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Energy efficient one-pot synthesis of durable superhydrophobic coating through nylon micro-rods

T. Simovich, A.H. Wu, R.N. Lamb[*]

Surface Science and Technology Group, School of Chemistry, The University of Melbourne, Victoria 3010, Australia

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ABSTRACT

A durable and superhydrophobic coating was fabricated at room temperature through encapsulating nylon micro-rods in a hydrophobic silica shell. This was achieved through the precipitation of miniemulsified nylon under high shear to generate micro-rods with high aspect ratio in the presence of methyltrimethoxysilane. The resultant coating structure resembles a network of highly entangled micro-rods that give rise to both surface roughness and hydrophobicity, resulting in contact angles greater than 155°. The embedded nylon polymer within the micro-rods imparts significant mechanical durability to the surface, resulting in a coating hardness of 2H using the pencil hardness test.

1. Introduction

Extremely waterproof surfaces are created through a mixture of chemical hydrophobicity and multiscale surface roughness [1,2]. The superhydrophobic condition is defined by high water contact angles of >150° and relatively small <5° sliding angles [2]. Technical interest stems from an inherent self-cleaning [1,3] property which has been applied with varying degrees of success in applications ranging from fog free [1,3] windows and mirrors [1,3] to marine anti-fouling [4] and fabric protection [5,6].

A key requisite for this observed superhydrophobicity is hierarchical roughness, which typically comprises of micron scale with a nanoscale overlay topography. This can be achieved in a myriad of ways [7–10] from etching of polymers to the creation of durable nanoparticle hybrid coatings. The latter is a scalable approach that was first reported over 15 years ago [11,12], intrinsically however, coating hardness decreases with increasing surface roughness [13]. Methods to mitigate this intrinsic limitation included the use of removable templates (usually polymeric) in the presence of a sol–gel, forming crater-like topography [14] and recently, allowed control over optical transparency of superhydrophobic films [15]. While this method offered additional control over film properties, the energy-intensive methods required to remove the polymeric templates significantly restricts scalability [16].

In this work, a new method of engineering a durable superhydrophobic coating using nylon particles as both a structural template and mechanical support is reported. As a structural template, nylon is readily removed through treatment with mild acids or warm water [17–19]. Nylon also exhibits suitable mechanical properties with high impact resistance [20] commonly utilized to strengthen other materials [21]. When embedded, the mechanical properties of nylon can be imparted into the bulk structure, thus enhancing the overall hardness of the coating.

2. Materials and methods

2.1. Materials

Nylon (MW approx. 10,000 g/mol) and Formic acid 95% and methyltrimethoxysilane (MTMS) Sigma–Aldrich. Methanol 99% Chem-Supply and Cyclohexane AnalaR Normanpur. Dimethylsiloxane-ethylene oxide block copolymer (50–55% non-siloxane) (PDMS-PEO) Gelest Inc. All reagents were used as received.

2.2. Synthesis of nylon particles

Nylon (300 mg) dissolved in Formic acid (7.5 g) was added to a solution of polydimethylsiloxane co-block polyethylene-oxide (1 g, PDMS-PEO) in cyclohexane (75 g). The mixture was emulsified by magnetic stirring for up to 24 h and further emulsified under high shear by blending using a Sunbeam SM6400 600 Watt blender for 5 min. Methanol (7.5 g) was added drop wise after the first 180 s of blending.

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[*] Corresponding author. Tel.: +61 3 8344 4180.
E-mail addresses: tomers@student.unimelb.edu.au (T. Simovich), ahwu@unimelb.edu.au (A.H. Wu), rnlamb@unimelb.edu.au (R.N. Lamb).

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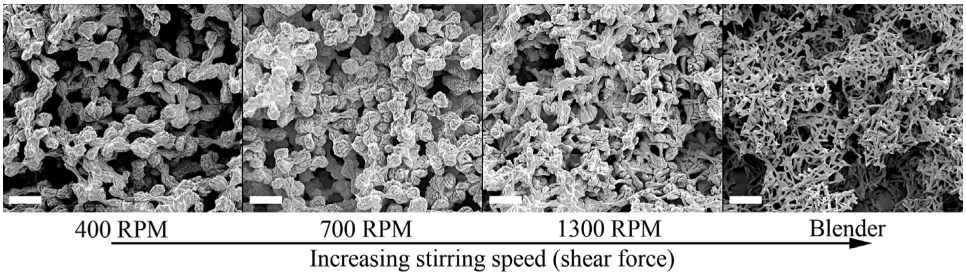

Fig. 1. SEM images of nylon micro-particle morphology as a function of applied shear (scale bar = 10 μm).

2.3. *Fabrication of nylon superhydrophobic coating*

A sol consisting of methyltrimethoxysilane (2.4 g) in methanol (50 mL), water (5 mL) and hydrochloric acid (12 M, 3 drops) was sonicated for 3 h to form a gel. A small amount (2.4 g) of the gel was then added to the nylon suspension. The mixture was then sonicated for a further 30 min and spray coated (Scorpion HVLP Spray Gun) onto glass slides. The coating was then cured at a minimum of 70 °C for 1 h for drying. Coated slides were then submerged in Hydrochloric acid (0.1 M, 150 mL, pH: 1) for 1 h while the solution was lightly stirred and then washed with water before drying.

2.4. *Measurement of coating durability*

ASTM pencil hardness standard [22] test was adopted for coatings hardness quantification. Varying pencil grades from 8B to 9H were used. The hardest pencil grading that did not scratch the surface was designated as the coating hardness.

2.5. *Surface analysis*

XPS data was acquired using a VG ESCALAB220i-XL spectrometer equipped with a hemispherical analyzer. The incident radiation was monochromatic Al Kα X-rays (1486.6 eV) at 220 W (22 mA and 10 kV). Survey (wide) scans were taken at analyzer pass energies of 100 eV. Survey scans were carried out over 1200–0 eV binding energy range with 1.0 eV step size and 100 ms dwell time. Base pressure in the analysis chamber was below 7.0×10^{-9} mbar. All data was processed using CasaXPS software and the energy calibration was referenced to the C 1s peak at 285 eV.

ATR-IR data was acquired using Bruker Tensor 27 Sample Compartment RT-DLaTGS Spectrometer with 4 cm^{-1} resolution with a range from 4000 cm^{-1} to 400 cm^{-1}. Data was analyzed using OPUS 6.5 software.

3. Results and discussion

Nylon particles were successfully synthesized through the use of water-in-oil miniemulsion precipitation. Fig. 1 shows the SEM of the produced particles as a function of applied shear, which are rod-shaped with an average length of 5 μm and a maximum achievable aspect ratio of 6:1. The rod-like nature of the particles is dictated by both surfactant concentration and applied shear force during precipitation [23].

Table 1
Shear force (stirring speed) during particle synthesis and resulting aspect ratio, contact angle and hardness of micro-rods and coatings (0.33% solid content).

Shear speed	Aspect ratio (length:width)	Contact angle	Hardness
400 RPM	2.7:1	90.6°	9B
700 RPM	2.1:1	56.6°	6B
1000 RPM	2.75:1	57.2°	3B
1300 RPM	5.3:1	68.5°	4B
Blender	6:1	159.9°	2H

3.1. *Particle morphology*

In particular, the elongated shape of nylon particles is attributed to surfactant concentration used. Concentrations of 0.16 g L^{-1} (8.9×10^{-5} M [24]) yield spherical particles while excess well above the CMC generate globular, sphero-cylindrical or rod-like shapes [23,25,26]. The latter's advantage is higher aspect ratios which significantly enhances the coating surface roughness. To further increase the aspect ratio, rod thickness was controlled by varying the applied shear resulting in thicker rod extremities but results in lower coating hardness, whereas higher stirring speeds generated linear rods with even thickness along the length of the rod (Table 1). Although the particles are in the micron range, a nano scale roughness is still present through ridges or "veins" running along the length of the particles primarily due to shear conditions.

3.2. *Coating characterization*

Spray coating of the pure nylon particles results in 5–10 μm thick films (Fig. 2a) that are hydrophilic, highly porous with needle like topography due to the rod-like nature of the nylon particles. The addition of MTMS into the nylon suspension conformally coats the nylon particles (Fig. 2b), which when acid treated, all exposed nylon is removed leaving behind a similar porous needle-like surface (Fig. 2c).

The surface of the as-produced MTMS-coated nylon superhydrophobic coating exhibits complete wetting characteristics. This

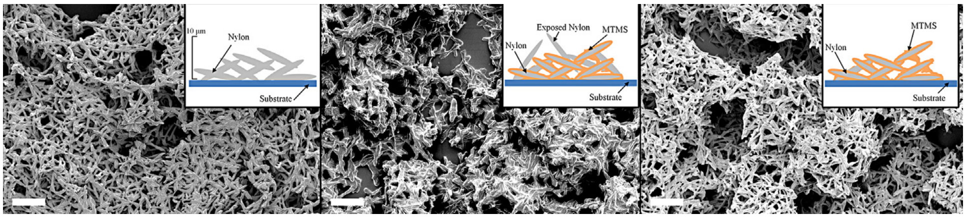

Fig. 2. SEM images and inset schematics illustrating the similarity in surface morphology of (a) as-produced nylon micro-rods, (b) MTMS-coated nylon micro-rods, and (c) acid-treated MTMS-coated nylon micro-rods (Scale bar = 10 μm).