



Transforming an intrinsically hydrophilic polymer to a robust self-cleaning superhydrophobic coating via carbon nanotube surface embedding



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ABSTRACT

A single-step method, including surface embedding of nanoparticles into a polymer matrix, was employed to fabricate superhydrophobic thermoplastic polyurethane (TPU)/carbon nanotube (CNT) nanocomposite coatings. The main aim was to prove that surface roughness plays a more important role in designing superhydrophobic surfaces as compared with the surface energy. Therefore, TPU was used as the model hydrophilic polymer and CNTs were employed as non-hydrophobic nanoparticles. It was found that, at a certain pressing time, CNTs form an efficient hair-like morphology which is able to highly enclose air within its as-formed pores leading to superhydrophobic behavior. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and confocal microscopy were utilized for characterization of samples. SEM and confocal microscopy results proved that surface roughness played the key role in the final wettability behavior. Based on XPS results, it was also found that a very long pressing time led to partial migration of TPU macromolecules into the CNTs' pores, and hence, superhydrophobicity was reduced. The effects of mechanical abrasion and nanoparticle type on wettability behavior of samples were evaluated as well. In conclusion, it is suggested that surface roughness factor should be highly considered in designing superhydrophobic nanocomposite coatings rather than surface energy.

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1. Introduction

In the field of nanotechnology, polymer matrix based nanocomposites have become a prominent area of research and development [1–8]. One of the current and emerging areas is design and fabrication of superhydrophobic nanocomposite surfaces which have been comprehensively investigated using a vast range of materials including metals, polymers, nanoparticles, etc. [9–13]. Superhydrophobicity and self-cleaning property are both highly desirable for commercially available and widely used polymers; therefore, several methods have been reported to transform common polymers into superhydrophobic surfaces [14–17].

Polyurethane is one of the most versatile materials which has been widely used in coatings, adhesives, thermoplastic elastomers and composite industries. Thermoplastic polyurethane (TPU) generally consists of a soft segment, a high molecular weight polyester or polyether macrodiol, and a hard segment which is made of diisocyanate and low

molecular weight diol or diamine. The soft segments are flexible and non-polar whereas the hard segments contain polar urethane groups which can form hydrogen bonds and crystalline structure [18]. Regarding the surface property of coated TPU films, hydrophilic hard segments adversely influence water and oil repellency due to their rather high surface energy.

Many studies can be found in the literature devoted to fabrication of hydrophobic and superhydrophobic PU coatings and surfaces. Wu et al. [19] have successfully synthesized hybrid films of water-borne 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, fluoropolyurethane films containing fluorinated polyhedral oligomeric silsesquioxane were synthesized [20]. Water contact angle (WCA) of the F-PU film was 109° indicating the migration of fluoro segments onto the surface; however, due to the absence of suitable surface roughness, such low surface energy was not sufficient for achieving superhydrophobicity. Another group reported fabrication of superhydrophobic fluoro-PU coatings through combined addition of hydrophobic nanosilica and

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fluorinated nanoparticles [21]. They found that only a combination of 30 wt.% nanosilica and 10 wt.% fluorinated 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] investigated 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.

Carbon nanotube (CNT) is one of the most interesting candidates to create a micro/nanoscale roughness owing to its rigid cylindrical nanostructure with a diameter ranging from 1 nm to dozens of nanometers and length varying from hundreds of nanometers to micrometers. Numerous studies have been devoted to the use of CNTs for fabrication of superhydrophobic surfaces [24–30]. For example, Yang et al. [27] have developed transparent superhydrophobic surfaces by means of polystyrene functionalized CNTs through living free radical polymerization. In another work, Wang et al. [28] have prepared pressure-proof superhydrophobic surfaces using spray coating technique for applying CNT/ethanol suspension onto the pre-fabricated polydimethylsiloxane (PDMS) surface. Many studies have also focused on the superhydrophobic aligned CNT films [29,30]; however, it has been demonstrated that water droplets are not stable on aligned CNT surfaces for a prolonged time due to their high surface energy. Therefore, to surmount such issue, low surface energy polymers have been utilized to improve the water repellency behavior of those surfaces. However, the electrical conductivity of such surfaces were diminished by the presence of insulated polymer coatings hindering their applications as electrode materials and interconnected conductors. Another issue concerning the CNT-containing composites is their poor solubility within the polymer matrix. To overcome the mentioned problems, a facile yet effective approach was recently reported for fabrication of superhydrophobic and highly conductive coatings by simply pressing a layer of CNTs on the surface of polymer melts [31,32]. The CNTs are partially embedded inside and partially exposed outside the coating surface through the pressing process.

As mentioned above, it is well-documented in the literature that surface roughness, at both micro- and nanoscales, together with low surface energy are generally required for achieving ultra-high water-repellency behavior [33]. In the current study, an attempt is made to induce self-cleaning behavior on an intrinsically hydrophilic polymer which is TPU via CNTs 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 contribution of the current article in this research area is to design and 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, non-hydrophobic CNT nanoparticles were used to induce proper levels of surface roughness. It was proved that under certain processing conditions, it is possible to impart self-cleaning behavior on a hydrophilic surface. Moreover, various tests were employed for further corroboration of the obtained results such as SEM, confocal microscopy and XPS.

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/cm³ was obtained from Bayer, Germany. Multiwalled CNTs with an average outside diameter of 50–80 nm, length of 10–20 μm and a purity of above 95 wt.% were supplied by US research Nanomaterials Inc. and used as received. 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 m²g⁻¹ and primary particle size of 12 nm. It was produced by treating SiO₂ with hexamethyldisilazane, [(H₃C)₃Si–NH–Si(CH₃)₃].

2.2. Preparation of nanocomposite coatings

The procedure used to fabricate the nanocomposite coatings with different CNT contents is the same as the method used for TPU/nanosilica coating. First, TPU sheets with dimensions of 100 mm × 100 mm × 2 mm were prepared through 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, they were placed into the pre-fabricated molds followed by distributing 15 mg of CNT powder (~2 vol.%) on the surface of the substrate and the pressing process was carried out at a pressure of 4 MPa. The mold was heated to 180 °C at which macromolecules are very mobile and capable of penetrating into the CNTs' pores since the majority of polymer chains are in amorphous state in the case of used TPU (DSC results not shown here). Therefore, it is not necessary to perform the experiment at the polymer melting temperature. The processing time was varied from 1 to 60 min, and at a fixed processing time, the effect of nanoparticle type was also studied by using silica nanoparticles. After cooling to the ambient temperature, samples were demolded, and in order to remove those nanoparticles which were not firmly embedded in the TPU substrate, all the samples were soaked in ethanol and then ultrasonically cleaned for 10 min. After that, samples were also rinsed with ethanol, and then, dried in an oven at 70 °C. For simplicity, the samples were named CNT1, CNT5, CNT10, CNT30, CNT60 and Silica10 in which the numbers account for the processing time.

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 $\gamma_{lv} = 72.8 \text{ mN}\cdot\text{m}^{-1}$ at 25 °C) on the sample surfaces.

Morphologies of the coating surfaces were evaluated on a digital scanning electron microscope (KYKY-EM3200, KYKY Technology Development, Beijing, China) operated at 25 kV. To avoid electric charging all samples were plated with gold coating.

All the roughness parameters were acquired for 800 × 800 μm² field size surfaces 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 K_α (h·ν = 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. Later, all recorded peaks were shifted by the same amount, which was necessary to set the C 1s peak of the CNT carbon atoms to 283.99 eV [34]. 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. High-resolution element spectra were deconvoluted by means of a computer routine (Kratos Analytical, Manchester, UK). Free parameters of component peaks were their binding energy (BE), height, full width at half maximum and the Gaussian–Lorentzian ratio.

In order to study mechanical resistance of the superhydrophobic nanocomposite coating, the shear resistance test used in [35] was

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