Applied Surface Science 307 (2014) 234–240

Contents lists available at ScienceDirect

Applied Surface Science

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

Permanent superhydrophobic polypropylene nanocomposite coatings by a simple one-step dipping process

Cintia B. Contreras[a], Gabriela Chagas[b], Miriam C. Strumia[a,**], Daniel E. Weibel[b,*]

[a] IMBIV-CONICET, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Haya de la Torre y Medina Allende, Edificio de Ciencias II, Ciudad Universitaria, Córdoba 5000, Argentina
[b] Laboratório de Fotoquímica e Superfícies, Departamento de Físico-Química, Instituto de Química, UFRGS, Av. Bento Gonçalves, 9500, Bairro Agronomia, CEP: 91501-970, CP 15003 Porto Alegre, RS, Brazil

ARTICLE INFO

Article history:
Received 4 February 2014
Received in revised form 1 April 2014
Accepted 2 April 2014
Available online 13 April 2014

Keywords:
Superhydrophobicity
Nanostructuration
Contact angle hysteresis
Titanium dioxide
Coating

ABSTRACT

Superhydrophobic nanocomposite coatings on injection-molded polypropylene (PP) samples were prepared by dipping in xylene solvent containing titanium dioxide nanoparticles (NPs) functionalized with trimethoxypropyl silane. Alternatively, PP samples were dipped in a mixture of functionalized NPs and dissolved PP pellets. As a general result, dip-coated PP samples reached a permanent superhydrophobic state with a contact angle hysteresis (CAH) depending on NPs concentration and surface chemistry. SEM and profilometer measurements show a general trend in the decrease of CAH with the increase of aggregates and roughness. However some results showed that surfaces with the same roughness presented different CAHs. XPS measurements showed that low CAHs and self-cleaning properties were obtained only when the Ti–OH relative concentration on the surface was about 20%. At higher Ti–OH relative concentrations, the surface kept a superhydrophobic static state but lost its self-cleaning properties. This work highlights the fact that both control of the roughness together with chemical surface composition of polar groups have to be taken into account for a precise tuning on the superhydrophobic dynamic component of the surface.

1. Introduction

The control of the wettability of solid surfaces is drawing increasing interest from both theoretical and practical approaches. Wettability is directly related to surface energy and is one of the primary surface properties of solid materials; it is mainly governed by chemical composition and microstructure. Over the last decade, the importance of the nanostructure superimposed on micrometer-scale topology in nature surfaces has been demonstrated [1]. Similarly, artificial superhydrophobic surfaces have been developed on the basis of the lotus leaf or several other natural examples [2–5], such as *Cicada orni*'s wings [3,6] and water strider's legs [7]. Those naturally produced surfaces are water repellent: water droplet rolls off the surface and simultaneously removes its contaminants (self-cleaning effect). The control of surface wettability is crucial in many practical applications, such as thin film technology, lubrication, antifouling paints, self-cleaning windows, microfluids, textiles and anti-snow-sticking surfaces. In recent years, extensive experimental and theoretical research has been devoted to the so-called superhydrophobic surfaces, those that exhibit high water contact angles (WCA) (>150°) and low contact angle hysteresis (CAH) (drops roll off easily even at small inclinations) [3,8–11].

On the basis of two theoretical models mainly, Wenzel's [12] and Cassie-Baxter's [13], numerous methods have been recently used to prepare controlled rough surfaces [2,14]: wet chemical reaction, hydrothermal reaction, electrochemical deposition, self-assembly layer-by-layer, plasma etching, chemical vapor deposition, sol–gel and polymerization reactions. For example, plasma etching processes coupled to chemical coating have demonstrated to be useful to produce superhydrophobic surfaces [10,15–18]. WCA > 170° were obtained using C_4F_8 [15,16] as a gas precursor. Chemical etching has also been used to obtain superhydrophobic surfaces on metals such as copper (154°) [19] or alumina (165°) [20]. Those methodologies usually produced surface roughness in a non-controllable way and new approaches to the problem were developed seeking to control the shape, distribution and

* Corresponding author at: Universidade Federal de Rio Grande do Sul (UFRGS), Físico-Química, Instituto de Química, Avenida Bento Gonçalves, 9500, Bairro Agronomia, 91501-970 Porto Alegre, RS, Brazil. Tel.: +55 5133086204.
** Corresponding author. Tel.: +543515353860.
E-mail addresses: mcs@fcq.unc.edu.ar (M.C. Strumia), danielw@iq.ufrgs.br, danielweibel@yahoo.co.uk (D.E. Weibel).

http://dx.doi.org/10.1016/j.apsusc.2014.04.019
0169-4332/

periodicity of surface topography in the micro scale. By dicing [21] or laser photolithography [8] several hydrophobic micro structures were prepared; experimental results were compared with those of Wenzel–Cassie models. Superhydrophobic alumina films have been successfully developed on industrial aluminum foils by a simple anodization method following by chemical surface modification [22,23].

Most of the above mentioned approaches usually involve many steps or intricate processes that cannot be directly applied to polymers. Polymer materials are widely used in many segments of the industry; its uses and features are defined by characteristics that the material offers, along with its surface. Coating is a crucial step in adjusting the surface properties of the materials including polymers. In this sense, alternative methods to prepare superhydrophobic surfaces on commodities polymers have been recently reported [24–30]. Many polymers present hydrophobic surface properties; however, they are not superhydrophobic and, in contrast to hard materials, such as metals or ceramics, after surface modification they suffer from hydrophobic recovery by regaining their original wettability. For instance, this thermodynamic effect in polypropylene (PP) films is well known when surfaces are modified to hydrophilic properties. PP surfaces modified by different types of plasma treatment show hydrophobic recovery within few days or weeks [31–34]. In polyolefin surfaces, a likely mechanism of hydrophobic recovery is the rotational and/or translational motion of polymer chains and chain segments [32]. These mechanisms determine the observed "loss" of functional groups within the first few monolayers of the surface and lead to a decrease in surface energy. Those thermodynamic processes also take place when hydrophobic groups are grafted into polymer surfaces; alternative methodologies are then used to generate permanent morphology on the surface and increase hydrophobicity [15,35].

Polymeric materials are substituting metals, ceramics and glasses; new applications for superhydrophobic polymers are expected in fields such as antifouling or foul-release coatings, non-wetting textiles, non-icing or ice repellant surfaces, self-cleaning solar cell coatings, among others [2,4,5]. Polymer coating is a very well established method to obtain new surface properties in polymeric materials and recent reports on the preparation of superhydrophobic polymeric substrates using diverse methodologies show the progress in the preparation of self-cleaning polymer surfaces [24,25,36–38]. In particular, polyolefins have broad industrial applications ranging from packaging to building materials and automotive parts and they are widely used where hydrophobicity and clean surfaces are required. A growing interest in converting their hydrophobic surfaces into superhydrophobic ones has also recently developed [39–44]. For instance, Rioboo et al. [41] prepared superhydrophobic PP surfaces by casting or dip-coating solutions of PP of various molecular weight and tacticity. They have investigated the superhydrophobic behavior in terms of initial film thickness and initial solution concentration. Hydrophobic surfaces were obtained at low film thickness. By increasing polymer concentration and, consequently, film thickness, the transition between hydrophobic and superhydrophobic surface is induced.

In this study, we developed a simple one-step dip-nanocomposite coating method to produce PP superhydrophobic films. For the nanocomposite coating, commercial titanium dioxide (TiO_2) nanoparticles (NPs) were first functionalized with trimethoxypropyl silane (TMPSi). Then injection-molded PP samples were simply immersed for a few seconds in hot xylene solutions containing dissolved functionalized TiO_2 NPs or a mixture of dissolved PP together with functionalized TiO_2 NPs. With this approach superhydrophobic surfaces with static water contact angles greater than 160° and very low contact angle hysteresis of less than 5° were produced. The surface properties of the films were characterized by profilometer measurements, scanning electron microscopy (SEM), Fourier transformed infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR) and X-ray photoelectron spectroscopy (XPS) analyses. The wetting property of the coating surface was determined by static and dynamic contact angle measurements.

2. Materials and methods

2.1. Materials

Polypropylene (PP) samples (Braskem S/A, 3.5 g/10 min) were injection-molded, washed ultrasonically with acetone for 30 min, dried at room temperature and then stored in a desiccator. The final PP substrates were about 30 × 10 mm size and 3 mm thickness. Trimethoxypropyl silane (TMPSi) of 97% purity was obtained from Aldrich. Xylene (mixture of isomers) was purchased from Merck (Brazil). Titanium dioxide nanoparticle powder, AEROXIDE® TiO_2-P25, was received from Degussa Corporation and used without any further treatment.

2.2. Production of PP-coated surfaces

TiO_2 NPs functionalization was carried out following the procedure previously published [45]. Briefly, TMPSi in xylene as solvent (5/95 v/v) was prepared by premixing TMPSi and xylene. TMPSi–xylene solution was then stirred for few minutes with a few grams of titanium dioxide.

Two methods were used to produce the superhydrophobic coatings on PP films (see Scheme 1):

(i) Series PPX, NPs–xylene

A varied quantity of NPs was dispersed in 20 mL of the TMPSi–xylene solution and sonicated for 3 h. The temperature of the solution was then increased to 125 °C and a PP stick was immersed. Finally, the stick was removed from the solution and dried in an oven at 100 °C. Different immersion times were studied: the stick was immersed and immediately removed after ~2 s, 3 or 5 s. The NPs concentration in the TMPSi–xylene solution assayed was 0.15, 1.5 and 10% w/v.

(ii) Series PPX-PP, NPs–xylene–PP

In this case, we followed the methodology used in the series (i) with the only difference that 0.3 g of PP pellets were dissolved in the NPs–TMPSi–xylene solution. Different immersion times were studied: the stick was immersed and immediately removed after ~2 s, 3 or 5 s. The NPs concentration in the TMPSi–xylene solution assayed was 0.15, 1.5 and 10% w/v.

Reference PP samples without NPs coatings were also prepared by dipping the PP sticks in xylene solutions following the methodology explained in series (i) and (ii) above.

2.3. Water contact angle measurements

Static water contact angle (WCA) was measured at ambient temperature using a drop of deionized water (4 μL) by gently depositing it on the substrate using a micro syringe. The images were captured using the "Drop Shape Analysis System" equipment, Kruss DSA 30. For each concentration and time, three different modified sticks were studied and all the measurements were repeated at least five times at different positions. For contact angle hysteresis (CAH), the advancing and receding contact angles were measured at the front and back of the droplet moving along the tilted surface, respectively. The tilting angle measurements were performed using a mechanical level goniometer. The images were captured using a digital video camera and analyzed for contact angle measurements using Surftens 3.0 or Image j software.