Applied Surface Science 368 (2016) 216–223

Contents lists available at ScienceDirect

Applied Surface Science

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

Self-cleaning behavior in polyurethane/silica coatings via formation of a hierarchical packed morphology of nanoparticles

Iman Hejazi [a], Gity Mir Mohamad Sadeghi [a,*], Javad Seyfi [b], Seyed-Hassan Jafari [c], Hossein Ali Khonakdar [d]

[a] Department of Polymer Engineering & Color Technology, Amirkabir University of Technology, P.O. Box 15875/4413, Tehran, Iran
[b] Department of Chemical Engineering, Shahrood Branch, Islamic Azad University, P.O. Box 36155-163, Shahrood, Iran
[c] School of Chemical Engineering, University of Tehran, P.O. Box 11155-4563, Tehran, Iran
[d] Iran Polymer and Petrochemical Institute, P.O. Box 14965/115, Tehran, Iran

ARTICLE INFO

Article history:
Received 1 December 2015
Received in revised form
27 December 2015
Accepted 21 January 2016
Available online 1 February 2016

Keywords:
Self-cleaning
Thermoplastic polyurethane
Superhydrophobic
Hierarchical

ABSTRACT

In the current research, a hierarchical morphology comprising of packed assembly of nanoparticles was induced in thermoplastic polyurethane (TPU)/silica nanocomposite coatings in order to achieve self-cleaning behavior. Moderately hydrophilic behavior of TPU hinders its transforming to a superhydrophobic material. In the presented method, a very thin layer of silica nanoparticles is applied to the surface of TPU sheets under elevated temperature and pressure. As temperature and pressure of the process remain unchanged, processing time was considered as a main variable. Based on scanning electron microscopy and confocal microscopy results, it was found that at a certain processing time, nanoparticles can form an utterly packed morphology leading to a self-cleaning behavior. Once the process was prolonged, TPU macromolecules found the chance to migrate onto the coating's top layer due to the enhanced mobility of chains at high temperature. This observation was further proved by X-ray photoelectron spectroscopy analysis and cross-sectional morphology. The presented method has promising potentials in transforming intrinsically hydrophilic polymers into superhydrophobic materials with self-cleaning behavior.

1. Introduction

Self-cleaning, anti-biofouling, anti-adhesive, antifogging and anti-icing properties are all extraordinary properties of superhydrophobic surfaces about which a great deal of research has been reported within the last decade [1–8]. Based on the general definition, the advancing and receding water contact angle values should be higher than 150° and the sliding angle should be no more than 10° [9]. Superhydrophobicity has been inspired from nature as well as other phenomena. Many plant leaves and insects for example lotus leaves and butterfly wings have the superhydrophobic property. Apart from the surface chemical composition which is an important factor for achieving superhydrophobicity, surface roughness has been considered a crucial parameter. The maximum water contact angle that can be achieved by a smooth non-porous surface of closest hexagonal packed $-CF_3$ groups is 120° which has been obtained in the case of Teflon surfaces [10]. Therefore, surfaces having contact angles higher than 150° can only be attained through inducing roughness and porosity [11].

Numerous methods have been reported for preparation of superhydrophobic surfaces [12–16]. Those methods can be mainly categorized into two approaches: either make a rough surface from a low surface energy material or modify a rough surface with a material of low surface energy [17]. Among polymers, polyurethane (PU) is one of the most versatile materials and has been widely used in diverse applications [18]. Several reports have been made on fabrication of superhydrophobic PU surfaces and coatings. For example, Wu et al. [19] have successfully synthesized hybrid films of waterborne PU/fluorinated polymethylmethacrylate/hydrophobic silica with superhydrophobic behavior. They found that a proper combination of fluorine enrichment and a rough topography accounted for the observed ultra-water-repellent behavior. In another research, fluoro polyurethane films containing fluorinated polyhedral oligomeric silsesquioxane were synthesized [20]. Water contact angle (WCA) of the F-PU film was 109° implying the migration of fluoro segments onto the surface; however, due to the absence of proper surface roughness, the surface energy of the material was not sufficient for achieving

* Corresponding author. Tel.: +98 21 64542442; fax: +98 21 66468243.
E-mail address: Gsadeghi@aut.ac.ir (G. Mir Mohamad Sadeghi).

http://dx.doi.org/10.1016/j.apsusc.2016.01.258
0169-4332/

superhydrophobicity. Another group reported fabrication of superhydrophobic fluoro-PU coatings through concurrent addition of hydrophobic nanosilica and fluoric nanoparticles [21]. They found that only a combination of 30 wt.% nanosilica and 10 wt.% fluoric particles rendered the coating superhydrophobic. Bayer et al. [22] fabricated PU/organoclay films with high water-repellency through dispersing the moisture-curable PUs and hydrophobic organoclay in cyclomethicone in water emulsions. In another study, Wu et al. [23] studied superhydrophobic fluorinated PU films through electrospinning method and found that low surface energy could be less important as long as the nanoscale structure is present. As could be seen, all the studies, reported on superhydrophobic PU films, have utilized other materials with low surface energy such as fluorinated polyols or cyclomethicone.

Nanoparticles have been mainly used for controlling the surface roughness due to their availability and the fact that they can be synthesized with uniform size and tunable wettability through proper modification methods [24]. Among them, silica exhibits promising characteristics such as nontoxicity, high thermal and mechanical stability, and easy structural regulation, intrinsically high level of wettability, low dielectric constant, and low refractive index. Karunakaran et al. reported that to achieve a superhydrophobic nanocoating, 3-Aminopropyltrimethoxysilane (APTS)-functionalized silica nanoparticles were dip coated onto different substrates, followed by annealing [25]. They also used fluoro-modification to render the coatings superhydrophobic with sliding angle of less than 5°.

In this study, the self-cleaning behavior was attempted to impart on an intrinsically hydrophilic polymer like TPU through silica surface embedding. TPU has numerous polar groups within its chain and is able to establish strong polar interactions with water droplets. In fact, the main aim of the current article is to produce superhydrophobic surfaces with self-cleaning behavior using an intrinsically hydrophilic material which has always been regarded as a challenge in the literature. To this end, hydrophobic silica nanoparticles were used to impart suitable levels of surface roughness. It can be proved that under specific processing conditions, self-cleaning behavior can be attained on a hydrophilic surface.

2. Materials and Methods

2.1. Materials

Aromatic polyether/polyester based TPU, Desmopan 5377A granules with melting temperature of 191–210 °C and density of 1.14 g/cm^3 was obtained from Bayer, Germany. The hydrophobic fumed silica used in this study is a commercial product (Aerosil® R 8200) which was purchased from Evonic Industries (Essen, Germany) and used as received. Aerosil R8200 has a specific surface area of 135–185 m^2 g^{-1} and primary particle size of 12 nm. It was produced by treating SiO_2 with hexamethyldisilazane, [$(H_3C)_3Si–NH–Si(CH_3)_3$].

2.2. Preparation of nanocomposite coatings

The method used to produce the nanocomposite coatings with different nanosilica contents is as follows: First, TPU sheets with dimensions of 100 mm × 100 mm × 2 mm were prepared via compression molding of TPU granules on a smooth-surface mold. Afterwards, the sheets were cut into smaller size (25 mm × 35 mm × 2 mm) in order to obtain uniform wettability results throughout the whole surface. Then, 8 mg of nanosilica powder were poured onto the surface of the substrate and the pressing process was conducted at a pressure of around 4 MPa. It is not necessary to perform the experiment at the polymer melting temperature, thus the pressing temperature was fixed at 180 °C. However, the processing time was changed from 1 to 60 min. After cooling to the room temperature, samples were soaked in ethanol and then ultrasonically cleaned for 10 min to remove any nanoparticles which were not firmly embedded in the TPU substrate. Finally, samples were also rinsed with ethanol, and then, dried in an oven at 70 °C. In fact, the schematic representation of the used method along with the cross-sectional morphology and wettability are illustrated in Fig. 1. For simplicity, the samples were named Silica1, Silica5, Silica10, Silica30 and Silica60 in which the numbers account for the processing time.

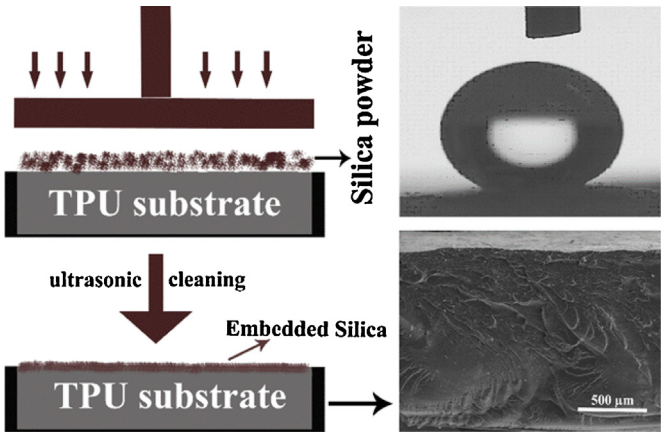

Fig. 1. Schematic representation of the pressing method for fabrication of TPU/silica coatings (left) and cross-sectional morphology along with the water drop profile for the superhydrophobic sample (right).

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 was conducted at least three times across the sample surface using the sessile drop method by dispensing 4 μL drops of de-ionized water (surface tension γ_{lv} = 72.8 mN m^{-1} at 25 °C) on the sample surfaces.

Morphologies of the coating 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 for 800 μm × 800 μm field size surfaces by means of a 3D confocal microscope μsurf explorer, provided by NanoFocus AG, Oberhausen, Germany.

X-ray photoelectron spectroscopy (XPS) analysis was performed by using XPS spectroscopy (BESTEC, Germany) with a monochromatic AlKα X-ray source (1486.6 eV photons), operated at 180 W (12 kV and 15 mA) and under ultrahigh vacuum conditions.

3. Results and discussion

3.1. Wettability behavior

Fig. 2 depicts the water contact angle values for all the fabricated coatings. As mentioned earlier, the used TPU was rather hydrophilic which can be confirmed by the wettability results shown in Fig. 2. As is demonstrated, embedding nanoparticles onto TPU sheets resulted in a significant increase in the WCA values. However, the fabricated coatings were not superhydrophobic until the processing time has reached 5 min, which can be chosen as the optimum processing time in production of TPU-based