abrasion cycle. The test sample surface was then examined by an optical microscope.

3. Results and Discussion

3.1. Effects of SiO$_2$ Nanoparticle Loading

To evaluate the effects of different components on the physical properties of the coatings, static WCA and optical transmittance were measured on different specimens. When plotting the relationships between the physical properties and the component ratios of the coatings, the component ratios in the coating solutions were converted to solid component ratios in the coatings. Figure 1 shows the WCA and optical transmittance of the superhydrophobic coatings with different SiO$_2$ nanoparticle loadings. The PU and FAP ST-200 were 5 and 2.5 wt.%, respectively, in the coating solutions. It is obvious that the WCA of these coatings shows an increasing trend with the increase of the SiO$_2$ nanoparticle loading (Figure 1a). The sample with 27.9 wt.% SiO$_2$ nanoparticles has the highest WCA of 153.5°. Further increase of SiO$_2$ nanoparticles leads to a slight decrease in WCA. Figure 1b shows that the optical transmittance of the coatings decreases with increasing SiO$_2$ nanoparticle loadings. But all the coatings measured keep an optical transmittance of larger than 77%. The decrease in optical transmittance is mainly attributed to the increased scattering of visible light by more pores and agglomerates with the increase of SiO$_2$ nanoparticles.

The surface morphologies of the coatings with different SiO$_2$ nanoparticle loadings were examined by SEM. Figure 2 shows the SEM images of the superhydrophobic coatings with various loadings of SiO$_2$ nanoparticles. It can be seen that when SiO$_2$ loading is less than 34.1 wt.%, the SiO$_2$ nanoparticles are dispersed well in the coatings, without obvious agglomerates formed. With the increase of the SiO$_2$ nanoparticles in the coatings, the coatings’ surface roughness becomes higher and higher. Therefore, their hydrophobicity increases gradually to reach the superhydrophobic state. The combination of low surface energy, which is provided by the component ST-200, and the increased roughness leads to the increased hydrophobicity. However, when SiO$_2$ loading reaches 34.1 wt.%, larger agglomerates formed (Figure 2f). The formation of these agglomerates has little impact on the hydrophobicity of the coating. In terms of the optical light transmittance, due to the difference of refractive indexes between the SiO$_2$ nanoparticles and the polymer matrix, the more SiO$_2$ nanoparticles added, the more light is reflected and scattered, which causes the decreased optical transmittance. In addition, when SiO$_2$ loading reaches 34.1 wt.%, the formed agglomerates causes more light scattering as well, and hence, a rapid decrease in optical transmittance.
Figure 1. (a) WCA and (b) optical transmittance of the superhydrophobic coatings with different SiO$_2$ nanoparticle loadings.

The nanoparticle loading has little impact on the hardness of the coating as all the tested samples present a hardness of 5H or higher. In terms of adhesion strength, with a SiO$_2$ loading of 27.9 wt.% or lower in the coatings the fabricated coatings have an adhesion rate of 0, which means no coating was peeled off by the adhesion test. These excellent hardness and adhesion imply that these coatings not only have superhydrophobicity, but also high mechanical performance.

In the current coating system, PU mainly functions as a binder and host to hold the SiO$_2$ nanoparticles and forms continuous coating, which also provides high abrasion resistance. The FAP ST-200 reduces the coatings’ surface energy. SiO$_2$ nanoparticles construct micro-/nanometer hierarchical rough surface structures and increase surface roughness significantly. The combination of high surface roughness and low surface energy leads to the superhydrophobicity of the coatings.
3.2. Effects of PU Loading

The effects of PU loading were also studied while ST-200 and SiO$_2$ nanoparticles were kept at 2.5 and 2.0 wt.%, respectively, in the coating solutions. The WCA and light transmittance of these coatings are present in Figure 3. As shown in Figure 3a, the WCA of these coatings increases slightly with increasing PU loading and reaches the maximum of 158.5° at a PU loading of 45.7 wt.%, while the rolling angle of this sample is about 3°,
showing the excellent hydrophobicity of this coating. However, with an excessive amount of PU added, the WCA drops and decreases rapidly from 158.5° to 112.4° at a PU loading of 67.8 wt.%. Figure 3b demonstrates that the optical transmittance of the superhydrophobic coatings keeps almost the constant and remain higher than 85%, with PU loading up to 55.9 wt.%. Further increasing PU beyond 55.9 wt.%, the optical transmittance is increased gradually and reaches 92% at a PU loading of 67.8 wt.%.

Figure 3. (a) WCA and (b) optical transmittance of the coatings with different PU loadings.

All the tested samples, but the one without SiO₂ nanoparticles added, have a pencil hardness of 6H or higher. In terms of adhesion, the samples with a PU loading of 45.8 wt.% or higher have an adhesion rate of 0.

To understand the effects of PU on coatings’ performance and surface morphologies, SEM images of three coatings with different PU loadings were taken (Figure 4). A porous structure was observed on the sample with 17.4 wt.% PU (Figure 4a). A large amount of SiO₂ nanoparticles can be clearly distinguished at higher magnification (Figure 4b). With more PU added (45.7 wt.%), the SiO₂ nanoparticles are covered partially by PU and the coating still exhibits a porous structure with micro/nano-scale roughness (Figure 4c,d). However, with excessive amount of PU (67.8 wt.%) in the coating, it presents a totally different surface morphology compared to the coatings with lower PU contents. A more flattened structure was observed on the surface (Figure 4e), and only a few nanoparticles can be found on the crack area (Figure 4f). With an excessive amount of PU added in the coating, most of the SiO₂ nanoparticles were covered by PU, therefore, the roughness of the coated surface was significantly reduced. The surface morphology is transformed from a Cassie Baxter state to a Wenzel state. Hence, the hydrophobicity is severely deteriorated.
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Figure 4. SEM images of the superhydrophobic coatings with different PU polyurethane loadings, (a,b) 17.4 wt.%, (c,d) 45.8 wt.%, (e,f) 67.8 wt.%, the insets are optical images of water droplets on the specific coatings.

The surface roughness of coatings with different PU loadings were measured to investigate the impact of surface roughness on the hydrophobicity and transmittance (Figure 5). With a PU loading of 67.8 wt.%, the coating exhibits a flattened surface (Figure 5a) which has a root mean square roughness, $R_q$, of 24.0 nm, such coating has a WCA of 112.4$^\circ$ and an optical light transmittance of 92.1%. When the PU loading is 62.8 wt.%, the coating presents a rougher surface (Figure 5b) with an $R_q$ of 48.0 nm, such coating exhibits a WCA of 138.5$^\circ$ and an optical light transmittance of 88.3%. A higher roughness results in a better hydrophobicity and lower transparency. For the coating with a PU loading of 45.8 wt.%, the coating exhibits an even rougher surface (Figure 5c), the $R_q$ is 127.0 nm, and such coating has a WCA of 158.5$^\circ$ and an optical light transmittance of 87.7%. It is concluded that the surface roughness has a positive effect on the hydrophobicity but a negative effect on the transparency of the coating.
Figure 4. SEM images of the superhydrophobic coatings with different PU166 polyurethane loadings, (a, b) 17.4 wt.%, (c, d) 45.8 wt.%, (e, f) 67.8 wt.%, the insets are optical images of water droplets on the specific coatings.

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(a) (b) (c)

Figure 5. AFM results for coatings with different PU loadings (a) 67.8 wt.%, (b) 62.8 wt.% and (c) 45.8 wt.%.

3.3. Effects of Fluorinated Acrylic Copolymer ST-200

In addition to SiO$_2$ nanoparticle and PU components, the FAP ST-200 was found to have a significant impact on the physical properties of the composite coatings as well. The relationship between the physical properties of the coatings and the amount of the ST-200 is shown in Figure 6. For these samples, PU and SiO$_2$ nanoparticles were 5.0 and 2.0 wt.%, respectively, in the coating solutions. As shown in Figure 6a, the WCA increases with the increment of ST-200, until reaching the highest value of 155.8° at a ST-200 loading of 21.6 wt.%. ST-200 is a low surface energy fluorinated polymer. With more and more ST-200 added, the coatings’ surface energy becomes lower and lower until it gets close to that of ST-200 itself. Together with the surface roughness created by the SiO$_2$ nanoparticles, the coatings’ hydrophobicity becomes higher and higher. When an excessive ST-200 is added, especially when ST-200 loading is beyond 29.3 wt.%, WCA declines rapidly. However, as plotted in Figure 6b, the optical transmittance of these coatings remains almost the constant, implying that the FAP ST-200 has little effect on coatings’ optical property.
Figure 5. AFM results for coatings with different PU loadings (a) 67.8 wt.%, (b) 62.8 wt.% and (c) 45.8 wt.%.

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Figure 6. (a) WCA and (b) optical transmittance of the superhydrophobic coatings with different ST-200 loadings.

All the tested samples have an adhesion rate of 0. The sample with the highest WCA has a pencil hardness of 4H. When ST-200 loading reaches 45.3 wt.% or higher, the coatings' hardness reaches 7H.

The coatings' morphologies with different ST-200 loadings are presented in Figure 7. It is clear that when the ST-200 loading is 21.7 (Figure 7c,d) or 12.1 wt.% (Figure 6a,b), the coatings have a porous structure with micro/nano-scale roughness. With more ST-200 added into the coating, the surface energy of the coating was reduced, which leads to the improved hydrophobicity of the coating. However, when the ST-200 reaches 45.3 wt.% (Figure 7e,f), the surface roughness was reduced, which is due to the fact that most SiO2 nanoparticles were wrapped and covered by the ST-200. The hydrophobicity of the coating depends on both the appropriate surface roughness and the low surface energy of the coating. In this case, the excessive amount ST-200 added in the coating may reduce the surface energy of the coating, however, the surface roughness was significantly reduced. Therefore, with an excessive amount ST-200 added, the hydrophobicity of the coating is compromised.
Figure 7. SEM images of the superhydrophobic coatings with different ST-200 loadings, (a,b) 12.1 wt.%, (c,d) 21.7 wt.%, and (e,f) 45.3 wt.%, the insets are optical images of water droplets on the specific coatings.

3.4. Abrasion Resistance

The coating’s robustness was examined by an abrasion test, in which a selected coating sample with 45.77 wt.% PU, 28.60 wt.% ST-200 and 22.88 wt.% SiO$_2$ nanoparticles, was rubbed against a piece of 800-mesh sand paper. The WCA of the sample after each cycle of abrasion is shown in Figure 8. The sample had an initial WCA of about 159$^\circ$. Its WCA decreased gradually with increasing abrasion cycles. After a total of 25 abrasion cycles, the final WCA of the sample was about 110$^\circ$, which is still hydrophobic after a total abrasion
distance of 300 cm with a weight load of 200 g, showing the high abrasion resistance of this sample.

Figure 8. WCA of the tested coating vs. abrasion cycles.

Figure 9 shows the optical images of the rubbed sample before and after the abrasion test. Before the abrasion test the sample had a rough surface with uniform textures. After the abrasion test, scratches formed on the sample surface and its surface roughness was reduced so that its hydrophobicity was decreased significantly.

Figure 9. Optical images (200×) of the abrasion tested sample: (a) before and (b) after 25 abrasion cycles.

3.5. Practical Applications

To evaluate the applicability of these superhydrophobic coatings, the coating solution for the sample with 22.9 wt.% SiO$_2$ nanoparticle, 45.8 wt.% PU and 28.6 wt.% ST-200, was sprayed onto glass, Al$_2$O$_3$ ceramic, fabric and Al substrates. The optical images of water droplets on these samples are shown in Figure 10. It is clear that water droplets on these samples are all close to a sphere and can roll off from the surface easily, showing the high WCA and superhydrophobicity, which implies that the coatings can be applied to a wide range of substrates and have great potential for different application fields.
4. Conclusions

By a facile mixing and dip coating method, superhydrophobic coatings have been successfully fabricated using solutions containing SiO$_2$ nanoparticles, PU-166 polyurethane and ST-200 FAP. With the optimal formula used, the coating exhibits excellent hydrophobicity, with a WCA of 159° and a rolling angle of 3°. Besides, the coating has a pencil hardness of 6H and adhesion rate is 0, which demonstrate that the coating has an adequate level of mechanical strength. Moreover, the transparency and hydrophobicity of the coating was well balanced. The coating demonstrates good transparency as the optical light transmittance is 88%. Good transparency and hydrophobicity are achieved in one coating. Also, the effects of different coating components on the coating properties are systematically investigated. As the SiO$_2$ nanoparticles increases, the hydrophobicity of the coatings becomes higher, but the optical transmittance decreases due to the increased surface roughness. The increment of PU-166 has a positive effect on the transparency but a negative effect on the hydrophobicity of the coating, as it significantly decreases the surface roughness of the coating. As for ST-200, it has little effect on the transparency of the coating. In terms of hydrophobicity, at a low content, the addition of ST-200 improves the hydrophobicity of the coating as it lowers the surface energy of the coating. However, with an excessive amount added, the hydrophobicity is severely compromised as the ST-200 destroyed the micro/nano-scale hierarchical roughness. Overall, the fabrication is simple,
requires no expensive equipment and energy consumption is reasonable. All these merits make it a suitable approach for upscale application.

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