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Preparation of superhydrophobic polyimide films modified with organosilicasol as effective anticorrosion coatings

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ABSTRACT

In this study we prepared superhydrophobic polyimide (PI) hybrid coatings for anticorrosion application by adjusting their surface roughness and surface composition through spray-coating with silylated perfluoroalkylsilane-modified organosilicasol (silylated fluoro-organosilicasol), which increased the surface hydrophobicity. After silylation with 1,1,1,3,3,3-hexamethyldisilazane (HMDS), the silylated fluoro-organosilicasol further transformed the PI surface into a superhydrophobic state with a static water contact angle of greater than 160° and a low hysteresis of 10°. We examined the mechanism behind the enhancement in superhydrophobicity through analyses of the surface topology and chemical composition of the films, using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM), and electron spectroscopy for chemical analysis (ESCA). These analyses suggested that both surface roughness and silylation of the fluoro-organosilicasol making more CF₂ groups on the outmost surface rendered the surface hydrophobicity. The anticorrosion properties of these superhydrophobic coatings were also examined through Tafel measurement. These PI hybrid coatings demonstrated lower corrosion current density and nobler corrosion potential and higher polarization resistance. The enhancement in anticorrosion performance was believed to be contributed from the superhydrophobicity and dual barrier protection from the fully-covered fluoro-organosilicasol, insulating the metal from corrosive species in the medium. This superhydrophobic coating technique with good stability guaranteed better corrosion protection and also has great potential for application to other polymeric films.

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1. Introduction

Polyimide (PI) is already a widely used flexible polymer exhibiting good thermal, chemical, and mechanical properties [1]. PIs are also utilized as stable organic coatings for anticorrosion purposes due to the advantages listed above. However, the limitation of PI as an organic coating lies in the water absorption [2], which is a drawback for its use in coating for anticorrosion. The adoption of fluorine-containing monomers can enhance the hydrophobicity of PI [3] but superhydrophobicity cannot be simply achieved with monomer substitution since the surfaces have to be rough. The major limitation toward achieving superhydrophobicity of PI surfaces, however, lies in its flatness and poor workability after imidization. According to previous studies, a flat surface presenting regularly aligned closest-hexagonal-packed CF₃ groups can achieve a water contact angle of only 120° [4]. To prepare superhydrophobic PI, appropriate control of the surface roughness is the critical factor toward enhancing hydrophobicity, according to the Wenzel and Cassie equations, which both describe the wetting behavior of rough surfaces [5].

Although many approaches have been developed for the fabrication of superhydrophobic surfaces, including electrospinning [6], etching [7], plasma treatment [8,9], chemical vapor deposition (CVD) [10,11], addition of a sublimation material [12,13], molding [14,15], electrodeposition [16], and sol-gel processing [17–20], the modification techniques on PI surfaces remain a challenge. Recently, nanoparticles (NPs) have become popular modifying agents for controlling surface roughness [21]. With their precise size control, tunable surface chemistry, and high processability through spin- or dip-coating, NPs appear to be excellent materials for producing superhydrophobic coatings [22–30]. These techniques for preparing superhydrophobic PI coating could be promising in application for anti-corrosion and anti-contamination use in harsh environment [31–33].

In this paper, we describe the endowing of superhydrophobicity onto the surface of PI films for anticorrosion using a simple method: spray-coating with an excellent anchor on the surface. Here, we employed fluoroalkylsilane-modified organosilicasol (DMAC-ST), which is spherical colloidal silica mono-dispersed in the organic solvent N,N-Dimethyl acetamide with particular particle size, to create rough features on the surfaces of soluble PI. We modified the organosilicasol DMAC-ST in a two-step process: first with fluoroalkylsilane (tridecafluoro-1,1,2,2-tetrahydrooctyl-1-triethoxysilane, F8261) to hydrophobize DMAC-ST [29], then with the silylation agent 1,1,1,3,3,3-hexamethyldisilazane

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(HMDS) further to remove residual SiOH groups [30]. After surface modification, we spray-coated the silylated fluoro-organosilicasol onto the PI surfaces. Through this simple process, we could anchor the sprayed silylated fluoro-organosilicasol onto the film's surface to provide suitably rough surface features, thereby enhancing the hydrophobicity and minimizing contact angle hysteresis. Furthermore, we believe the combination of silylated fluoro-organosilicasol and PI can provide good water repellency and dual barrier protection for anticorrosion on steel. Using contact angle measurements, scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared (FTIR) spectroscopy, and electron spectroscopy for chemical analysis (ESCA) and Tafel polarization curves for corrosion measurement, we characterized the mechanism of superhydrophobicity enhancement and the anticorrosion behaviors of the PI hybrid coatings.

2. Experimental

2.1. Materials

2,2'-Bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,2-Bis [4-(4'-aminophenoxy)phenyl] hexafluoropropane (6FBAPP) were purchased from ChrisKev. Organosilicasol (DMAc-ST ZL, 20 wt% spherical colloidal silica mono-dispersed in N,N-dimethylacetamide (DMAc); particle size: 70–100 nm; Nissan Chemical), tridecafluoro-1,1,2,2-tetrahydrooctyl-1-triethoxysilane (F8261, 95%+; Alfa Aesar), 1,1,1,3,3,3-hexamethylidisilazane (HMDS) (98%; ACROS), hydrochloric acid (HCl, 37%; Merck), N,N-dimethylacetamide (DMAc, 99%+; Tedia) and toluene (99%+; Tedia) were stored in desiccators and used as received. Stainless steel 304 (SS304) plates with 0.1 mm thickness were purchased from a local supplier and mechanically abraded with different grades of emery paper and then polished with 0.3 mm alumina powder. The polished SS304 plates were washed with distilled water and ethanol.

2.2. Synthesis of PI-coated SS304 film

6FBAPP with equal mole numbers to 6FDA was first added in three portions to DMAc solvent in a 250-mL three-neck round-bottomed flask equipped with a mechanical stirrer and N₂ inlet. After the diamine had completely dissolved, an equal number of moles of 6FDA was added, in three portions, to the solution. After the 6FDA had completely dissolved in the reaction mixture, the solution was further stirred for 2 h to obtain a higher molecular weight of poly(amic acid). This poly(amic acid) solution was then coated onto SS304 plates and subjected to thermal imidization sequentially at 100, 150, 200 °C for 1 h each. Bare SS304 and PI-coated SS304 plates were cut into square films with 2.5 × 2.5 cm² per piece to undergo further measurement.

2.3. Synthesis of silylated fluoro-organosilicasol

DMAc-ST was diluted to 0.5 wt% by adding DMAc solvent and then F8261 (an equal weight to the DMAc-ST solid content) was added slowly to the solution. The DMAc solution was stirred at 100 °C for 24 h to form fluoro-organosilicasol. The pH of this solution was then adjusted to 1.2 by adding concentrated HCl (37%). HMDS was slowly added dropwise to the acidified solution to silylate the fluoro-organosilicasol; this reaction took place in an ultrasound bath over 12 h at room temperature. The supernatant liquid was then removed through baking at 160 °C for 6 h and the silylated fluoro-organosilicasol was collected and dried. The nonsilylated fluoro-organosilicasol was also subjected to the same procedure for the sake of comparison.

2.4. Preparation of superhydrophobic PI-coated films

Silylated fluoro-organosilicasol and fluoro-organosilicasol were separately dispersed in DMAc and toluene (1:1) so that the solid content

was 5 wt% in each solution. The solutions containing the silylated and nonsilylated fluoro-organosilicasols were separately spray-coated (one, two, or four cycles with constant time per cycle) onto several PI-coated SS304 films; the volume of each spray was fixed at 0.01 mL over an area of 2.5 × 2.5 cm². Spray-coating was performed using a spray pistol and N₂ gas under a constant pressure (50 psi). PI coating films modified with the silylated and nonsilylated fluoro-organosilicasols are denoted herein as PI-FH_x and PI-F_x, respectively, where x represents the number of sprays. These modified PI-coated SS304 films were baked at 50 °C for 10 min and then at 160 °C for 2 h to ensure that no solvent remained. The baking process also served to anchor the particles to the surface.

2.5. Characterization

The surface wettability of the samples was determined using a contact angle meter by measuring the water contact angle of one drop (10 μL) of deionized water at room temperature. Three measurements were performed for each sample to evaluate the average static contact angle (θ) after 5 s. Films were tilted at 10° to record the dynamic motions of the water droplets on the sample surfaces. Contact angle hysteresis was investigated by measuring advancing and receding contact angle through tilting experiment. Surface morphologies and particle distributions were investigated using a thermal field emission scanning electron microscope (JEOL JSM-6500 F). An atomic force microscope (Innova Scanning Probe Microscope) was used to derive surface roughness profiles. All AFM measurements of the PI, PI-F_x, and PI-FH_x series were performed in the tapping mode in a dry environment at room temperature over a sampling area of 5 × 5 μm². The images had a resolution of 512 × 512 pixels and were acquired at a scanning rate of approximately 0.5 Hz. The images obtained were processed using diSPMLab software (Veeco). FTIR spectra of fluoro-organosilicasols prepared with and without HMDS treatment were recorded using a PerkinElmer Spectrum 100 Optica spectrometer. The surface chemistry of the PI, PI-F_x, and PI-FH_x series was characterized through ESCA (Ulvac-PHI PHI 1600) with a 15 kV Al/Mg X-ray source and the Mg K_α emission at 1253.6 eV. A single-scan spectrum (0–1100 eV) and narrow scans for C 1 s (280–300 eV) were recorded for each sample with pass energies of 1 and 0.1 eV, respectively. The background was subtracted using the Shirley formula; deconvolution was performed by fitting the spectra to multiple peaks, each being a Gaussian function; the charge effect was compensated by setting the binding energy of aromatic C atoms, not linked to O or N atoms, at 285.0 eV. Cross-cut tests were used to determine the adhesion of the surface coating. Specimens were cross-cut to create 100 squares pieces within 1x1 cm² and 3 M 600 tape was applied over the cut. Then the tape was pulled

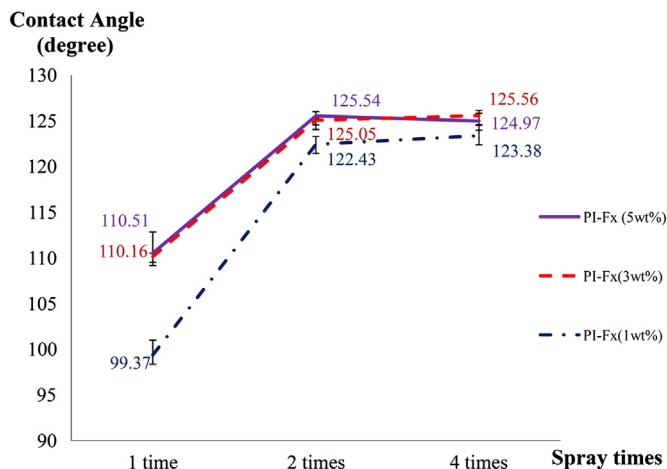


Fig. 1. Contact angle curves of PI-F_x films coated with different concentrations of the modified particles and subjected to different numbers (one, two, or four) of spray coatings.

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