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Wettability of terminally anchored polymer brush layers on a polyamide surface

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Surface wettability of terminally anchored hydrophilic polymer brush layers on polyamide–silicon (PA–Si) surfaces was evaluated with respect to surface topography at the nanoscale. Hydrophilic polyvinylpyrrolidone (PVP) and polyacrylamide (PAAm) brush layers were synthesized via graft polymerization onto a PA–Si surface previously activated by surface treatment with atmospheric pressure plasma. Hydrophilicity (or wettability) of the PA substrate, as quantified by the free energy of hydration, was increased upon surface coverage with the PVP and PAAm brush layers by 13–24% (-101.4 to -111.3 mJ/m^2) and 19–37% (-106.1 to -122.4 mJ/m^2), respectively. Surface hydrophilicity increased with both increasing surface roughness (0.55–2.89 nm and 1.54–5.84 nm for PVP and PAAm, respectively) and polymer volume (1.3×10^6–7.3×10^6 nm^3/μm^2 and 3.3×10^6–2.8×10^7 nm^3/μm^2 for PVP and PAAm surfaces, respectively). The present study suggests that a specific level of surface wettability can be attained by tailor-designing the polymer brush layer's physicochemical characteristics (e.g., surface roughness, wettability, and polymer water affinity) by adjusting surface topography and surface chemistry, which are controlled by surface activation and polymerization conditions. The above indicates that there is merit in structuring various surfaces with hydrophilic brush layers to increase surface wettability in membrane filtration, biomedical devices, and lubrication applications.

1. Introduction

Surface wettability (or surface hydrophilicity) is of considerable importance in a variety of applications such as membrane separations [1–3], lubrication [4], fibers (e.g., textiles) [5,6], and biomedical applications [7–9]. In particular, surface modification via graft polymerization (or "grafting from") to form a dense polymer layer of terminally and covalently anchored polymer chains ("brush" layer), has gained popularity in recent years as a surface modification method aimed at increasing surface hydrophilicity [1–3,7,10–12], increasing [4,11,13] or decreasing [1–3,7–9] the target solute affinity for the surface, decreasing surface adsorption of proteins (i.e., biofouling) [10,12], decreasing friction [4], imparting biocompatibility [7–9], and increasing adhesion [5,6].

In order to increase surface wettability via graft polymerization, the surface must possess reactive sites for polymer chain anchoring. Surface activation techniques include, for example, chemical modification (e.g., via ozonation, benzoyl peroxide (BPO), azoisobutyronitrile (AIBN), certain transition metal ions (Ce^{4+}, Cr^{6+}, V^{5+}, Co^{3+}), etc.) [14], UV [15–19] or gamma irradiation [20–22], and plasma activation [2,10,14,23–26]. Plasma surface activation is of particular interest since a high surface density of active sites can be created on a wide range of inorganic [25,27] and organic [2,23] surfaces. High surface density of anchored chains is desirable in order to reduce chain–chain separation and form a polymer layer in the "brush" regime [28–30]. In this regard, the development of atmospheric pressure plasma (APP) has made it possible to achieve a high density of surface active sites under atmospheric pressure conditions, paving the way for scale-up of the sequential integration of APP surface activation with graft polymerization. It is worth noting that while there is extensive literature on the application of low pressure plasma (LPP) to surface treatment and integration with both polymer grafting ("grafting to") and graft polymerization, the requirement of LPP chamber is a limiting factor for large-scale deployment [31]. Other plasma surface treatment approaches such as corona discharge and dielectric barrier discharge have enabled operation under atmospheric pressure condition, but typically produce plasma discharge which is of insufficient uniformity for producing grafted polymer layers with sufficient uniformity at the submicron – or even nano-scales [32–34]. In contrast, the APP jet approach provides a plasma stream that is spatially and temporally uniform with a higher

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plasma density (~10^{16} particles/cm^3) relative to dielectric barrier discharge plasma sources (~10^{12} particles/cm^3). Furthermore, the APP jet approach offers several advantages for scale-up potential and is not restricted to flat or thin substrates as is the case with other APP surface treatment systems [23].

Once a surface is activated via plasma treatment, graft polymerization is achieved by contacting the substrate surface with a vinyl monomer solution, leading to the formation of a layer of terminally and covalently anchored polymer chains. The kinetics of growth of such surface chains (R_P) from active surface sites typically follows a first order reaction, with respect to monomer concentration in solution ([M]) [27,35],

$$R_p = k_p\left(\frac{f_d k_d}{k_t}\right)^{1/2}[SI]^{1/2}[M] \quad (1)$$

where k_p, k_t, and k_d are the rate constants for surface chain propagation (via sequential monomer addition), chain termination (via combination and disproportionation), and initiator decomposition, respectively, f_d is the initiator thermal decomposition efficiency (for first order decomposition), and [SI] is the concentration of active surface species (e.g., peroxides [36]). The grafted polymer yield (e.g., mg polymer/cm^2) and grafted polymer thickness are governed by the polymerization conditions (e.g., monomer type and concentration, grafting time, and temperature) [36–38]. For example, higher polymer graft yield is expected with increasing temperature, initial monomer concentration, as well as reaction time. It has been reported that the above approach of surface graft polymerization enables the formation of a high chain surface density layer of terminally and covalently attached chains (i.e., "brush layer") at a reasonably low level of polydispersity [23]. It is noted, however, that if there is significant formation of free radical species in solution (e.g., primarily due to thermal initiation at excessive high reaction temperatures), termination of surface chains can impede chain growth by monomer addition, thereby increasing the polydispersity of surface chains [25]. Therefore, for certain applications that may require low polydispersity, controlled radical polymerization can be used with the present approach of surface plasma activation [39].

Surface activation by APP is typically accomplished by exposure of the surface to plasma (e.g., using argon, helium, nitrogen, oxygen or other suitable gas) for a short duration (order of seconds to minutes) [2,6,40]. Graft polymerization post-APP treatment is typically preformed with vinyl monomers with reported initial monomer concentrations typically in the range of 1–30% v/v [1,41,42], although concentrations as high as 70% v/v have been reported [43]. Graft polymerization is generally carried out at mild temperatures (50–80 °C, [1,2,25,27,36,40]), but higher temperatures have been reported for grafting in non-aqueous solvents [27,44]. Studies have shown that APP, followed by either graft polymerization ("grafting from") [1,2,6,40] and polymer grafting ("grafting to") [7,42] with hydrophilic monomers enabled synthesis of terminally anchored polymer brush layers with reported water contact angles in the range of 5–75°. The degree of polymer grafting is quantified in most studies in terms of grafting mass density which has been reported to be in the range of 0.01–3.0 mg/cm^2 [7,43,45,46]. Although published studies concerned with atmospheric pressure plasma induced graft polymerization (APPIGP) have generally reported on wettability and grafting density, few have provided information regarding surface topography (e.g., via AFM analysis) which suggests a range of root-mean-square surface roughness, R_{rms}, of 0.18–220 nm [1,2,7,25,27,36,43,44]. While existing studies have demonstrated that APP surface activation followed by synthesis of a polymer brush layer via graft polymerization ("grafting from") and/or polymer grafting ("grafting to") lead to different levels of polymer surface chain density and surface wettability, such studies have not explored the relationship between surface topography at the nanoscale and wettability.

Studies have shown that, in addition to the importance of surface chemistry, surface topography at the nanoscale [1,2,25,27,36,43,44] and sub-micron scale [7] can have a measurable impact on surface wettability. Accordingly, the present contribution focused on evaluating the impact of surface topography at the nanoscale/sub-micron range, for a hydrophilic polymer brush layer, on surface wettability (i.e., hydrophilicity). The brush layer was synthesized on a thin polyamide surface created on a smooth silicon wafer substrate (Fig. 1). A polyamide (PA) substrate, which has a hydrophobic character relative to the hydrophilic brush layer, was selected for brush layer anchoring given the popularity of this polymer as a membrane material for nanofiltration (NF) and reverse osmosis (RO) membranes as well as in various other applications [1,2,36]. In particular, it is noted that there have been increasing efforts over the last decade to modify the surfaces of PA membranes in order to increase both surface hydrophilicity and resistance to biofouling and fouling by organics and colloidal matter. Indeed, using the APPIPG approach, previous work [36] has demonstrated that hydrophilic polymer brush layers can be effective in increasing local membrane surface hydrophilicity in addition to surface screening, thereby imparting fouling resistant character to RO membranes. The brush layers were synthesized in the current work by a two-step process consisting of surface activation by an APP source (via surface impingement) followed by surface graft polymerization with two different anionic water soluble vinyl monomers. The effect of surface activation and graft polymerization conditions on the resulting surface topography (e.g., surface feature height distribution and surface roughness) was assessed and subsequently surface wettability was quantified with the aim of elucidating the impact of topography of the hydrophilic brush layer.

2. Materials and methods

2.1. Materials

Prime-grade silicon ⟨1 0 0⟩ wafers (Wafernet, Inc., San Jose, CA) of 100 mm in diameter and 0.050–0.055 mm in thickness were cut into 0.5″ × 0.5″ squares and used as substrates to facilitate surface analysis. Concentrated H_2SO_4 (Fisher Scientific, Pittsburgh, PA) and reagent grade H_2O_2 (Sigma–Aldrich, St. Louis, MO) were used to prepare the piranha solution (3:1 mixture of sulfuric acid and 30% hydrogen peroxide) for silicon wafer cleaning. The polyamide surface for anchoring the hydrophilic brush layers was prepared using poly(ethyleneimine) (PEI, M_w = 750,000 g/mol), 1,3-phenylenediamine (MPDA, ⩾99%), and trimesoyl chloride (TMC, 98%) (Sigma–Aldrich, St. Louis, MO). The monomers for graft polymerization were 1-vinyl-2-pyrrlidone (nVP) (>99%, Aldrich, St. Louis, MO), and acrylamide (AAm) (Fisher Chemicals, 99%, Fair Lawn, NJ). Solutions of PEI, nVP, and AAm were all prepared using ultra-pure deionized water produced by filtering the distilled water through a Milli-Q filtration system (Millipore Corp., San Jose, CA). Hexane (Sigma–Aldrich, St. Louis, MO), was the solvent for preparing the TMC solution. Monomer solutions were degassed using industrial grade nitrogen (97%, Air Liquide, Los Angeles, CA).

2.2. Surface nanostructured polyamide surfaces

Surface nanostructured-polyamide-silicon (SNS-PA–Si) surfaces were synthesized in three sequential steps: (1) surrogate surface preparation, (2) plasma surface activation, and (3) graft polymerization. The silicon wafers were first thoroughly cleaned in a piranha bath (90 °C, 3:1 sulfuric acid to 30% hydrogen peroxide,