Poly(ethylene glycol)-grafted silica nanoparticles for highly hydrophilic acrylic-based polyurethane coatings

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A silane coupling agent bearing poly(ethylene glycol) (PEG) chains was synthesized using triethoxysilylpropyl isocyanate and excess PEG, with molecular weights of 400 or 1000 g/mol (PEG400 and PEG1000) and chemically bonded to SiO2 nanoparticles, to obtain PEG-modified SiO2 nanoparticles (SiO2-PEG) with pendant hydroxyl groups. The PEG modification was demonstrated by Fourier transformed infrared spectroscopy, thermogravimetric analysis, and through the dispersion behavior of SiO2-PEG nanoparticles in water. The SiO2-PEG nanoparticles were further incorporated into acrylic-based polyurethane (APU) coatings. Transparent and crack-free nanocomposite coatings with SiO2-PEG content up to 35 and 40 wt.% were achieved for SiO2-PEG400 and SiO2-PEG1000, respectively. The high quality of the product was owed to the improved compatibility of SiO2 nanoparticles with the APU matrix after PEG modification. Due to the rearrangement of hydrophilic/hydrophobic segments, a highly hydrophilic surface, with a water contact angle (WCA) as low as 38.7°, was attained for the SiO2-PEG embedded coatings after induction with water. Moreover, SiO2-PEG400 was more efficient in enhancing the surface hydrophilicity of the APU coatings than SiO2-PEG1000 at the same SiO2-PEG content. In contrast, pure APU coatings and the APU coatings containing unmodified SiO2 nanoparticles displayed WCAs of 68.2° and 70.1°, respectively. Outdoor exposure experiments showed that the APU coatings containing SiO2-PEG nanoparticles had excellent dirt-resistance.

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1. Introduction

Highly hydrophilic/superhydrophilic organic coatings have good dirt resistance in air [1–3] and excellent antifouling performance under water [4–6]. Unfortunately, traditional top organic coatings, such as polyurethane coatings, fluorocarbon polymer coatings, and polysiloxane coatings, have weakly hydrophobic (water contact angle: 56°–65° < θ < 90°) or hydrophobic (90° ≤ θ ≤ 120°) surfaces [7], making them easily polluted by dust, oily dirt, proteins, and bacteria. Increasing the surface hydrophilicity of organic coatings is thus urgently required.

There are several possible routes to acquire surface hydrophilicity for traditional organic coatings. For example, O2 plasma treatment is frequently adopted to create hydrophilic surfaces for polyacrylate coatings [8]; however, this method needs a special apparatus and has to be employed in factory rather than on-site. Recently, 3D-grafting of hydrophilic polymers on the top layer of organic coatings has been developed to acquire highly hydrophilic surfaces with good durability [9–11]. Nevertheless, the organic coatings have to be specially designed to match the chemical grafting of the hydrophilic polymer. Certainly, highly hydrophilic or superhydrophilic surfaces can be readily obtained by casting a layer of superhydrophilic coatings on the traditional organic coatings. In any case, the fabrication of superhydrophilic coatings is not an easy task. Dong et al. [12] fabricated superhydrophobic coatings based on SiO2 nanoparticles and quaternized poly(2-dimethylaminoethyl methacrylate) with trimethoxysilyl pendant groups (PQDMAEMA); however, the authors only reported casting the coatings on glass substrates. Moreover, the synthesis of PQDMAEMA was complex.

From the viewpoint of practical application, the formation of a highly hydrophilic or superhydrophilic surface by changing an additive to traditional organic coatings is desirable. Among the additives, photocatalytic TiO2 nanoparticles are rather efficient in creating superhydrophilic surfaces through photocatalytic oxidation and degradation of polymer coatings, as well as from their inherent photoinduced superamphilicity [13–16]. But TiO2 nanoparticles will considerably shorten the service life of organic coatings. Fluoride siloxane, for example, commercially named...
GH-701, is another additive frequently used to fabricate highly hydrophilic fluoroethylene vinyl ether (FEVE) coatings [17] because it can transfer to the surface and subsequently create hydrophilic silanol groups via moisture-aided hydrolysis. However, this additive is too sensitive to water, easily causing the pigmented coatings to form a gel during storage. In addition, the further condensation of silanol groups and the loss of the additive during service lead to unstable hydrophilicity of the surface. In order to overcome the shortcomings of the fluoride siloxane additive, we recently synthesized light responsive SiO2 nanoparticles with wettable changing from hydrophobic to hydrophilic [18]. The nanoparticles enriched at the surface of the fluorocarbon FEVE coatings due to their low surface free energy. After UV irradiation, a highly hydrophilic surface with a water contact angle (WCA) of 33.3° was acquired. Nonetheless, the preparation of light responsive SiO2 nanoparticles was complicated and costly. Therefore, the facile synthesis of cheap functional additives is still required for the preparation of highly hydrophilic organic coatings.

In this study, we synthesized a silane couple agent bearing a polyethylene glycol (PEG) segment (PEG-S). The PEG-S was subsequently grafted to the silica nanoparticle to get PEG-modified SiO2 (SiO2-PEG) nanoparticles with pendant hydroxyl groups at their surface. This structure can alleviate the loss of hydrophilic PEG from organic coatings and endow the nanoparticles with chemical reactivity during curing of coatings. These SiO2-PEG nanoparticles were also introduced into acrylic-based polyurethane (APU) coatings. The APU nanocomposite coatings acquired hydrophilic surfaces with a WCA as low as 38.7° after induction with water, indicating the positive effect of the addition of SiO2-PEG nanoparticles. The influence of the molecular weight of PEG segments was also investigated.

2. Experimental

2.1. Materials

Fumed silica (SiO2, 7 nm, AROSIL® 380) with a surface area of 380 ± 30 m²/g was supplied by Evonik (Germany) and dried at 55 °C in a vacuum oven overnight before use. 3-(Triethoxysilyl) propyl isocyanate (IPTES, 95%), PEG400 and PEG1000 (corresponding to PEG with molecular weights of 400 and 1000 g/mol, respectively), and ammonia solution (28.0%-30.0% NH3 basis) were purchased from Aladdin (Shanghai, China). The PEG was dried by azetropic distillation in toluene prior to use. Absolute ethanol (>99.7%) and tetrahydrofuran (THF, >99.0%) were purchased from Sinopharm Chemical Reagent Corp (Shanghai, China). Acrylic polyol resin (SMS15/70ABC) was obtained from Shanghai Huarong Chemical Co., Ltd (Shanghai, China). Isocyanate curing agent (Tolonate® HDT-90) was purchased from Rhodia (France). All other raw materials came from commercial sources and were used as received, unless otherwise noted. The water used in the experiments was deionized.

2.2. Synthesis of SiO2-PEG nanoparticles

The SiO2-PEG nanoparticles were synthesized on the basis of the “grafting” strategy, which is similar to our two step approach, previously reported in literature [18]. The process is schematically shown in Scheme 1.

A silane coupling agent bearing a PEG chain (PEG-S) was synthesized through the reaction of IPTES with excess PEG (IPTES/PEG = 1:1.5 mol/mol). PEG400 (or PEG1000, 17 mmol) was mixed with IPTES (11.3 mmol) and stirred at 75 °C for 12 h in a sealed bottle. The mixture obtained was used without any additional treatment.

The SiO2-PEG nanoparticles were prepared by the surface modification of SiO2 nanoparticles with PEG-S. Specifically, the SiO2 nanoparticles (7.0 g) were dispersed in absolute ethanol (150 mL) via ultrasonication for 30 min and stirred at 60 °C. The as-obtained PEG-S mixture was then dropped into the SiO2 dispersion, followed by the addition of ammonia solution (three droplets). The reaction system was stirred at 75 °C for 24 h. After the reaction was completed, the products were separated by repeated centrifugation at 13000 rpm for 25 min and washed three times with THF. The resulting products (SiO2-PEG400 or SiO2-PEG1000) were dried at 55 °C in a vacuum oven overnight and then stored in a desiccator for further use.

2.3. Preparation of APU nanocomposite coatings

The desired amounts of SiO2-PEG were dispersed into the mixture of SMS15/70BAC resin (0.5 g) and THF (2.5 g) by bead milling. The curing agent, HDT-90 (0.2 g), was then added and stirred for another 15 min. Once the mixing step was complete, the product was coated on a clean glass slide using a bar applicator (50 μm) and cured at room temperature overnight to obtain the final APU nanocomposite coatings.

2.4. Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 (Thermo-Fisher, Waltham, Massachusetts, USA) with a resolution of 4 cm⁻¹ and scanned 32 times in the range of 4000–400 cm⁻¹. The reactions of PEG-S were monitored based on the FTIR spectra. The functionalized silica nanoparticles were blended with KBr to fabricate pellets for FTIR analysis. The amount of organic components attached to the SiO2-PEG nanoparticles were analyzed by thermogravimetric analysis (TGA, Q500, TA Instruments, New Castle, Delaware, USA) at a heating rate of 20 °C/min from 30 to 800 °C under a nitrogen atmosphere. The particle size distribution of the SiO2-PEG nanoparticles in water was determined by dynamic light scattering (DLS, Nano-ZS90, Malvern Instruments Ltd, Great Malvern, UK). Transmission electron microscopy (TEM) images were collected using a Tecnai G2 20 TWIN (FEI, Hillsboro, Oregon, USA) microscope operating at 200 kV. The SiO2-PEG nanoparticles were dispersed in water and dried on a copper grid. WCA measurements were carried out by an OCA 15 contact angle analyzer (Dataphysics, Filderstadt, Germany) using a 3 μL deionized water droplet. The resulting angle was determined as the average value from measurements taken on over five different sites of the same sample. Optical images were recorded by a 3D digital microscope (KH-7700, HIROX, Tokyo, Japan). Scanning electron microscopy (SEM) observations were conducted using a Philips XL 30 (Czech Republic) emission microscope at an accelerating voltage of 5 kV. The surface composition was measured by X-ray photoelectron spectroscopy (XPS, PHI 5300 ECSA instrument, Perkin Elmer, Christiansburg, Virginia, USA) using an Al Kα source at a power of 250 W with a take-off angle of 45°.

3. Results and discussion

3.1. Synthesis of SiO2-PEG nanoparticles

SiO2-PEG nanoparticles have been fabricated mostly using poly(ethylene glycol) methyl ether [19–22] or poly(ethylene glycol) methyl ether methacrylate [23]. As a consequence, the terminal groups of the bonded PEG chains are methoxyl groups, which lead to the lack of chemical reactivity of the SiO2-PEG nanoparticles. SiO2-PEG nanoparticles having terminal hydroxyl groups had been previously synthesized via a sol-gel process with PEG200 and tetraethyorthosilicate [24]. Nevertheless, in the cited report, the
grafting of PEG200 was conducted for the purpose of anti-protein adsorption of SiO₂ nanoparticles rather than for the enhancement of hydrophilicity of organic coatings.

In the present study, PEG chains with different molecular weights (400 and 1000 g/mol) were chemically bonded to the SiO₂ nanopowder, providing on one side the highly hydrophilic surface and on the other side the high chemical reactivity of SiO₂ nanoparticles with functional groups such as isocyanate and amine. The preparation of SiO₂-PEG nanoparticles is schematically described in Scheme 1. To make sure that only one hydroxyl group of PEG reacted, excess PEG was used in the synthesis of PEG-S. The removal of residual PEG is difficult but not necessary since only PEG-S can chemically attach to the surface of SiO₂ nanoparticles. The non-essential purification makes the synthesis of SiO₂-PEG feasible in practical applications.

To demonstrate the synthesis of PEG-S, FTIR spectroscopy was used to characterize the reaction products of PEG with IPTES. Their spectra are shown in Fig. 1. The strong peak at 2270 cm⁻¹, belonging to the isocyanate group of IPTES, disappears; instead, a new peak at 1719 cm⁻¹ arises due to the appearance of a urethane carbonyl group in both PEG400-S and PEG1000-S. These facts directly confirmed the complete reaction of PEG with IPTES. Unfortunately, the terminated hydroxyl group of PEG-S cannot be proved from FTIR spectra because of the interference of residual PEG molecules.

The surface functionalized SiO₂ nanoparticles were also characterized by FTIR. Fig. 2 shows the FTIR spectra of SiO₂, SiO₂-PEG400 and SiO₂-PEG1000. After the SiO₂ nanoparticles were modified by PEG-S, both SiO₂-PEG400 and SiO₂-PEG1000 displayed a new peak at 1703 cm⁻¹, corresponding to the stretching vibration of carbonyl groups from PEG-S. In addition, the intensity of the peaks for C–H stretching around 2980 cm⁻¹ obviously increases after surface modification, indicating the presence of −CH₂− groups relating to PEG-S molecules. The results demonstrate that both PEG400-S and PEG1000-S were successfully grafted to SiO₂ nanoparticles.

Fig. 3 shows the TGA curves of SiO₂, SiO₂-PEG400 and SiO₂-PEG1000 nanoparticles. One main weight loss stage of unmodified SiO₂ nanoparticles happens below 100 °C, which should be due to the evaporation of physically adsorbed water molecules. This low-temperature weight loss stage is not observed for SiO₂-PEG400 and SiO₂-PEG1000 nanoparticles. Instead, SiO₂-PEG400 and SiO₂-PEG1000 nanoparticles display a large weight loss stage in the temperature range of 200 °C–600 °C. This weight loss may
be attributed to the thermal decomposition of the grafted PEG. Interestingly, the weight loss is nearly the same (about 13%) for SiO$_2$-PEG400 and SiO$_2$-PEG1000 nanoparticles, although PEG1000-S has longer chains than PEG400-S. This means that the grafting density of SiO$_2$-PEG1000 is lower than that of SiO$_2$-PEG400. Such a result is reasonable because PEG1000-S has a higher steric hindrance in the “grafting to” reaction.

Having previously synthesized PEG2000-S with PEG2000 ($M_n = 2000$ g/mol), we used it here to modify SiO$_2$ nanoparticles. Due to its high molecular weight, PEG2000 has low solubility in ethanol, making it easy to extract form the solution along with the SiO$_2$-PEG2000 nanoparticles. On the contrary, mixtures of SiO$_2$-PEG2000 and PEG2000 in water are both rather stable. SiO$_2$-PEG2000 could not be separated from the aqueous dispersion even by centrifugation at 16000 rpm for more than 50 min. This phenomenon suggested that PEG2000 could also be grafted to SiO$_2$ nanoparticles using the synthetic route presented here. Nevertheless, due to the low purity of the SiO$_2$-PEG2000 nanoparticles, they were not adopted in the fabrication of highly hydrophilic coatings that followed.

Because of the hydrophilic character of the grafted PEG chains, SiO$_2$-PEG nanoparticles were dispersed into water to examine their dispersion behavior. Fig. 4 shows pictures of the aqueous dispersions of unmodified SiO$_2$, SiO$_2$-PEG400 and SiO$_2$-PEG1000 nanoparticles before and after storage for 12h. Most of unmodified SiO$_2$ nanoparticles precipitated, while no obvious changes were observed in the aqueous dispersions of SiO$_2$-PEG400 and SiO$_2$-PEG1000 nanoparticles. This fact indicated that the grafting of the hydrophilic PEG chain to SiO$_2$ nanoparticles improved their dispersion stability in water. On the other hand, the good dispersion stability of SiO$_2$-PEG400 and SiO$_2$-PEG1000 nanoparticles indirectly demonstrated the chemical attachment of PEG chains on the surface of SiO$_2$ nanoparticles.

The particle size of the aqueous dispersions of unmodified SiO$_2$, SiO$_2$-PEG400 and SiO$_2$-PEG1000 nanoparticles was determined by the DLS method. The results are summarized in Table 1. Significant improvement of the dispersion stability of SiO$_2$ nanoparticles in water was revealed after modification with PEG-S. The dispersion size of SiO$_2$ nanoparticles was reduced from 295 nm to 149 nm and 185 nm when grafted with PEG400-S and PEG1000-S, respectively. The fact that the dispersion size of SiO$_2$-PEG1000 was larger than that of SiO$_2$-PEG400 was ascribed to the large hydrodynamic size of the SiO$_2$ nanoparticles with long PEG chains attached.

The TEM images of aqueous dispersions of unmodified SiO$_2$, SiO$_2$-PEG400 and SiO$_2$-PEG1000 nanoparticles are presented in Fig. 5. Silica agglomerates with an average size of about 280 nm were found for the unmodified SiO$_2$ nanoparticles. However, SiO$_2$-PEG400 and SiO$_2$-PEG1000 dispersions exhibited reduced agglomeration. Statistical analyses indicate that their average sizes are about 240 nm and 200 nm, respectively, in agreement with the DLS results reported above.

### Table 1

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Diameter (nm)</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified SiO$_2$</td>
<td>294.9 ± 6.7</td>
<td>0.344 ± 0.021</td>
</tr>
<tr>
<td>SiO$_2$-PEG400</td>
<td>149.1 ± 5.3</td>
<td>0.177 ± 0.016</td>
</tr>
<tr>
<td>SiO$_2$-PEG1000</td>
<td>185.2 ± 5.6</td>
<td>0.217 ± 0.015</td>
</tr>
</tbody>
</table>

3.2. Fabrication of APU/SiO$_2$-PEG nanocomposite coatings

Hydrophilic hybrid coatings had been previously fabricated through a sol-gel process using PEG, IPTES, silica sol, and tetraethylorthosilicate [25]. The raw materials in this report are similar to those of SiO$_2$-PEG nanoparticles; however, they were the constituents of the hydrophilic coatings rather than being used as additives of other organic coatings. In any case, SiO$_2$-PEG nanoparticles are suitable additives to enhance the surface hydrophilicity of traditional organic coatings. Herein, SiO$_2$-PEG nanoparticles were incorporated into 2K APU coatings to examine their efficiency as hydrophilic fillers of organic coatings. APU coatings were chosen because SiO$_2$-PEG nanoparticles can chemically react with the curing agent, isocyanate, similarly to the reaction of acrylic polyl resin with isocyanate. The chemical binding of SiO$_2$-PEG nanoparticles with the APU matrix may reduce its loss in rainy days or underwater, thus enhancing its long-term durability. Clearly, a hydrophilic surface can be acquired only when SiO$_2$-PEG nanoparticles stick out of the surface. Due to their high surface free energy, the hydrophilic SiO$_2$-PEG nanoparticles tend to stay inside the APU matrix. To assure the presence of SiO$_2$-PEG nanoparticles in the outermost layer of the coatings, relatively high quantities of SiO$_2$-PEG nanoparticles were introduced into the APU coatings. Preliminary tests showed that all coatings were opaque and had poor film-forming abilities with SiO$_2$-PEG contents above 40 wt.%, based on the total weight of the coating. Therefore, silica contents of 30–40 wt.% were finally utilized.

Fig. 6 presents the photos of the APU nanocomposite coatings with different amounts of SiO$_2$-PEG400 or SiO$_2$-PEG1000. For the sake of comparison, the photos of pure APU coatings and the coatings containing different amounts of unmodified SiO$_2$ nanoparticles are also shown. All the coatings based on unmodified SiO$_2$ nanoparticles exhibited a white coloring for SiO$_2$ content in the range of 30–40 wt.%. The opacity of the coatings could be caused by the light scattering of the aggregates of SiO$_2$ nanoparticles, and the cracks and pores in the coatings (see the optical and SEM images below). High transparency was achieved for the coatings prepared with 30 and 35 wt.% of SiO$_2$-PEG400 or with 30–40 wt.% of...
SiO\textsubscript{2} nanoparticles, were SiO\textsubscript{2}-PEG1000 ified pigment cracks PEG and was coatings containing nanoparticles. Moreover, SiO\textsubscript{2}-PEG1000 nanoparticles have better compatibility with the APU matrix than SiO\textsubscript{2}-PEG400 nanoparticles. These results agree with the conclusion drawn by Corbierre et al. [26] that a lower grafting density and a higher organic chain molecular weight are beneficial for the dispersion of nanoparticles in a polymer matrix.

Fig. 7 shows the optical images of the surface of the coatings containing 30, 35 and 40 wt.\% of unmodified SiO\textsubscript{2} or SiO\textsubscript{2}-PEG nanoparticles. Pure APU coatings had a rather smooth surface, whereas many cracks appeared on the surfaces of the coatings with unmodified SiO\textsubscript{2} nanoparticles, regardless of the SiO\textsubscript{2} content. The coatings with SiO\textsubscript{2}-PEG400 had rough surface but were free of cracks until the SiO\textsubscript{2}-PEG400 content was increased up to 40 wt.\%. SiO\textsubscript{2}-PEG1000 coatings did not display any cracks even at 40 wt.\% SiO\textsubscript{2}-PEG1000 content. The surface morphology of the coatings was further observed by SEM, as shown in Fig. 8. Even at high magnification, pure APU coatings still displayed a smooth surface. Rough and porous surfaces were clearly observed for all the coatings with unmodified SiO\textsubscript{2} nanoparticles. The coatings with SiO\textsubscript{2}-PEG400 or SiO\textsubscript{2}-PEG1000 have similar surface morphology. At 30 and 35 wt.\% nanoparticles, some pits, but no distinct pores, were revealed. At 40 wt.\% porous surfaces were evident. The cracks and the pores could therefore explain the declined transparency of the coatings after incorporation of SiO\textsubscript{2} nanoparticles.

The cross-section of APU coatings containing 35 wt.\% of unmodified SiO\textsubscript{2} or SiO\textsubscript{2}-PEG nanoparticles were additionally observed by SEM, as presented in Fig. 9. The coatings with unmodified SiO\textsubscript{2} were highly porous, as suggested by their surface appearance. This observation suggested that 35 wt.\% was already beyond the critical pigment volume concentration of the coatings. The low critical pigment volume concentration of the unmodified SiO\textsubscript{2}-embedded coatings could be caused by the aggregates or agglomerates of SiO\textsubscript{2} nanoparticles, entrap some polymer binders, leading to a high actual pigment volume concentration. Therefore, the cross-section morphology further demonstrated that the pores are responsible for the opacity of the coatings. As for the APU coatings with SiO\textsubscript{2}-PEG400 and SiO\textsubscript{2}-PEG1000 nanoparticles, the coatings were dense although SiO\textsubscript{2} nanoparticles were visible in their cross-sections. The dense character explained their high transparency. The above morphologies additionally demonstrate that grafting of PEG can also improve the dispersion of SiO\textsubscript{2} nanoparticles in APU coatings.

### 3.3. Wettability of APU/SiO\textsubscript{2}-PEG nanocomposite coatings

The WCAs of APU coatings with unmodified SiO\textsubscript{2} nanoparticles or SiO\textsubscript{2}-PEG nanoparticles were measured. To our surprise, the unmodified SiO\textsubscript{2} nanoparticles cause a sharp rise in WCA values, from 77.6\(^\circ\) to 127.3\(^\circ\). The WCAs of the APU coatings embedded with SiO\textsubscript{2}-PEG400 and SiO\textsubscript{2}-PEG1000 also gradually increased from 77.6\(^\circ\) to 101.4\(^\circ\) and to 104.7\(^\circ\), respectively. This should be due to the fact that hydrophobic segments of APU coatings thermodynamically dominate the top surface in the air. The hydrophobic segments combining with the nanoparticles-induced rough surface consequently lead to high WCAs. Unmodified SiO\textsubscript{2}-embedded coatings have rougher surface and hence higher WCA.

Since rearrangement of hydrophilic/hydrophobic polymer chains at the surface is possible in an aqueous environment, highly hydrophilic surfaces may be produced with the help of water. To examine whether or not water can induce the formation of hydrophilic surfaces on the SiO\textsubscript{2}-PEG embedded APU coatings and control samples, and to simulate the rainy/non-rainy days in outdoor service, “water/air” cycles were carried out. This was done by immersing the synthesized coatings in deionized water for 24 h; the samples were then taken out of water and dried at room temperature until water was no longer visible on the surface. The WCA of the samples was determined as the wettability of the “water” stage. Next, the samples were further dried in air for 24 h and their WCA was measured and taken as the wettability of the “air” stage. Such water/air cycle was repeated several times in order to monitor changes of surface wettability in service.

Fig. 10 displays the WCAs of the coatings with various contents of SiO\textsubscript{2}-PEG nanoparticles as a function of the number of
Fig. 7. Optical images of the surface of APU coatings with different amounts of SiO₂ nanoparticles.

Water/air cycles. After the first water stage, the WCAs of the coatings with both SiO₂-PEG400 and SiO₂-PEG1000 sharply declined to a value below that of pure APU coatings, regardless of SiO₂-PEG content. This suggests that water can expel the hydrophobic segments to make the hydrophilic SiO₂-PEG400 or SiO₂-PEG1000 exposed at the surface. However, when the first air stage was completed, the WCAs of all SiO₂-PEG-embedded coatings showed an increase close to that of pure APU coating but much smaller than their original values. This must be due to the aging-induced recovery of hydrophobic segments at the surface. After several water-air
cycles, the WCAs of both the water stage and the air stage tend to reach a plateau. In particular, the equilibrium WCAs in water stage are 59.3°, 49.5°, 25.3° for SiO2-PEG400 embedded coatings and 67.2°, 54.9°, 38.7° for SiO2-PEG1000 embedded coatings when the SiO2-PEG content increases from 30, 35–40 wt.%. This indicates that a higher SiO2–PEG content leads to a lower equilibrium WCA. We particularly examined by XPS analysis the surface composition of APU/SiO2–PEG1000 coatings before and after water immersion.

Fig. 8. SEM images of the surface of APU coatings with different amounts of SiO2 nanoparticles.
as summarized in Table 2. Clearly, as the SiO$_2$-PEG1000 content increases in the coatings, the C atomic fraction decreases and Si atomic fraction increases, well illustrating the change of the coatings composition. The unexpected Si atoms in pure APU coatings may result from the glass substrate. After immersion in water, the C atomic fraction further declines and Si atomic fraction remarkably rises. Moreover, the coating with 40% SiO$_2$-PEG1000 has a higher Si atomic fraction at the surface than the sample with 35% SiO$_2$-PEG1000. These results demonstrated that the acquisition of a highly hydrophilic surface should be attributed to the larger quantity of SiO$_2$-PEG nanoparticles accumulated at the surface. Although the coatings with 40 wt.% SiO$_2$-PEG400 possess the lowest WCA (25.3°) they are also opaque and characterized by the presence of cracks, as described above. Therefore, the lowest WCA that can be reached for a crack-free and clear APU, using SiO$_2$-PEG fillers, is 38.7°, i.e., the WCA of the coatings with 40 wt.% SiO$_2$-PEG1000. In addition, it is obvious that, when working with fixed amounts of SiO$_2$-PEG, SiO$_2$-PEG400 is more efficient in increasing the surface hydrophilicity than SiO$_2$-PEG1000. Perhaps, the lower compatibility of SiO$_2$-PEG400 with APU caused a lower reactivity of the grafted PEG400 chains during the curing step. As a consequence, PEG400 chains have higher mobility and thus more easily rearrange at the surface of the coatings in water [27]. The relatively rougher surface of the coatings with PEG400 may be another reason for the higher hydrophilicity of the coatings.

For the sake of comparison, pure APU coatings and unmodified SiO$_2$ based coatings were also exposed to water/air cycles. A slight decrease of WCA was found for pure APU coatings, which should be caused by the migration of polar groups from the coatings to the surface [28]. Its equilibrium value is 68.2°, being much higher than the lowest WCAs of SiO$_2$-PEG based coatings. The WCA of the coatings with unmodified SiO$_2$ remarkably reduced as the number of water/air cycles increased, but its equilibrium WCA was about 70.1°, which was close to that of the pure APU coatings. Highly hydrophilic coatings were not obtained through the direct addition of hydrophilic nanoparticles, owing to the lower mobility of the silanol groups in the unmodified silica compared to those in the PEG chains of the SiO$_2$-PEG nanoparticles [29].

### 3.4. Outdoor dirt resistance

To understand the influence of SiO$_2$-PEG nanoparticles on the dirt-resistance of APU coatings, the nanocomposite coatings containing 35 wt.% SiO$_2$-PEG400, 35 wt.% SiO$_2$-PEG1000 and 40 wt.% SiO$_2$-PEG1000 as well as pure APU coatings were exposed to the outdoors environments for 42 days. All the samples were mounted on an outdoor exposure rack with a tilting angle of 45° and
facing south. Fig. 11 displays the optical microscopy images of the surfaces of different coatings before and after outdoor exposure. Pure APU coatings became seriously contaminated by dirt, whereas all nanocomposite coatings remained clean. The phenomenon demonstrated that SiO₂-PEG nanoparticles can efficiently improve the dirt-resistance of APU coatings. It also suggests that highly hydrophilic coatings have good dirt-resistance outdoors. These results agree with the observations made for polyvinylidene fluoride coatings [2]. Since PEG segments have the ability to resist protein adsorption [30–33], SiO₂-PEG nanoparticles may also have potential applications in medical implants and underwater anti-fouling coatings.

4. Conclusions

PEG-grafted SiO₂ (SiO₂-PEG) nanoparticles with alcoholic hydroxyl groups at their surface were readily obtained by chemically attaching the PEG-functionalized silane coupling agent, synthesized from the reaction of IPTES with excess PEG. The acquisition of SiO₂-PEG was confirmed by FTIR, TGA, and through the dispersion behavior of SiO₂-PEG nanoparticles in water. The molecular weight of PEG did not exhibit a significant impact on the mass fraction of PEG attached.

SiO₂-PEG nanoparticles were incorporated into acrylic-based polyurethane coatings. In comparison with unmodified SiO₂ nanoparticles, the compatibility of SiO₂-PEG with polyurethane coatings was greatly improved. Moreover, SiO₂-PEG1000 demonstrated better compatibility than SiO₂-PEG400, leading to crack-free and transparent coatings even for SiO₂-PEG1000 contents up to 40 wt.%. The coatings containing SiO₂-PEG nanoparticles formed highly hydrophilic surfaces in the water-air cycle. On the contrary, pure acrylic-based polyurethane coatings and the unmodified SiO₂ nanoparticles-embedded coatings displayed WCAs as high as 70° even after induction with water. Due to their highly hydrophilic surface, the coatings with SiO₂-PEG nanoparticles have excellent outdoor dirt-resistance.

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References


