Applied Surface Science 419 (2017) 454–459

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Aluminum surface modification with fluoroalkyl methacrylate-based copolymers to attain superhydrophobic properties

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ARTICLE INFO

Article history:
Received 30 November 2016
Received in revised form 24 April 2017
Accepted 26 April 2017
Available online 8 May 2017

Keywords:
Aluminum surface
Superhydrophobicity
Polymer coatings
Glycidyl methacrylate and fluoroalkyl methacrylates copolymers

ABSTRACT

We propose a novel approach to create a superhydrophobic coating on an aluminum surface by attaching random copolymers that are based on glycidyl methacrylate and a number of fluoroalkyl methacrylates that contain 3–7 fluorine atoms in their monomer units. To texture the aluminum surface, short-term etching with hydrochloric acid solutions was used. The coatings that are based on glycidyl methacrylate and fluoroalkyl methacrylate copolymers maintain superhydrophobic properties for longer than 40 h under saturated vapor conditions.

1. Introduction

During the last decade, materials with superhydrophobic properties have received significant attention in terms of fundamental research and practical application. Superhydrophobic materials are characterized by a water contact angle that is greater than 150° and a low contact angle hysteresis that does not exceed 1–3°. The unique functional properties of superhydrophobic materials have potential application as anti-icing, anti-corrosion and anti-biofouling coatings for metal constructions, protective coatings for electronics, and as self-cleaning surfaces [1–3].

The concept of superhydrophobic material production is based on reciprocal action of the following two factors: multidimensional roughness and low free energy of the subsurface layer [4,5]. Research literature contains information about a number of substrate surface texturing methods such as lithography, electroplating, anodic oxidation and chemical vapor deposition, plasma and laser treatment, sol-gel process, and etching [6–14]. However, the majority of these methods require special equipment and chemicals, which limits their applicability [15]. Therefore, it is essential to develop approaches for surface texturing of materials (especially for metals) that can be used for treating large workpieces using the available chemical reagents.

As a rule, surface energy reduction of a substrate is achieved by attaching hydrophobic agents with long fluoroalkyl or hydrocarbon substituents, for example organosilicon compounds. One disadvantage of these substances is the complexity of their synthesis [16,17]. Moreover, coating defects may be formed during the modification with low molecular weight hydrophobic agents due to the non-uniform surface coverage and the absence of chemical bonds with the adjacent molecules of the modifying agent, or between the modifying agent and the substrate. This causes coating degradation and reduction of hydrophobic characteristics [18]. The alternatives to low molecular weight hydrophobic compounds are copolymers that contain both hydrophobic and reactive groups in their monomer structure that provide multiple bonds between macromolecules and the substrate surface. Furthermore, it is possible to create an additional level of nanoroughness by attaching high molecular weight compounds to the surface.

It is well known that fluorine containing polymers have many practical applications in industry for surface coating, stone preservation, in optics and microelectronics etc. because of their unique surface properties such as low surface free energy and water/oil repellency [19,20]. The surface energies are determined by the structures present in the top layer (1 nm or less from the air surface). High water/oil contact angles on the surface of fluorine

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http://dx.doi.org/10.1016/j.apsusc.2017.04.222
0169-4332/

containing polymers are result of the presence of C—F bonds which have low polarizability and the strong electronegativity of the fluorine atom [21]. Early it was determined that on the surface of polymers the surface energy of constituent groups decreases in the order CH_2 (36 mN/m) > CH_3 (30 mN/m) > CF_2 (23 mN/m) > CF_3 (15 mN/m) [22,23].

Some previous works [24–27] were devoted to the synthesis of copolymers of perfluoroalkyl acrylates and alkyl acrylates: methyl methacrylate, butyl acrylate, etc. and to study the surface energy characteristics of polymer films on their basis. However, the solubility of fluoropolymers in organic solvents decreases as the fluorine content increases in the monomer unit.

It is known that fluoroalkyl methacrylates with a low fluorine content [e.g., poly(2,2,2-trifluoroethyl methacrylate) and poly(1,1,1,3,3,3-hexafluoroisopropyl acrylate)] are characterized by a surface energy that does not exceed 22 mJ/m^2, which is comparable to the parameters of perfluorinated compounds [28,29]. Consequently, fluoroalkyl methacrylates with low fluorine content seem to be viable for providing water-repelling properties to the surfaces of materials.

In this work we investigated the water-repellent properties of the polymer coatings on the basis of copolymers of fluoroalkyl methacrylates (FMAs) containing three to seven fluorine atoms in their monomer unit and glycidyl methacrylate (GMA) on the textured aluminum surface (Diagram 1). In our previous work [30], we studied the modification of non-textured aluminum surfaces with polymers that are based on fluoroalkyl methacrylates. This modification results in highly hydrophobic coatings with a contact angle of up to 120°. The problem of achieving a stable superhydrophobic state on aluminum surfaces is still relevant. To achieve this state, it is necessary to provide a reliable chemical attachment of low surface energy polymers to the substrate and to solve the problem of obtaining multi-level roughness of the subsurface layer of the support. To texture aluminum surfaces, a simple and promising mineral acid etching method is proposed that does not require complicated equipment. The reduction of free surface energy is achieved via the modification of textured supports with copolymers that are based on FMAs and GMA. FMAs ensure water-repelling properties, and GMA acts as an “anchor” due to the presence of epoxide groups that are capable of interacting with hydroxyl groups of the substrate.

Thus, the purpose of this work is to synthesize the copolymers that are based on glycidyl methacrylate and fluoroalkyl methacrylates (containing three to seven fluorine atoms in their monomer units) and their further attachment to the textured aluminum surface to attain superhydrophobic properties.

2. Materials and methods

2.1. Materials

The following materials and chemicals were used in this work: rectangular aluminum (A5 grade) plates with the dimensions of 15 × 10 and a 0.8 mm thickness, hydrochloric acid (38%), solvents [methyl ethyl ketone (MEK), n-hexane, acetone, and deionized water], glycidyl methacrylate (GMA) (97%), 2,2,2- trifluoroethyl methacrylate (TEMA) (98%), 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (HIMA) (99%), 2,2,3,3,4,4,4-heptafluorobutyl methacrylate (HBMA) (97%), and azobisisobutyronitrile (AIBN) (98%). These materials were purchased from Aldrich. GMA was distilled under vacuum at 50 °C before use.

2.2. Preliminary treatment of the aluminum surface

Aluminum samples were cleaned according to the previously published procedure [30]. Aluminum surface was textured via etching with hydrochloric acid solutions with concentrations ranging from 2 to 5 M. The acid and other etching products were washed away by boiling the samples in deionized water followed by ultrasonic bath treatment for 5 min at 45 °C. Then, the aluminum samples were dried in an oven for 40 min at 140 °C.

2.3. Synthesis of random copolymers of GMA and FMAs

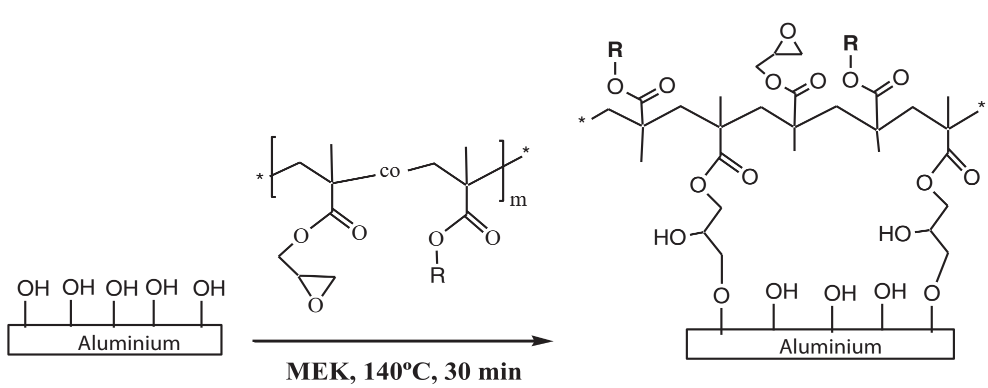
The synthesis of copolymers was conducted in MEK for 24 h at 70 °C with a GMA:FMA mole ratio of 0.6:1. The overall concentration of monomers was 1 mol/L. AIBN was used as an initiating agent. The copolymer was precipitated in cold hexane and then was dried under reduced pressure for 24 h.

2.4. Attachment of synthesized copolymers to the aluminum surface

In total, 3 wt% solutions of GMA- and FMA-based copolymers were prepared in MEK. Textured aluminum samples were placed into the copolymer solution for 30 min. Then, the samples were removed from the solution and placed into an oven for 30 min at 140 °C. Following this, the samples were weighed. Then, the samples were washed in MEK two times and dried at 80 °C until the mass remained constant.

2.5. Research methods

The composition of the synthesized copolymers was studied with a Vario EL Cube CHNOS elemental analyzer (Germany) using



R = CH_2CF_3; $CH(CF_3)_2$; $CH_2CF_2CF_2CF_3$

Diagram 1. Modification of the aluminum surface with the copolymers of glycidyl methacrylate and fluoroalkyl methacrylates.