



Superhydrophobic high impact polystyrene (HIPS) nanocomposites with wear abrasion resistance



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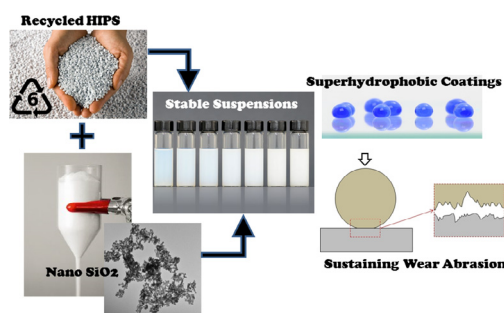
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HIGHLIGHTS

- Superhydrophobic nanocomposite metal coatings from recycled and non-toxic polymers.
- Wear abrasion resistant superhydrophobic high impact polystyrene nanocomposites.
- Tribological and wear abrasion properties can be tuned by thermal annealing.
- Application process can be easily scaled-up.

GRAPHICAL ABSTRACT



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ABSTRACT

Superhydrophobic and wear abrasion resistant high impact polystyrene (HIPS)/silica nanocomposite coatings for metal surfaces have been produced by spray. An environmentally friendly perfluorinated acrylic copolymer (PFAC) primer coating layer was applied first, in order to enhance adhesion with the substrate and prolong abrasion resistance. The best nanocomposite composition was found to be 50% silica nanoparticles with respect to HIPS by weight. This coating displayed the lowest friction coefficient compared to other nanocomposites with lower or higher silica concentrations. Tribological experiments on the best performing nanocomposites indicated that wear tracks or marks had no debris, cracks or complete material removal. Furthermore, Taber[®] abrasion tests confirmed tribological findings and showed that the best nanocomposites resisted superhydrophobic degradation up to 35 continuous linear abrasion cycles (15 kPa). Nanocomposites made with general purpose polystyrene instead of HIPS could only resist up to 15 Taber[®] abrasion cycles. The reason was attributed to the mechanical energy dissipation capability of rubber domains in HIPS. Thermal annealing of the coatings had a deterministic effect on the durability of the coatings against wear induced loss of superhydrophobicity. Annealed and non-annealed coatings were characterized by Fourier transform infrared and X-ray photoelectron spectroscopy. Due to ease of fabrication, resultant mechanical robustness, use of non-toxic materials, and low-cost industrial scale availability of HIPS, nanoparticles and the primer polymer, these coatings can be effortlessly transformed into larger scale non-wettable protective treatments for metals.

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1. Introduction

High impact polystyrene (HIPS) thermoplastic also known as rubber toughened polystyrene was developed as a ductile alternative to the highly brittle and rigid general purpose polystyrene [1].

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In general, HIPS is made by thermal or radical polymerization of styrene monomer with polybutadiene rubber [2]. Its classical microscopic structure is composed of an amorphous polystyrene matrix containing a uniform dispersion of composite spheroid domains, the latter being responsible for properties of HIPS such as opacity, craze plasticity, elongation, and energy absorption [3]. HIPS polymer has many advantages compared to other rigid and brittle thermoplastics such as flexibility, impact resistance, easy machinability, shatterproof, and low cost. It is also approved by the Food and Drug Administration (FDA) for food contact and packaging applications [4]. Due to its extensive use in many diverse applications such as packaging, toys, bottles, housewares, electronic appliances, and light-duty industrial components to name a few, efficient processes of recycling and reusing HIPS have also been developed [5,6].

Development of polymer nanocomposites based on HIPS has so far been motivated by improving its flame retarding and heat deflection properties [7,8]. Some common nanoscale fillers or additives already utilized are exfoliated clay or layered silicates [9], titanium dioxide [10], silica nanoparticles [11] and carbon black [12]. Although polystyrene has been extensively investigated in literature for the production of non-wettable surfaces [13–17], to the best of our knowledge, HIPS has not been used in the fabrication of non-wettable coatings (superhydrophobic and/or superoleophobic). Note that superhydrophobic/superoleophobic coatings are defined as coatings that display static water/oil contact angles greater than 150° and droplet roll off angles below 10° [18,19]. To date, non-wettable materials based on polystyrene have targeted potential applications such as corrosion prevention [20], self-healing [21], water-oil separation [22], hydrophobic textiles [23], and water purification [24]. Typical fabrication methods implemented include electrospinning [8], polystyrene microspheres assembly and dip coating [25], plant leaf replication [26,27] and solution spray coating [28]. However, no information is available on the wear abrasion resistance of non-wettable surfaces or coatings made up of polystyrene or polystyrene composites. Review of recent literature on wear abrasion resistance of non-wettable polymer nanocomposite coatings indicates that existence of rubbery phases in the coating formulations can significantly improve resilience against abrasion-induced non-wetting texture damage [29]. Since HIPS thermoplastics already contain dispersed micron-sized rubber particles, it could be a model polymer matrix for wear resistant non-wettable nanocomposites.

Hence, it is the aim of this work to evaluate performance of HIPS as a binder matrix against abrasion-induced wear in superhydrophobic nanocomposite coating applications. Superhydrophobic HIPS-SiO₂ nanocomposite coatings were prepared by spray coating from solutions. Upon optimization of the SiO₂ nanoparticles concentration within HIPS, abrasion-induced wear properties were measured and discussed. Both pure HIPS and HIPS-SiO₂ nanocomposite coatings displayed very poor metal substrate adhesion properties that obstructed proper tribological measurements. This drawback was eliminated by applying an environmentally friendly perfluorinated acrylic copolymer primer layer. Post-annealing conditions were also found to be critical in improving the performance of the coatings. Presence of the primer layer also ensured highly satisfactory results against loss of superhydrophobicity as a result of abrasion tests.

2. Materials and methods

2.1. Materials

HIPS polymer (rubber content ~8–13 wt%) originating from recycled urban waste was purchased from Heathrow Scientific USA. According to the manufacturer, the weight average molecular weight (M_w) of polystyrene is 260,000 and number average molec-

ular weight (M_n) is 150,000. The rubbery phase is polybutadiene with M_w and M_n of 120,000 and 100,000, respectively. Approximately, 35% of the rubber is grafted to the polystyrene. Polystyrene beads with M_w and M_n of 198,000 and 187,000 were purchased from Sigma-Aldrich and used as received.

A commercial aqueous perfluorinated acrylic copolymer (PFAC; Capstone ST-100) was purchased from The Chemours Company, USA [30]. It contains approximately 20 wt% polymer dispersed in water. Hydrophobically modified fumed silica, AEROSIL® R812, with an average particle size (7–40 nm) [31] was kindly donated by Evonik industries, Germany. Aluminum substrates (with dimensions: length: 5.0 cm, width: 2.5 cm, thickness: 1.0 mm) were purchased from RS components. Reagent grade trifluoroacetic acid (TFA), chloroform and acetone were purchased from Sigma-Aldrich and used as received without any further modification.

2.2. Preparation of the nanocomposites

The commercial water-dispersed perfluorinated acrylic copolymer (PFAC) has been developed as a penetrating stain resistant sealant for porous structures. Direct glazing on smooth surfaces by spray or roll coating does not produce smooth and adhesive coatings. Hence, it needs to be extracted from its aqueous dispersion [32]. In order to extract (precipitate) PFAC from the stabilized water dispersion, equal volumes of TFA and as-received aqueous dispersion were mixed at room temperature using a vortex mixer for five minutes. Resultant solid precipitate (an elastic rubbery polymer) was collected by decanting the supernatant, washing several times with distilled water, drying overnight under ambient conditions and dissolving in acetone in such a way that a 10% by weight solution was formed [33,34]. Primer coating formulation was made by further diluting the solution with acetone. The optimum solution concentration for spraying was determined to be 4% w/v. Flakes of HIPS polymer were dissolved in chloroform such that a 2 wt% solution was made. Afterwards hydrophobic silica nanoparticles were mixed into the solution so as to produce polymer/nanoparticle (HIPS/SiO₂) suspensions with varying nanoparticle weight percent with respect to the polymer (0%, 10%, 20%, 30%, 40%, 50% and 60%). To ensure good dispersion of silica nanoparticles in solution, the mixtures were sonicated in a sonic bath for 3 hours at 59 Hz. Aluminum substrates were cleaned by acetone prior to spray-deposition. Different HIPS/SiO₂ solutions were then sprayed onto aluminum substrates using an internal mix airbrush spray system (model VL-SET, Paasche). Spray coating was driven by high-pressure airstream at 200 kPa pressure. Distance between the sample and nozzle head was approximately 15 cm. In order to compare the wear abrasion performance of HIPS/SiO₂ coatings against general purpose polystyrene, identical polymer/nanoparticle solutions were also made with polystyrene. Polystyrene/SiO₂ coatings had identical wetting characteristics, however they did not resist wear abrasion as will be shown later.

For abrasion resistance, PFAC solution was first sprayed onto aluminum substrates. After evaporation of acetone solvent under ambient conditions annealing was performed on a hot-plate for 5 min at 180 °C. This will be designated as the primer coating. HIPS/SiO₂ solutions were spray coated on the primer coating using identical spray pressure and distance conditions. The solvent was evaporated for 1 h under ambient conditions and HIPS/SiO₂ nanocomposites were annealed at 180 °C for 5 min over a hot-plate. A final thermal annealing step was made by exposing the surface of the coatings to 220 °C for 2 min using a heat gun.

2.3. Morphological characterization

Scanning electron microscope (SEM, JEOL JSM-6490AL) with 10 and 15 KV accelerating voltage was used. Specimens were coated

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