



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



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ABSTRACT

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 superhydrophilic 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 charging 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 superamphiphilicity [13–16]. But TiO₂ nanoparticles will considerably shorten the service life of organic coatings. Fluoride siloxane, for example, commercially named

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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 wettability 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 azeotropic 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 (SM515/70ABC) 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 SM515/70ABC 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 (80 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 tetraethylorthosilicate [24]. Nevertheless, in the cited report, the

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