Surface & Coatings Technology 225 (2013) 66–74

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Superhydrophobic dual-sized filler epoxy composite coatings

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ARTICLE INFO

Article history:
Received 17 May 2012
Accepted in revised form 9 March 2013
Available online 22 March 2013

Keywords:
Superhydrophobicity
Hierarchical roughness
Composite coating
Sandblasting
Erosion

ABSTRACT

We propose an accessible method of superhydrophobic coating fabrication, in the form of an epoxy resin composite with hard nano- and microfillers, combined with surface sandblasting and wet chemical hydrophobization. The fillers – glass microbeads and Al_2O_3 nanoparticles, dispersed in the bulk composite – provide a dual-sized roughness, if exposed on the surface. Sandblasting with corundum particles and subsequent air plasma etching exposes and enhances the micro- and nano-scale roughness, while wet chemical modification with 1H,1H,2H,2H-perfluorodecyltrichlorosilane reduces surface free energy to the level required for superhydrophobic materials. The coatings exhibit superhydrophobic behavior, with water contact angle of 152° and contact angle hysteresis of 8°. Hierarchical surface structure of coatings is preserved after erosive wear tests and superhydrophobicity is restored upon re-hydrophobization.

1. Introduction

The phenomenon of superhydrophobicity has been receiving increasing attention in the past decade, driven by the expectations for such applications as water repellent and self-cleaning coatings [1] or, more recently, anti-icing coatings [2]. Water droplets take on a spherical shape and roll off easily from objects that combine low surface free energy with a specific surface texture, usually consisting of hierarchical roughness — at the micro- and nano-scales. Such structures are known in nature and have been synthesized utilizing various procedures, most often by fabrication of a material with hierarchical surface structure and subsequent surface hydrophobization, to ensure required low surface energy. The techniques utilized for microfabrication of the structure include photolithography, nanoimprint lithography, reactive ion etching, soft lithography, anodization, *etc.* [1,3–7]. The applications of such procedures are limited by their complexity and low cost effectiveness [8]. In an attempt to obtain more feasible superhydrophobic materials, fillers have been used to generate roughness, either by deposition of nanoparticles on flat or microstructured substrates (by spin coating, dip coating or spraying) [9–14] or by incorporating fillers in a composite coating [15–20]. In one such a procedure, the microscale roughness was generated on an epoxy paint surface by sandblasting it with alumina (Al_2O_3) particles. A solution of epoxy adhesive loaded with silica (SiO_2) nanoparticles was subsequently deposited on the surface, which – upon hydrophobization – led to water contact angle (WCA) of 167.8° and sliding angle of 7° [21]. Silica and other nanoparticles, such as alumina, tin oxide or calcium carbonate, have been dispersed in polymethacrylate, polyvinylidene fluoride, polyacrylate, polytetrafluoroethylene, epoxy, acrylic, perfluoroalkyl methacrylic copolymer and other polymers and copolymers [15,22–24]. Dual-scale roughness, obtained in procedures involving deposition of nanoparticles or composite coatings on flat substrates, has most often resulted from nanoparticle agglomeration. Micrometer-sized agglomerates act as the first order structure, while individual nanoparticles, protruding from the agglomerates, define the second order structure. Mechanical durability of such surfaces, usually problematic, is one of the concerns in current research on superhydrophobic surfaces [25–30]. Pareo et al. designed a PMMA-based composite material for self-cleaning applications, loaded with hollow glass microsized spheres, nanosized silica particles and aluminum hydroxide prismatic microflakes [29]. The material exhibited increased resistance to outdoor weathering, accompanied by improvement in mechanical properties such as elastic modulus and Rockwell hardness. Weathering resistance resulted in a large part from application of polymeric hydrophobic methoxy-functionalized fluoromethacrylic protective film on composite surface. Elbert and Bhushan demonstrated high wear resistance of coatings created by spraying micro- and nano-sized silica particles onto micropatterned and flat epoxy substrates, in multiscale tests involving an atomic force microscope (AFM), a ball-on-flat tribometer, and a water jet apparatus [30].

Superhydrophobic surfaces in many potential outdoor applications, such as antennas, power lines or aircraft outer surfaces, need to demonstrate resistance to erosive action of airborne sand or dust particles. The aim of this study was to develop a superhydrophobic coating with improved durability of its hierarchical topography in erosive environment. The hierarchical texture is defined in the bulk

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http://dx.doi.org/10.1016/j.surfcoat.2013.03.017

of the coating by dual-sized fillers – glass microbeads and Al_2O_3 nanoparticles – dispersed in epoxy resin, and the microroughness is enhanced by sandblasting with corundum particles. Epoxy binder was chosen primarily for its compatibility with epoxy paints, frequently used as topmost coatings in outdoor applications. The composite exhibits superhydrophobicity after wet chemical hydrophobization.

2. Materials and methods

2.1. Preparation of epoxy composites

The process through which the nanocomposite coating is made is illustrated in Fig. 1. First, a composite of low viscosity diglycidyl ether of bisphenol-A epoxy resin (Epidian 5, Z. Ch. Organika-Sarzyna, Poland, the average molecular mass of 390, the epoxide equivalent weight of 192–204, the viscosity of 30000 mPa·s at 25 °C), crosslinked with an amine hardener (IDA, Z. Ch. Organika-Sarzyna, at the proportion of 1:1 w/w) with aluminum oxide nanoparticles (ALNP, Nanostructured & Amorphous Materials Inc., USA, gamma-Al_2O_3, 99%, the mean diameter of 11 ± 3 nm, as determined by means of atomic force microscopy) and SiO_2 microbeads (GMB, the mean diameter of 26 ± 7 μm, as determined by means of optical microscopy), was prepared by ultrasound assisted mixing. The mixing was performed in the following sequence: Epidian 5 + ALNP (at ALNP weight fractions in the range of 5–18%, in relation to total Epidian 5 and IDA weight) + GMB (at a maximum GMB loading that allowed for uniform casting of the composite, typically in the proportion of 2.2:1.0 to total Epidian 5 and IDA weight) + IDA. The degassed composite was cast on microscope glass slides (the coating thickness was about 2 mm) and allowed to crosslink for seven days at room temperature (RT, ~22 °C). The coatings were then sandblasted using corundum particles (particle diameter of *ca.* 250 μm, at sample–nozzle distance of 2 cm and air pressure of 0.8 MPa) and ultrasonically cleaned in deionized (DI) water.

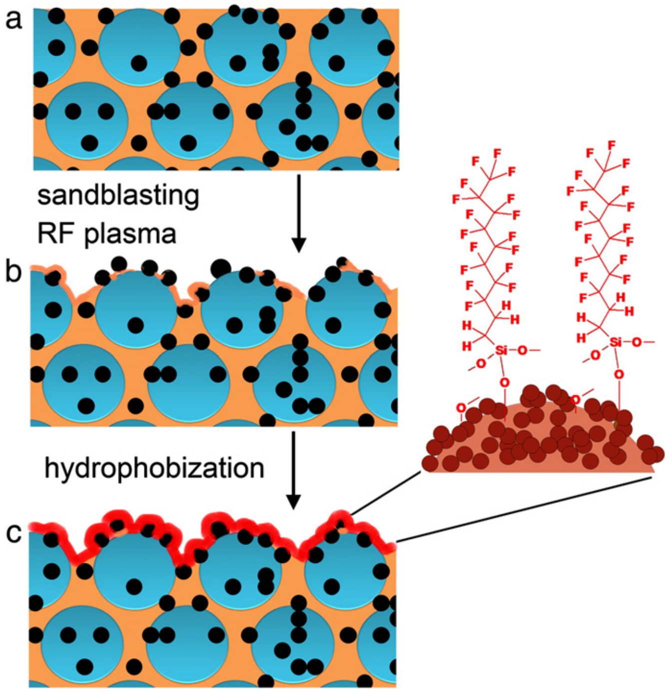

Fig. 1. Schematic of nanocomposite coating fabrication process: casting of 2 mm epoxy resin/ALNP/GMB composite coating on a microscope slide (a), sandblasting of coating surface with corundum particles and air plasma etching/activation (b) and surface chemical modification of the coating with FDTS (c). Filler sizes and outer layer thicknesses are not to scale for clarity.

2.2. Chemical surface hydrophobization

Prior to hydrophobization the surfaces were subjected to radio frequency (RF) air plasma (Harrick PDC-32G plasma cleaner, 10 min at 18 W), for etching of epoxy binder, exposing nanoparticles on the surface. Plasma treatment also provides removal of impurities and generation of reactive –OH groups on epoxy surface [31], as well as Al–OH groups on exposed alumina nanoparticle surface, both types easily undergoing silanization [32]. Chemical modification by chloroalkyl silanes proceeds more effectively for such activated surfaces, as demonstrated by Haensch et al. [33]. Finally, to impart hydrophobic properties to the surface, the coatings were modified with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS, $CF_3(CF_2)_7(CH_2)_2SiCl_3$, 96%, ABCR GmbH & Co. KG), by dipping them in 1 vol.% solution in toluene, for 30 min at RT. Due to the presence of fluorine atoms in FDTS chain, surface modification by this highly hydrophobic compound proceeds in two concurrent processes (Fig. 2). The first one consists in a direct reaction of chemically active Si–Cl groups of FDTS with surface groups generated in plasma activation process, such as –OH, –COOH and Al–OH. This process leads to formation of a modifier which is chemically bonded to the substrate [34].

In the second process chlorosilane reacts with a thin water layer on the surface, present due to air humidity. Chlorosilane hydrolysis takes place, with products condensing on the surface [35]. Nanometer-sized fluoropolymer clusters deposit this way, increasing roughness of the modified surface, which is beneficial for the structure under consideration (see Section 3.1).

After modification, the surfaces were cleaned with toluene, to remove the excess, unbonded FDTS, dried and heated at the temperature of 40 °C for 24 h, to enhance fluoropolymer condensation on the surface.

2.3. FT-IR spectroscopy

To verify the hydrophobization process, FT-IR spectra were recorded using a Bio-Rad FT F175 spectrometer, equipped with a GATR™ grazing angle ATR accessory (The GATR features a 65° incident angle and a Ge ATR crystal) and a MCT detector. This technique is very sensitive to surface modifications — spectroscopic information is collected from the material depth of a few tens of nanometers. 125 spectra were accumulated at 4 cm^{-1} resolution for each sample. A spectrum of aluminum substrate modified with FDTS was recorded at the same conditions as unmodified and FDTS-treated Epidian 5/IDA epoxy resin substrates, as a reference for adsorption band analysis.

The hydrophobization process was verified using FT-IR spectroscopy. Three absorption maxima at 1243, 1216 and 1142 cm^{-1}, characteristic of stretching vibrations of C–F bonds in $-CF_2-$ groups, can be recognized in the reference spectrum of FDTS-modified aluminum substrate (Fig. 3). All these bands are also present in the spectrum of FDTS-modified neat epoxy resin. The one with the maximum at 1243 cm^{-1}, is not separated from the substrate signal, but significantly increases its intensity. The two others, at 1216 and 1142 cm^{-1}, are well separated. The presence of these three adsorption bands provides evidence that fluorinated alkyl chains are presented on the surface of modified epoxy resins.

2.4. Surface morphology examination

The surface morphology of the coatings was characterized at each preparation stage, using optical microscopy and scanning electron microscopy (SEM, JEOL JSM-5600, operating in secondary electron imaging mode, at accelerating voltage of 20 kV, emission current of