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Interfacing superhydrophobic silica nanoparticle films with graphene and thermoplastic polyurethane for wear/abrasion resistance

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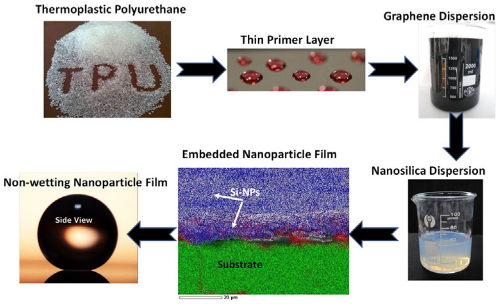
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Nanoparticle films are one of the most suitable platforms for obtaining sub-micrometer and nanometer dual-scale surface texture required for liquid repellency. The assembly of superhydrophobic nanoparticles into conformal and strongly adherent films having abrasion-induced wear resistance still poses a significant challenge. Various techniques have been developed over the years to render nanoparticle films with good liquid repellent properties and transparency. However, forming abrasion resistant superhydrophobic nanoparticle films on hard surfaces is challenging. One possibility is to partially embed or weld nanoparticles in thin thermoplastic primers applied over metals.

Experiments: Hexamethyldisilazane-functionalized fumed silica nanoparticle films spray deposited on aluminum surfaces were rendered abrasion resistant by thermally welding them into thermoplastic polyurethane (TPU) primer applied a priori over aluminum. Different solvents, nanoparticle concentrations and annealing temperatures were studied to optimize nanoparticle film morphology and hydrophobicity.

Findings: Thermal annealing at 150 °C enhanced stability and wear resistance of nanoparticle films. A thin thermal interface layer of graphene nanoplatelets (GnPs) between the primer and the nanoparticle film significantly improved superhydrophobic wear resistance after annealing. As such, superhydrophobic nanocomposite films with the GnPs thermal interface layer displayed superior abrasion-induced wear resistance under 20 kPa compared to films having no GnPs-based thermal interface.

1. Introduction

Dual length scale surface roughness with micro and nanostructures that are essential for the "lotus effect" or for liquid repellency can be conveniently obtained by depositing nanoparticle layers on various surfaces as long as the nanoparticle surfaces are

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functionalized with hydrophobic moieties [1]. In fact, commonly referred to as "all-nanoparticle thin-film coatings" [2], these nanostructured films are useful platforms to produce multifunctional coatings such as antireflective, heat transfer control and UV resistant systems with controlled wetting properties. In addition, some nanoparticle films such as amorphous nanocarbon deposited on surfaces by flame impingement (i.e., candle flame) were found to be inherently superhydrophobic due to carbon surface hydrophobicity [3]. Nanoparticle films obtained from stimuli-responsive surface functionalization are also highly beneficial for tuning local wettability gradients on surfaces [4]. To date, a number of well-described techniques to deposit nanoparticle films have been reported, such as sol-gel approaches [5], electrodeposition of semiconductor and metal nanoparticles [6,7], the Langmuir-Blodgett technique to deposit nanoparticle monolayers [8,9], and in-situ nanoparticle generation on polymeric surfaces [10]. Hydrophobic nanoparticle films can also be deposited on pre-textured surfaces [11], such as polyelectrolytes [12] to induce nanoscale texture as well as hydrophobic chemistry.

Silica (SiO_2) nanoparticles have been extensively used in the construction of superhydrophobic surfaces and coatings [13], not only due to their abundance and low cost, but also due to the fact that once properly assembled, transparent non-wetting nanoscale coatings can be fabricated [14]. They can also be deposited from various precursors and after a proper subsequent silanization process, and can be transformed into hydrophobic or oleophobic nanotextured films [15]. A more industry-friendly approach is to deposit hydrophobized silica nanoparticles by spray painting [14] or by dip coating on large substrates [16]. There also exist studies in which colloidal silica nanoparticle suspensions are aged under conditions in which the silica nanoparticles undergo controllable aggregation in solution before application to a substrate via spin-coating. This was done in order to tune optical/anti-reflection properties of nanoparticle films [17]. Although, all these applications of nanoparticle films are very promising, as stated by Lee et al. [18], mechanical stabilization (i.e., coating durability) of such as-assembled films should be performed in order to target various demanding applications in which nanoparticle films should be mechanically stable [19].

One of the most critical issues related to the durability or stability of liquid repellent nanoparticle films is their ability to adhere or bind to the surface over which they are deposited. Generally, it is difficult to permanently bind nanoparticle films on metallic or ceramic surfaces [20,21]. Thermal embedding is a useful tool to attach and weld the nanoparticle films on substrates. Although, generally high temperatures (>600 °C) are required to embed ceramic or metallic nanoparticles into substrates like glass [20], recent works also attempted to achieve this at lower temperatures [21]. Alternatively, thin thermoplastic polymer layers as primers on solid surfaces can act as embedding media for nanoparticle films [22–25] at much lower temperatures. In this study, we follow this approach in order to investigate the durability and wear abrasion resistance of hydrophobic silica nanoparticle films on aluminum surfaces primed with a thin thermoplastic polyurethane (TPU) coating.

TPUs are probably among the fastest evolving polymers [26,27]. They are well-known for their outstanding versatility due to the fact that their co-polymer chemistry can be tuned to yield soft rubbery elastomer-like materials, rigid plastics, or soft-hard hybrids, so that their toughness, elongation, abrasion resistance and thermal response can be engineered [28,29]. TPU polymers feature good abrasion resistance [30], flexibility at low temperatures [31], and good biocompatibility [32]. Recent literature on non-wetting coatings displaying abrasion resistance properties indicates that presence of rubbery phases in the coating structure can help increase the resistance to abrasion [33]. Since many TPU polymers have been formulated to have soft and hard co-polymer segments, the soft segments can act as rubbery mechanical energy dampening sites [34].

In this study, we demonstrate that spray-deposited all-nanoparticle films, originating from commercially available fumed silica nanoparticles modified with organosilane surface treatment, can be made resistant to wear abrasion by thermally embedding them into a thin TPU layer. Furthermore, we show that if a layer of graphene nanoplatelets is used as thermal interface between the nanoparticle layer and the TPU primer, resistance to wear abrasion while maintaining non-wetting state can be significantly enhanced.

2. Materials and methods

2.1. Materials

The hydrophobic fumed silica nanoparticles (silica NPs), Aerosil® R-812, with an average particle size (7–40 nm) were kindly donated by Evonik Industries, Germany. Polyether-based thermoplastic polyurethane (TPU), Elastollan 1185A granules with density 1.12 g/cm^3 and melting temperature of about 92 °C was purchased from BASF, Germany. Graphene nanoplatelets (GnPs, with commercial name Pure G+), with thickness: 8 nm, lateral size: 600 nm and number of layers: >8 [35] were kindly donated by Directa Plus, S.p.A. Italy. Commercial aluminum foils (2 cm × 2 cm, thickness: 1 mm) were used as substrates. Reagent grade chloroform, acetone, isopropanol and cyclopentanone were purchased from Sigma-Aldrich and used as received.

2.2. Preparation of the samples

All coatings were prepared by spray deposition from various organic solvents. For the polymer dispersion, TPU pellets were dissolved in chloroform to form a 2 wt% solution. Silica NPs and GnPs were dispersed in chloroform, separately, forming 2 wt% and 1 wt% solutions, respectively. All solutions and dispersions were ultrasonic processed for 1 min duration with probe sonic processing (SONICS, Vibra cell, USA) and subsequent 2 h in an ultrasonic bath at 59 Hz (SAVATEC, Strumenti scientifici, LCD Series, Italy). Afterwards, the solutions were sprayed onto the aluminum foils using an internal mix airbrush spray system (model VL-SET, Paasche), with 200 kPa pressure. The distance between the nozzle and substrate was kept approximately at 15 cm. Different samples were produced by spraying the polymer and nanoparticle or graphene solutions with or without post thermal annealing. Thermal annealing was performed on a hot plate at 150 °C for 10 min. Table 1 summarizes the different samples produced in order to obtain a robust and wear resistant coating.

2.3. Wetting analysis

Water contact angles (WCAs) and water roll off angles (RAs) were measured by OCAH 200 (Data Physics, Germany) contact angle goniometer. Five different measurements were collected

Table 1
Different nanoparticle films produced with or without TPU primer and GnP interface.

Code	Primer	Interface	Nanoparticle film	Annealing
S1	TPU	–	–	–
S2	TPU	–	–	150 °C
S3	TPU	–	Silica NPs	–
S4	TPU	–	Silica NPs	150 °C
S5	TPU	GnPs	Silica NPs	–
S6	TPU	GnPs	Silica NPs	150 °C