



Facile electrodeposition of superhydrophobic and oil-repellent thick layers on steel substrate



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ABSTRACT

The aim of this work is to produce liquid-repellent surface on stainless steel via simple electrodeposition. For this purpose, myristic acid, stearic acid ethanol solution and perfluorooctanoic acid aqueous solution were used. Resulting contact angles and surface energy values were studied. Superhydrophobic and superoleophobic behavior of samples prepared using perfluorooctanoic acid electrolyte were performed by contact angle 159° for deionized water, 153° for olive oil and low surface energy 0.60 mJ/m^2 . Relation between the non-wettable behavior of samples, surface structure, chemical composition and mechanical properties were observed by SEM with EDX analysis, FTIR spectroscopy and tribological measurement, giving the preference to fluorinated precursor and low voltage electrodeposition.

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1. Introduction

A repellency of the surfaces for various liquids is the point of the interest for many research teams [1,2]. Characterization of non-wettable behavior is realized by measuring the contact angle (CA) values of liquids on the surface [3]. As the result of the theoretical aspects introducing the Young's equation, Wenzel and Cassie–Baxter wetting models [4–6], the roles of surface energy, surface morphology and surface tension are crucial. For perspective application, there are two necessary steps to reach the repellency, namely creation of an appropriate morphology and the modification of surface energy by suitable chemical composition [7,8]. The bioinspiration lead to mimicking of natural morphology and production of artificial surfaces in laboratory conditions [9–11].

An application of liquid-repellent products introduces the large quantity of possible substrates for modification such as textiles [12], wood [13], plastics [14,15], paper [16,17] or glass [18,19]. Important substrates for industry are metals. The hybrid surface modification consists of enhancing the surface roughness with inorganic nanoparticles or chemical etching and additive modification of nanoparticles by organic precursors such as fluorinated organic compounds [20–22]. Many research teams present the preparation of superhydrophobic surface on metals such as aluminum [1,23,24], copper [25,26] or iron [27] by long-time

immersions of substrate with modified structure in stearic acid (SA), myristic acid (MA) [28,29] with analogue results given by replacing the precursors with perfluorooctanoic acid (PFOA) [30], providing water and oil repellency. Two-step methods consisting of the microstructure formation and hydrophobization were replaced by controlled electrolysis with ethanol solution of SA or MA as electrolytes [31,32–34]. This method is time-saving, simple and effective for metal substrate modification. However, the products exhibit no repellency for low surface tension liquids.

Herein, we report simple time-saving deposition method of liquid-repellent layers on the stainless steel. Furthermore, by introducing of PFOA in electrolyte, water and oil repellent coatings are formed, prioritizing PFOA before non-fluorinated organic acids requiring addition of inorganic salt. Substitution of ethanol with water in electrolyte containing PFOA could help to solve the problem of acid persistence in water [35,36] by recycling the contaminated fraction of water. Deposited layers can be applied to enhance the corrosion resistance or to introduce functional properties such anti-icing and self-cleaning.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

PFOA (Alfa Aesar, 95%), MA (Alfa Aesar, 98%), lanthanum(III) chloride heptahydrate ($\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, Alfa Aesar, 99%), SA (Lachema,

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Table 1
CA values for testing liquids and calculated surface free energy.

Sample	Liquid CA [deg]						Surface free energy [mJ/m ²]
	Distilled water	Glycerol	Ethylene glycol	Diiodomethane	Formamide	1-bromonaphthalene	
sMA	156 ± 2	149 ± 5	148 ± 4	106 ± 11	150 ± 3	63 ± 28	16.10
sSA	151 ± 3	148 ± 8	139 ± 8	122 ± 7	142 ± 12	64 ± 19	11.40
sPFOA	159 ± 2	154 ± 3	152 ± 2	141 ± 3	141 ± 4	144 ± 5	0.60

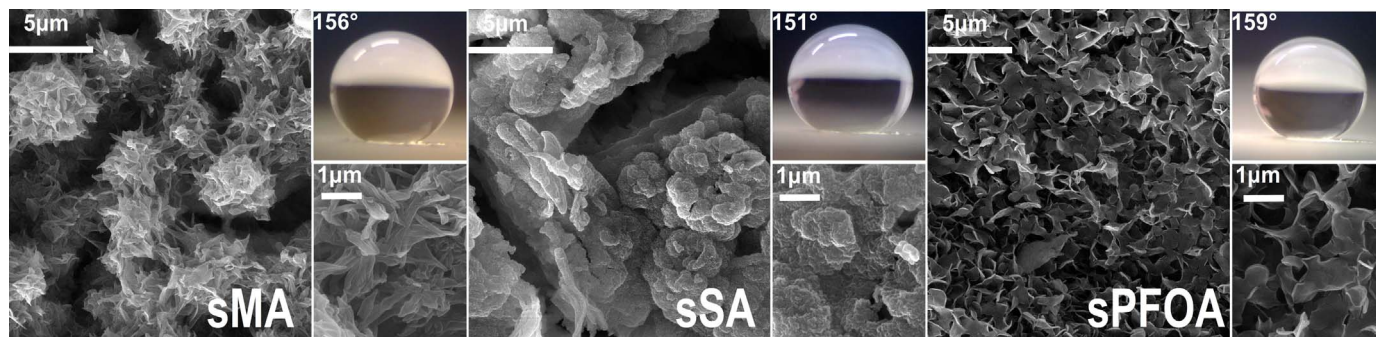


Fig. 1. SEM micrographs of surface structure (magnification 10 kx), inset of image detail (magnification 50 kx) and water droplet with stated WCA for sMA, sSA and sPFOA samples.

95%), potassium bromide (KBr, Sigma Aldrich, ≥ 99%), ethanol (Sigma-Aldrich, 95%), glycerol (Sigma-Aldrich, ≥ 99%), 1-bromonaphthalene, ethyleneglycol (Sigma-Aldrich, ≥ 99.5%), diiodomethane (Sigma-Aldrich, 99%), formamide (Sigma-Aldrich, ≥ 99.5%) and deionized water (conductivity 18.18 μS/cm at 13 °C; prepared at Masaryk university using RO 1-1CC unit by MEMSEP Ltd.) were used for experiments.

2.1.2. Surface characterization

CA and surface energy values, averaged from ten measurements, were obtained by Surface Energy Evaluation (see) System device with eponymous software (AdvEX Instruments) for 2.5 μl droplets. The surface energy was determined using the six-liquid Owens-Wendt regression model.

Norm-referenced neutral salt spray (NSS) corrosion tests were realized for 1000 h according to CSN EN ISO 9227 NSS to observe possible corrosion product formation. Macroscopic topography and surface roughness was characterized by confocal microscope Olympus LEXT OLS4000 operating with LEXT software.

For microstructure observation, SEM Tescan MIRA3 using secondary electron (SE) detector was employed. Each sample was coated by 19 nm of gold in order to prevent surface charging.

The film thickness was measured using DektakXT (Bruker) mechanical profilometer. The mechanical properties of the films were studied using TI950 (Hysitron) and Fischerscope H100 nanoindenters. The scratch resistance and film adhesion were studied by means of Revetest Xpress plus scratch tester (Anton Paar) equipped with a Rockwell type diamond indenter with a radius of 200 μm. The load was increased at a constant rate 16 N/min, while the scratch length was 16 mm.

Occurrence of chemical elements from precursors was stated in wt% by SEM-EDX mapping of the 25 μm² area.

FTIR spectrometer Bruker VERTEX 80v equipped with attenuated total reflectance (ATR) plate measured reflectance spectra of samples on steel substrate and transmittance spectra of KBr pellets containing pure precursors (concentration up to 1%).

2.2. Electrodeposition

Stainless steel plates 20 × 70 × 1.5 mm in size were cleaned in

ethanol, ethanol/deionized water, deionized water ultrasonic bath, each for 15 min and dried with the airflow.

Electrolytes with concentration of 0.1 M MA and 0.038 M of LaCl₃ · 7H₂O in ethanol, 0.05 M SA with 0.038 M LaCl₃ · 7H₂O in ethanol and 0.045 M PFOA in deionized water were prepared two hours prior the deposition. The distance between the electrodes was two centimeters. Using DC power supply DF3010 (Wentronic GmbH), working conditions were set to 30 V for 10 min for MA electrolyte according to [37], 15 V for 10 min for SA and 5 V for 20 min for PFOA solution. Optimal working conditions for SA and PFOA electrolytes were optimized in dependence on water CA (WCA) (see Table S1 Supplementary material). After the deposition termination, samples were retained in a fume hood until dried.

3. Results and discussion

3.1. Contact angle and surface energy measurement

WCA values were stated 156 ± 2°, 151 ± 3° and 159 ± 2° for prepared samples sMA, sSA and sPFOA respectively, exhibiting superhydrophobic behavior. However, the CA for olive oil (OCA) with surface tension of ≈ 32 mN/m was impossible to state for sMA and sSA due to their oleophilicity. OCA for sPFOA was stated in a range of 153 ± 3° exhibiting superoleophobic behavior. The high liquid CAs ensure the perspective usage of PFOA products. The Table 1 contains the CA values for liquids and surface energies, that were stated 16.10 mJ/m², 11.40 mJ/m² and 0.60 mJ/m² for sMA, sSA and sPFOA, respectively. Low deviations for sPFOA CA values predict eligible material uniformity. The Meng et al. [38] referred that surface energy exceeding the one-quarter of the liquid surface tension result in wettable behavior (CA < 90°). This fact fitted to surface energies of sMA, sSA and sPFOA in relation to OCA. The significant change of sPFOA surface energy corresponded to the presence of fluorine.

Reproducibility of layers was considerable, providing low deviations for numerous WCAs measurement (see, Table S2).

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