G Model
APSUSC-34299; No. of Pages 9
ARTICLE IN PRESS
Applied Surface Science xxx (2016) xxx–xxx
Contents lists available at ScienceDirect
Applied Surface Science
journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Assessment of morphology, topography and chemical composition of water-repellent films based on polystyrene/titanium dioxide nanocomposites

Beleta Bolvardi [a], Javad Seyfi [b,*], Iman Hejazi [c,*], Maryam Otadi [a], Hossein Ali Khonakdar [d,e], Astrid Drechsler [e], Matthias Holzschuh [e]

[a] *Chemical Engineering Department, Central Tehran Branch, Islamic Azad University, Tehran, Iran*
[b] *Department of Chemical Engineering, Shahrood Branch, Islamic Azad University, P.O. Box 36155-163, Shahrood, Iran*
[c] *Applied Science Nano Research Group, ASNARKA, P.C. 1619948753, Tehran, Iran*
[d] *Department of Polymer Engineering, Faculty of Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran*
[e] *Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, D-01069 Dresden, Germany*

ARTICLE INFO

Article history:
Received 9 July 2016
Received in revised form 30 October 2016
Accepted 31 October 2016
Available online xxx

Keywords:
Polystyrene
Superhydrophobic
Self-cleaning
Titanium dioxide
Roughness analysis

ABSTRACT

In this study, polystyrene (PS)/titanium dioxide (TiO_2) films were fabricated through simple solution casting technique via a modified phase separation process. The presented approach resulted in a remarkable reduction in the required amount of nanoparticles for achieving superhydrophobicity. Scanning electron microscopy (SEM) and 3D confocal microscopy were utilized to characterize surface morphology and topography of samples, respectively. An attempt was made to give an in-depth analysis on the surface rough structure using 3D roughness profiles. It was found that high inclusions of non-solvent and nanoparticles resulted in a stable self-cleaning behavior due to the strong presence of hydrophobic TiO_2 nanoparticles on the surface. Quite unexpectedly, low inclusions of nanoparticles and non-solvent also resulted in superhydrophobic property mainly due to the proper level of induced surface roughness. XPS analysis was also utilized to determine the chemical composition of the films' surfaces. The results of falling drop experiments showed that the sample containing a higher level of nanoparticles had a much lower mechanical resistance against the induced harsh conditions. All in all, the presented method has shown promising potential in fabrication of superhydrophobic surfaces with self-cleaning behavior using the lowest content of nanoparticles.

1. Introduction

Tremendous potential of superhydrophobic surfaces and coatings have made this subject extremely intriguing for researchers from both industrial and scientific viewpoints, and as a result, numerous studies have been reported on this subject within the last 15 years [1–6]. In order to achieve water contact angles (WCAs) above 150° and sliding angles (SAs) below 10°, the wettability of surface has to be designed by tuning surface roughness and chemical composition. It is well-known that enhancing the surface roughness and reduction of surface energy can dramatically improve the water-repellency of the surface [7]. The lotus flowers provide a great example in which superhydrophobicity is employed as the basis of a mechanism to control the surface morphology for the protection and self-cleaning of their surfaces [8]. Generally, in order to create a superhydrophobic surface, two strategies have been employed. One is induction of roughness to a low surface energy material and the other is to modify an intrinsically rough surface with low surface energy materials. Superhydrophobic surfaces with a hierarchical structure in both nano and micro-scales mimicking that of a lotus leaf have been abundantly reported in the literature [9–11]. A variety of methods were utilized for fabrication of such surfaces including chemical etching [12], surface embedding [13], phase separation [14], etc. Phase separation methods are simple and inexpensive yet effective, and have been utilized to fabricate self-cleaning surfaces since explored by Erbil et al. [15]. A modified version of phase separation method for fabrication of superhydrophobic surfaces has been recently presented by our group [16]. In this method, nanoparticles are used simultaneously with non-solvent and accelerate the phase separation process.

* Corresponding authors.
E-mail addresses: Jseyfi@gmail.com (J. Seyfi), Imanhe64@gmail.com (I. Hejazi).

http://dx.doi.org/10.1016/j.apsusc.2016.10.205

Please cite this article in press as: B. Bolvardi, et al., Assessment of morphology, topography and chemical composition of water-repellent films based on polystyrene/titanium dioxide nanocomposites, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2016.10.205

In this study, polystyrene (PS), which is a very popular thermoplastic and has numerous applications, was employed as the polymer matrix. For instance, to utilize PS in microfluidic devices, superhydrophobic property has to be developed [17]. In many researches, nanoparticles were used instead of non-solvent [18]; however, very high inclusions were necessary to induce superhydrophobic property which is commercially undesirable [19–22]. Moreover, very high loadings of nanoparticles may also result in poor mechanical stability and durability of the coatings due to the poor adhesion to the substrates. For instance, Qing et al. [19] reported that the weight ratio of ZnO nanoparticles to PS should be 7:3 in order to achieve superhydrophobicity on cotton textiles. In another study, it was reported that the concentration of molybdenum disulfide nanoparticles should be 55 wt.% to fabricate superhydrophobic polyurethane surfaces [22]. In the current study, titanium dioxide (TiO_2) nanoparticles are incorporated into the phase separation process and act synergistically in the presence of non-solvent, which results in a remarkable reduction in the required contents of nanoparticles to 5 and 10 wt.% for achieving superhydrophobicity. Therefore, the presented approach is commercially desirable, and also, highly efficient in fabrication of durable PS surfaces with self-cleaning property.

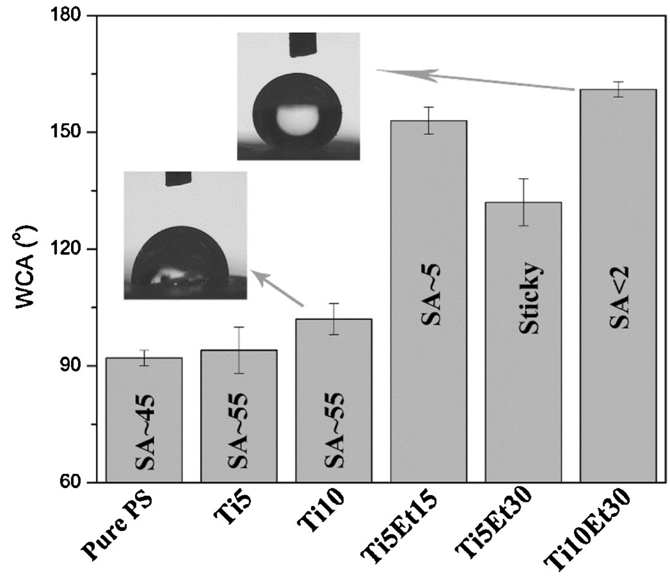

Fig. 1. WCA and SA values for different samples. Water droplet profiles are also shown for two samples.

2. Materials and methods

2.1. Materials

Polystyrene (M_n = 140,000 g/mol, M_w = 230,000 g/mol) was obtained from Sigma-Aldrich (St. Louis, MO, USA). The hydrophobic fumed titanium dioxide (titania) used in this study is a commercial product (AEROXIDE® TiO_2 T 805) which was purchased from Evonic Industries (Essen, Germany) and used as received. AEROXIDE® R805 has a specific surface area of 45 ± 10 m^2/g and primary particle size of 12 nm. It was produced by treating TiO_2 with octylsilane ($C_8H_{17}SiH_3$). Tetrahydrofuran (THF) and ethanol were supplied from Merck (Darmstadt, Germany) and used as received.

2.2. Preparation of PS/TiO_2 films

Solution casting technique was employed for all the samples. For preparation of TiX series of samples, different amounts of TiO_2 nanoparticles were added to a PS solution with a certain concentration (10 mg/mL), and then the suspension was vigorously stirred for 3 h followed by mixing in an ultrasonic bath for 1 h till a homogeneous solution was obtained. Afterwards, several drops of the suspension were casted on the previously cleaned glass substrates and left to dry overnight at ambient conditions. In the case of TiXEtY series of samples, after obtaining a stable and homogeneous suspension of nanoparticles within the PS solution, different volumes of non-solvent (ethanol) were added drop-wise to the suspension under stirring, and after 2 min, several drops were casted on the glass slides and left to dry overnight. TiX series of samples included Ti5 and Ti10 in which 5 and 10 wt.% of TiO_2 nanoparticles were added to the PS solution, respectively. Moreover, TiXEtY series of samples included Ti5Et15, Ti5Et30 and Ti10Et30 in which Et accounts for ethanol and the numbers 15 and 30 are the volume percentages of the added ethanol in the course of sample preparation.

2.3. Characterization

A video-based contact angle measurement system (OCA 15, DataPhysics Instruments GmbH, Filderstadt, Germany) was employed to determine the WCA values of the samples. The WCA measurements of each sample were conducted at least three times across the sample surface using the sessile drop method by dispensing 4 mL drops of de-ionized water on the sample surfaces. All WCA values were measured under ambient laboratory conditions at a temperature of 25 °C.

Morphologies of the films' surfaces were evaluated on a digital scanning electron microscope coupled with energy dispersive X-ray spectroscopy (EDX) (VEGA//TESCAN instrument, Czech Republic) operated at 25 kV. To avoid electric charging all samples were plated with gold coating.

All the roughness parameters were acquired at different magnifications including 20× and 100× by means of a 3D confocal microscope μsurf explorer, provided by NanoFocus AG, Oberhausen, Germany.

X-ray photoelectron spectroscopy (XPS) studies were carried out by means of an Axis Ultra photoelectron spectrometer (Kratos Analytical, Manchester, UK). The spectrometer was equipped with a monochromatic Al Kα (h n = 1486.6 eV) X-ray source of 300 W at 15 kV. During all measurements, electrostatic charging of the sample was avoided by means of a low-energy electron source working in combination with a magnetic immersion lens. The maximum information depth of the XPS method was not more than 8 nm. Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function. Spectrum background was subtracted according to the Shirley method. Free parameters of component peaks were their binding energy (BE), height, full width at half maximum and the Gaussian–Lorentzian ratio.

3. Results and discussion

3.1. Wettability

The water contact angle (WCA) and sliding angle (SA) values are illustrated for all the samples in Fig. 1. At first, the sole effect of nanoparticles was studied by measuring the WCA for Ti5 and Ti10 samples in which 5 and 10 wt.% of TiO_2 nanoparticles (with respect to the solid content) were used, respectively. It can be observed that addition of 5 and 10 wt.% of TiO_2 nanoparticles did not considerably change the WCA values. Based on the obtained results, the WCA was increased from 92° for the pure PS film to 94° and 102° for the Ti5 and Ti10 samples, respectively. The major reason