



High throughput atmospheric pressure plasma-induced graft polymerization for identifying protein-resistant surfaces

Minghao Gu^a, James E. Kilduff^b, Georges Belfort^{a,*}

^aHoward P. Isermann Department of Chemical and Biological Engineering and the Center for Biotechnology and Interdisciplinary Studies, Rensselaer Polytechnic Institute, Troy, NY 12180 3590, USA

^bDepartment of Civil and Environmental Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180 3590, USA

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ABSTRACT

Three critical aspects of searching for and understanding how to find highly resistant surfaces to protein adhesion are addressed here with specific application to synthetic membrane filtration. They include the (i) *discovery* of a series of previously unreported monomers from a large library of monomers with high protein resistance and subsequent low fouling characteristics for membrane ultrafiltration of protein-containing fluids, (ii) *development* of a new approach to investigate protein-resistant mechanisms from structure-property relationships, and (iii) *adaptation* of a new surface modification method, called atmospheric pressure plasma-induced graft polymerization (APP), together with a high throughput platform (HTP), for low cost vacuum-free synthesis of anti-fouling membranes. Several new high-performing chemistries comprising two polyethylene glycol (PEG), two amines and one zwitterionic monomers were identified from a library (44 commercial monomers) of five different classes of monomers as strong protein-resistant monomers. Combining our analysis here, using the Hansen solubility parameters (HSP) approach, and data from the literature, we conclude that strong interactions with water (hydrogen bonding) and surface flexibility are necessary for producing the highest protein resistance. Superior protein-resistant surfaces and subsequent anti-fouling performance was obtained with the HTP-APP as compared with our earlier HTP-photo graft-induced polymerization (PGP).

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1. Introduction

Surface modification of materials is an efficient and cost-effective way of imparting desired interfacial properties. Examples of different approaches include wet chemistry [1], phase separation [2,3] and radiation methods such as photo-oxidation [4], low pressure plasma [5], atmospheric pressure (AP) plasma [6] and electron beam [7]. Materials are also tailored with unique functional properties using for example, free radical graft polymerization. Here, materials are exposed to an activation source, and free radicals are formed as dissociation of excited sites. Then graft polymerization occurs simultaneously in the presence of a functional vinyl monomer. The resultant grafted polymer chains are covalently attached to the material surface with durable stability.

Photo-induced graft polymerization (PGP) has been widely used and accepted for modification of both intrinsically photoactive and non-photoactive (with initiating agents) materials [8–10].

Recently, atmospheric pressure plasma-induced graft polymerization (APP) has been employed for material surface functionalization [11–16]. A number of advantages of APP are: (1) AP plasma combines both UV and ion bombardment without the need to submerge the substrate in a vacuum, (2) AP plasma discharges with low breakdown voltage, uniform density of charge species and high concentrations of ions and radicals, and (3) properties of grafted polymer phase is controllable [11,17].

Lewis and Cohen [11] first reported the modification of a silicon surface with APP. Graft polymerization was controlled by plasma treatment time, radio frequency (RF) power, amount of adsorbed surface water and solvent type. They also combined free radical graft polymerization with controlled nitroxide-mediated graft polymerization of polystyrene using APP with hydrogen [12]. APP has also been used to modify synthetic material surfaces to develop stimuli-responsive polymer for drug delivery [13], improve dyeing and antistatic properties of fabrics [14], improve adhesion of fluorocarbon polymer films [15], and reduce mineral scaling propensity of reverse osmosis membranes [16].

A significant challenge for membrane filtration of biofluids is protein adhesion to the external and internal surface of synthetic

* Corresponding author. Tel.: +1 518 276 6948.
E-mail address: belfog@rpi.edu (G. Belfort).

membranes (we call this “membrane fouling”). Fouling greatly reduces membrane performance, i.e. causes permeation flux decline, effects selectivity and increases process cost. The main challenge for the past 20–30 years has been how do we choose the best surface chemistry to resist protein adhesion and hence membrane fouling for synthetic membrane filtration. The Whitesides group has published a set of criteria for selecting protein-resistant chemistries: They should (i) be hydrophilic, (ii) include hydrogen bond acceptors, (iii) do not include hydrogen bond donors, and (iv) be net electrically neutral. In the Discussion section, we address these criteria and their limitations.

Graft polymerization of synthetic membrane surface is an attractive approach without substantially changing the bulk properties of the base-membrane. Previously, we have used low pressure plasma graft polymerization (LPP) to modify the polyacrylonitrile and polysulfone ultrafiltration (UF) membranes so as to reduce membrane fouling [18,19]. After graft polymerization with hydroxyethyl methacrylate (HEMA), protein fouling was significantly reduced and membrane permeation flux during protein filtration was improved. Recently, we combined a high throughput platform (HTP) with PGP to synthesize, test and select the best protein-resistance membranes from a large library of monomers in less than a day. New and previously known monomers for protein resistance were identified with this HTP-PGP method [20,21]. Since APP has several advantages for materials modification (above), it could offer a new approach for modifying synthetic polymeric membranes.

In this work, the goals were to discover new protein-resistant monomers, explain the basis of protein resistance and develop high flux and low protein-binding (low fouling) UF membranes using APP. Together with a previously reported HTP method [20–22], a library of 44 commercial vinyl monomers was grafted onto commercial PES membrane surfaces. The performance of modified and unmodified PES control membranes were assessed using a static protein adsorption protocol. To evaluate our capability for developing protein-resistant membranes, the performance of HTP-APP was compared with our previously successful HTP-PGP results. We also investigated the mechanisms of why some surfaces resist protein adhesion better than others from structure-property relationships.

2. Theoretical

Solubility parameters have been used to predict the compatibility between solvents and polymers. Liquids with similar solubility parameters are mostly miscible, while polymers dissolve in solvents with solubility parameters close to those of the polymer.

The term solubility parameter was first introduced by Hildebrand and Scott [23]. The Hildebrand solubility parameter is defined as the square root of the cohesive energy density:

$$\delta = (-U/V)^{1/2} \quad (1)$$

U is defined as the molar internal energy, which is associated with the net attractive interactions between the materials. $-U$ is total energy of evaporation, which is a direct measure of the total energy of association of the liquid's molecules. V is the molar volume of the liquid.

The seminal assumption of the Hansen solubility parameter (HSP) approach is that the total energy of evaporation is due to (i) “non-polar” or dispersion interactions (δ_d), (ii) “polar” or permanent dipole–permanent dipole interactions (δ_p), and (iii) hydrogen bonding interactions (δ_h). δ_d , δ_p , and δ_h of HSP are estimated from molecular physical properties of each group in a monomer and is named the group contribution method [24]:

$$\delta_d = (\Sigma F_d)/V \quad (2)$$

$$\delta_p = (\Sigma F_p^2)^{1/2}/V \quad (3)$$

$$\delta_h = (\Sigma U_h/V)^{1/2} \quad (4)$$

where F_d ($J^{1/2} \text{ cm}^{2/3} \text{ mol}^{-1}$), F_p ($J^{1/2} \text{ cm}^{2/3} \text{ mol}^{-1}$) and U_h ($J \text{ mol}^{-1}$) are the molar attraction constant for the non-polar groups, the molar attraction constant for the polar group and the hydrogen bonding energy, respectively. All these values were adapted from the work of van Krevelene [25], except sulfur dioxide group [26]. V ($\text{cm}^3 \text{ mol}^{-1}$) is molar volume of monomer.

3. Experimental

3.1. Materials

96-well filter plates (Seahorse Labware, Chicopee, MA) were used for the HTP-APP experiment. 100 kDa PES membrane coupons (effective area 19.95 mm^2) were mounted and sealed by the manufacturer on the bottom of each well with the volume of $300 \mu\text{L}$. The membranes were washed and soaked in DI water overnight before use to remove any surfactant. Separate 100 kDa PES membranes (Pall Corp., Port Washington, NY) were used to characterize the membrane surface structure and the degree of grafting of the monomers after expose to APP. Five classes from 44 commercial vinyl monomers (Fig. 1) and butyl methacrylate (BMA), a control monomer, were purchased (Sigma–Aldrich, Saint Louis, MO). A description of these monomers is shown in Table S1 (Supplementary Information, SI). The monomers were tested without further purification. All monomer solutions were degassed before use to remove the existing oxygen. Except for #4 and BMA used water/ethanol (20/80 wt %/wt %) as the solvent, the other monomers were dissolved in water. Except for #4 at a concentration of 0.12 mol L^{-1} , the concentration of other monomers was 0.2 mol L^{-1} . 2,2-diphenyl-1-picrylhydrazyl (DPPH) and benzene were purchased from Sigma–Aldrich without further purification. Bovine serum albumin (BSA) and phosphate buffered saline (PBS) tablets were purchased (Sigma–Aldrich). Ultrahigh purity helium and nitrogen gas was used (Noble Gas Solutions, Albany, NY).

3.2. Methods

3.2.1. Peroxide assay

Radical concentrations were measured according to Suzuki et al. [27]. After the PES membranes were APP with helium (He), they were placed into 0.1 mM de-aerated DPPH benzene solution and reacted at $60 \pm 1 \text{ }^\circ\text{C}$ for 2 h. The amount of the DPPH consumed was measured from the difference in transmittance at 520 nm between the unmodified or control and the treated PES membranes.

3.2.2. HTP-APP

The atmospheric pressure AP plasma source (Model ATOMFLO, Surfex Technologies LLC, Culver City, CA) was operated at 200 V and was driven by RF power at 27.12 MHz. A beam of reactive gas species with 5 cm of length was generated from the plasma source. With the source-to-membrane distance of 13 mm, the 96-well membrane plate was exposed to the ultra-purity He at a flow rate of 30.0 L min^{-1} . An XYZ Robot (Surfex Technologies LLC, Culver City, CA) was used to control the plasma source over the plate with the scan speed (S) from 0.7 to 0.2 mm s^{-1} . The width (L) of the plasma source was 3.1 cm measured according to Gonzalez et al. [6]. The exposure time was calculated as the ratio of L/S. Following the

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