



Superhydrophobic polyethylcyanoacrylate coatings. Contact area with water measured by Raman spectral images, contact angle and Cassie–Baxter model

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ABSTRACT

Apolar fibers wired into a mesh-like microstructure forming a coating with a contact angle larger than 160° and fabricated by polycyanoacrylate polymerization are described. Interconnected fibers with diameters measuring approximately 5 μm are formed by texturized linear or folded nanowires. The structure forming the deposited film occupies ~1.5% of the coating's top geometric area. This value agrees with the water/coating contact area given by the Cassie–Baxter contact-angle model (~1.5%). The spatial distribution of the surface in contact with water was determined by Raman spectral imaging (~1.5%) using the polycyanoacrylate lines and by scanning electron microscopy (~2.0%).

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1. Introduction

Water repellency is important in many processes, such as the prevention of the adhesion of snow to antennas and windows, self-cleaning traffic indicators, the reduction of frictional drag on ship hulls, metal refining and stain-resistant textiles [1]. The two crucial factors in the wettability of solid surfaces are chemical composition and topography [2]. It is well known that microtextured or nanotextured hydrophobic surfaces can become superhydrophobic [3]. To achieve superhydrophobicity, the surfaces may be regularly structured, which provides useful models for quantitatively evaluating the relationship between contact angle and surface structure. Irregularly structured surfaces provide the advantage of simplicity and low cost of fabrication. To date, various methods, such as lithographic patterning [4], plasma etching [5], electrical deposition [6], phase separation [7], sol–gel synthesis [8] and electrostatic self-assembly [9], have been established to achieve superhydrophobicity. These existing techniques are typically complicated, expensive, and/or time-consuming. Herein, we present an alternative way to simply and inexpensively achieve superhydrophobic surfaces constructed by irregularly packed colloidal self-assembly.

Alkyl cyanoacrylate monomers are known for their high reactivity and the excellent adhesive properties of the resulting polymers; however, these unique features tend to make the synthesis of

well-defined and/or functionalizable poly(alkyl cyanoacrylate) architectures difficult [10]. The fuming of cyanoacrylate esters provides an effective means for developing latent fingerprints; in this process, the polymerization of cyanoacrylate esters is initiated by reactants in a fingerprint. Thus, the in situ development of polymer chains serves to highlight the fingerprints [11]. Recently, Mankidy et al. [12,13] prepared nanofibers of poly(ethyl-2-cyanoacrylate) by a vapor-phase polymerization technique directly on surface-modified glass substrates. Bogdan et al. [14] prepared nanocapsules by interfacial polymerization of ethyl-2-cyanoacrylate monomer in an oil-in-water emulsion. Li et al. [15] prepared hollow microspheres of poly(ethyl- α -cyanoacrylate) via vapor-phase polymerization using micro-water droplets as templates and initiators, which were used to construct surfaces with diverse wettability. Boday et al. [16] modified glass slides with polycyanoacrylate (PECA) by chemical vapor deposition and measured water contact angles of 129°. Troitskya et al. [17] developed a method of hydrophilic/hydrophobic patterning of solid surfaces based on polycyanoacrylate monolayers with water contact angles of 102–103° [18].

In this study, we describe a simple and inexpensive method for forming superhydrophobic coatings on glass using cyanoacrylate polymerization under controlled atmospheric relative humidity (RH) and curing temperature. The formation of PECA was analyzed by Raman and infrared spectroscopy. Optical microscopy and scanning electron microscopy (SEM) were used to investigate the changes in morphology occurring during polymerization and subsequently to infer the effects of microstructure on hydrophobicity,

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as characterized by contact angles. The Cassie–Baxter contact-angle model was used to determine the water/coating contact area, and the results were compared with those obtained by mapping the coating contact surface using confocal Raman microscopy.

2. Experimental

2.1. Sample preparation

PECA films were prepared on flat glass surfaces via vapor deposition by the polymerization of commercial poly(ethyl-2-cyanoacrylate) glue (Super Bonder®). The composition of the glue is >90% ethyl-2-cyanoacrylate, <10% polymethyl-methacrylate and <10% stabilizers, which include 1,4-dihydroxybenzene (hydroquinone). Temperature effects were studied during the process to control the roughness of the resulting polymer films. The glass slides (1 × 2 cm) used as substrates were cleaned with isopropyl alcohol and dried under argon flux. The glass substrates were then immersed for approximately 10 s in a 25% w/w ammonium hydroxide (NH₄OH) aqueous solution and immediately placed in a Petri dish containing a smaller container with 200 mg of cyanoacrylate glue. A film of NH₄OH was then formed on the glass; the film exhibited a variable thickness along its surface. During the fuming process, the reaction time (10 min) was held constant for the samples used. The effect of out temperature on the polymerization process was investigated.

2.2. Raman spectroscopy

Raman spectra were recorded using a commercial confocal Raman microscope (CRM 200, WiTec, Germany) operating with an intensity-stabilized single-mode He–Ne laser system (Melles-Griot) (usually $I_{\max} = 15$ mW). The laser radiation was coupled to the microscope via a single-mode fiber. The optical components (filters, gratings, and lenses) were adapted to the appropriate wavelength. The used Raman spectra were centered at $\nu_{\text{cyanoacrylate}} \sim 2970$ cm⁻¹, $\nu_{\text{water}} \sim 3400$ cm⁻¹. The following conditions were applied: integration time, 0.25 s; objective used for Raman spectral imaging, Nikon 60×, NA = 0.8 and excitation wavelength, 514 nm.

2.3. Confocal laser scanning microscopy

Confocal laser microscopy requires a point source that is focused onto the sample. The scattered light is collected and focused into a pinhole in front of the detector to ensure that only rays from the image focal plane can hit the detector. By varying the focus plane for various scans, it is possible to map various planes of an object and determine the area of the top plane of a sample. In our setup, where the laser light was delivered via a multi-mode optical fiber, the spot could be focused to a diffraction-limited size because a multi-mode optical fiber acts as a pinhole.

The energy shift in the Raman spectrum is associated with the excitation of a molecular vibration, which represents a type of fingerprint for the molecule involved in the scattering process, and the confocal Raman microscope has a spatial resolution that reaches the sub-micrometer regime. The laser is focused onto the sample, and an image is acquired by scanning the sample along the X–Y plane. Low scanning speeds are used in the Raman spectra imaging mode because a complete spectrum is obtained at every image pixel. During the scan, the data-acquisition electronics create a trigger signal for every image pixel.

The scan is performed line by line. The formation of the image is associated with point-like excitation and with a point-like detector. As in wide-field microscopy, the resolution at the focal plane

is diffraction-limited. Instrument parameters such as the scan rate and pin-hole diameter can be set to achieve maximum resolution. Variations in the actual sample intensities will be averaged, or integrated, into one intensity value in any image pixel. Small sample structures can be missed if the step size is too high or the pixel too large. The operator must consider the size of the objects and set the pixel size and step size to appropriate values to collect sufficient information to reconstruct the object, as given by the Nyquist theorem of sampling, which reads: The sampling frequency (D) must be at least $D/2$ to distinguish object information from the background. Oversampling will capture the same information but take a longer time and result in long acquisition times.

2.4. Infrared spectroscopy

IR spectra were measured on a FTIR Bomem MB-100 spectrometer by using KBr (IR grade, Aldrich) pellets directly placed in the sample holder. All spectra were collected at 2-nm intervals over the spectral range of 400–4000 cm⁻¹. Each spectrum was based on 64 co-added scans. The PECA polymer sample removed from the glass substrate was prepared by using an agate mortar and pestle to grind the solid polymer (1% w/w) with solid potassium bromide (KBr) and applying pressure to the dry mixture.

2.5. Optical microscopy

A Zeiss standard was used for the size calibration of the images obtained with a Zeiss Axioplan optical microscope equipped with a CCD color camera (Hitachi KP-D20BU).

2.6. Scanning electron microscopy

The substrates containing the organic films prepared under the conditions specified above were fixed in a metallic sample holder and coated with a thin layer of gold (60 nm) using a AJA ATC 1300-F sputtering system. The fragments were also observed using a Leica LEO 440i SEM with digital imaging magnification up to 300,000×, provided by secondary electrons, back-scattered electrons and specimen current measurement detectors operated at a voltage of 20 kV. Size measurements were performed for at least 15 different regions of each sample, and the presented results correspond to the averages of the obtained size values.

2.7. Contact angle measurements

All experiments were performed at 25 ± 0.5 °C and 65% RH. The samples were placed on a horizontal support; a microsyringe with a 5.0 μL capacity was positioned at the center of the substrate and connected to the micromanipulator. The micromanipulator was used to adjust the position of the needle tip of the syringe carefully above the clean solid slide. The tip of the syringe was positioned a few micrometers away from the surface of the solid to eliminate any effect of the impact when the droplet was released. The droplet volume was selected to be 1.5 μL. An image of the drop in contact with the desired sample surface was created using a digital camera, and the image was magnified by an optical lens. The profile of the drop was then processed using the free software ImageJ. The ImageJ contact angle plug-in (Drop Analysis) detects the edge of the drop and fits its profile to a circle or an ellipse.

The tangent to the triple-line contact is calculated and drawn by the ImageJ software to return the value of the contact angle with acute precision [19].

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