Enzyme-catalyzed Modification of PES Surfaces

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Scope & Target

To investigate a new "Green" enzyme-catalyzed modification of poly(ethersulfone) (PES) membranes, and to evaluate the behavior of the modified membranes.

Materials, Methods & Results

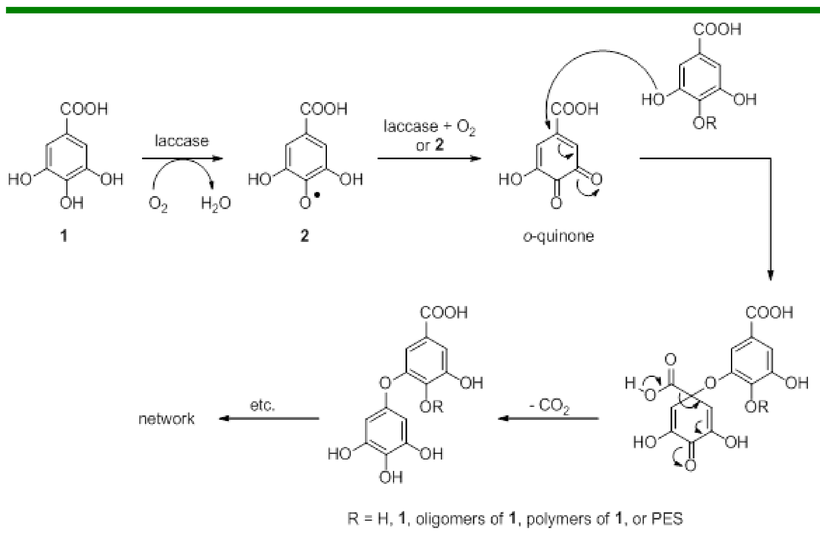

Figure 2a. Proposed mechanism of the laccase-mediated formation of an o-quinone from gallic acid, and its reaction with gallic acid (derivatives) in solution or with the PES membrane.

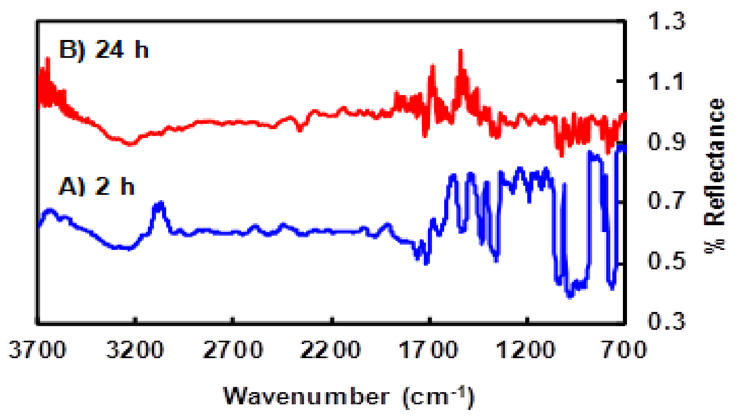

Figure 3a. IRRAS spectra for gallic acid-grafted membranes at both 2 (A) and 24 h (B) modification time. Reflectance is relative to an unmodified membrane.

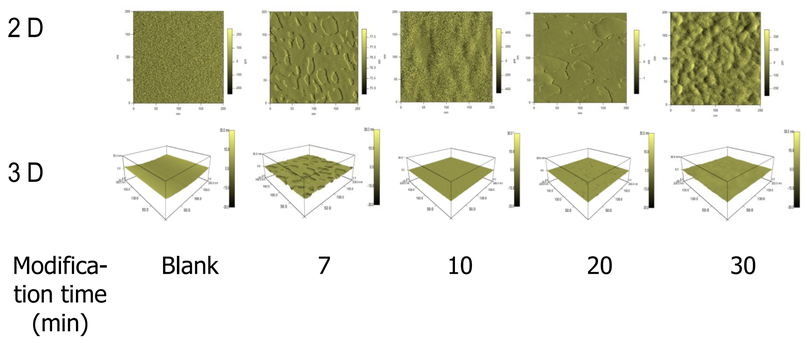

Figure 4a. AFM images (2D and 3D), blank and gallic acid modified PES model surfaces [4.8 mM gallic acid, 0.5 U·ml^{-1} enzyme, at pH 5, and 25 °C] obtained after 7, 10, 20, and 30 min modification time.

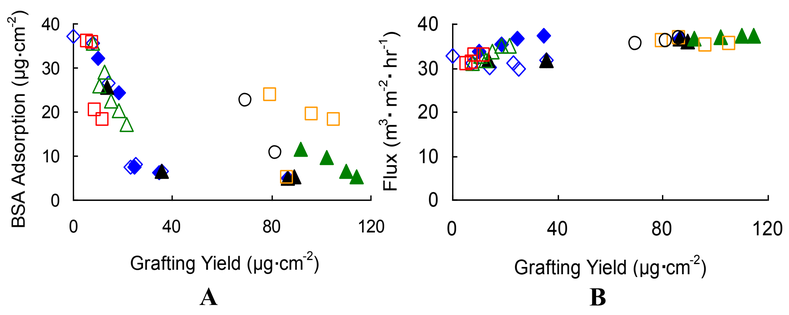

Figure 5a. A) BSA adsorption and **B)** Clean water flux, as function of grafting yield for different reaction conditions using gallic acid modifier.

References.

1. Nady, N.; Schroën, K.; Franssen, M.C.R.; van Lagen, B.; Murali, S.; Boom, R.M.; Mohy Eldin, M.S.; Zuilhof, H., Mild and Highly Flexible Enzyme-catalyzed Modification of Poly(ethersulfone) Membranes, ACS Appl. Mater. Interfaces, 3 (2011) 801-810.
2. Nady, N.; Schroën, K.; Franssen, M.C.R.; Mohy Eldin, M.S.; Boom, R.M.; Zuilhof, H., Laccase-Catalyzed Modification of PES Membranes with 4-Hydroxybenzoic Acid and Gallic Acid, J. Membr. Sci., 394-395 (2012) 69-79.
3. Nady, N.; Schroën, K.; Franssen, M.C.R.; Fokkink, R.; MohyEldin, M.S.; Zuilhof, H.; Boom, R.M., Enzyme-Catalyzed Modification of PES Surfaces: Reduction in Adsorption of BSA, Dextrin and Tannin, J. Colloid Interface Sci., 378 (2012) 191-200.

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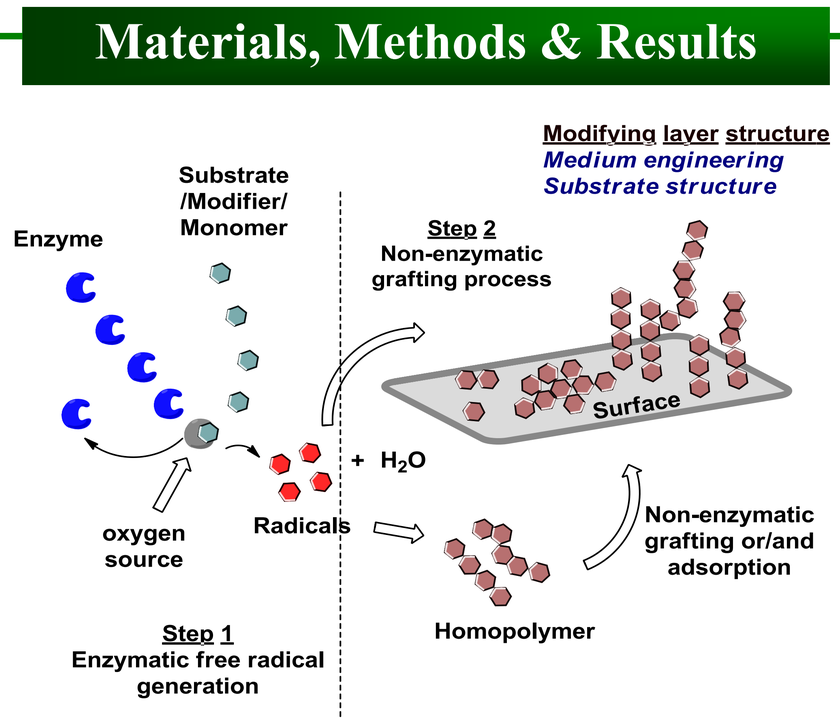

Figure 1. Schematic diagram of the enzyme-catalyzed modification method of PES surfaces.

4-Hydroxybenzoic (4-HBA) acid and Gallic acid were covalently coupled under mild conditions (neutral pH, room temperature, aqueous medium, see Fig. 1 & Fig. 2b) to PES membranes by C-O linkages using **laccase** from ***Trametes versicolor*** as biocatalyst [1]. Other monomers can be oxidatively grafted onto the attached monomers, to form oligomers or polymers, which may lead to additional C-O as well as C-C bond formation with concomitant coloration of the surfaces. For gallic acid, further oxidation of the formed radicals to *o*-quinones may take place inside the enzyme's active site or in solution as shown in Fig. 2a [2].

XPS and NMR measurements indicate the covalent deposition of new material to the membrane, which is confirmed by IRRAS (Fig. 3 a & b) studies that show the presence of carbonyl and hydroxy-groups (1708 cm^{-1} [C=O], 3200-3500 cm^{-1} [O-H]) on the modified membranes. ***The brush-shaped modifying layer*** was determined with AFM using 4-hydrozybenzoic acid modifier (Fig. 4b), whereas the added gallic acid appears as small islands after 7 min modification time, which then grow together and become denser and rougher upon longer reaction times as shown in Fig 4a. Laccase-catalyzed modification of PES membranes significantly suppressed protein adsorption but hardly affected membrane flux (Fig 5 a & b) or bulk membrane properties [2,3].

The structure of the modifying layer can be tuned by the modification conditions and the choice of substrate. In general, substrates with more reactive groups (like gallic acid) will lead to denser 3D networks, while molecules with only one hydroxyl group give linear or branched structures as shown in Fig 6, which swell and extend in water to give rise to entropic repulsion as shown in Fig.7.

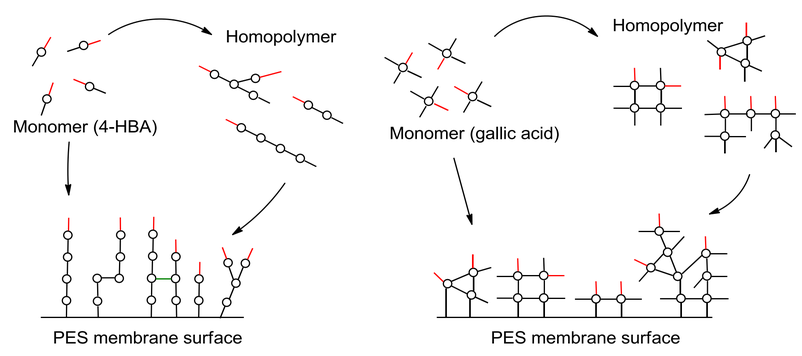

Figure 6. Schematic representation of modification layers formed by 4-hydroxybenzoic acid (4-HBA) and gallic acid. Black line: OH group or ether linkage; green line: C-C bond; red line: COOH group.

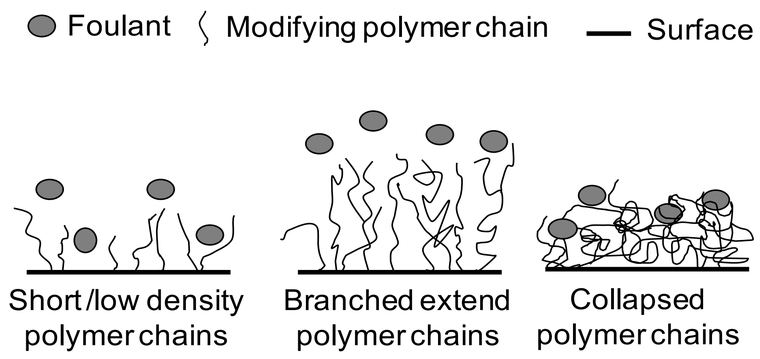

Figure 7. Effect of surface morphology on foulant repellence

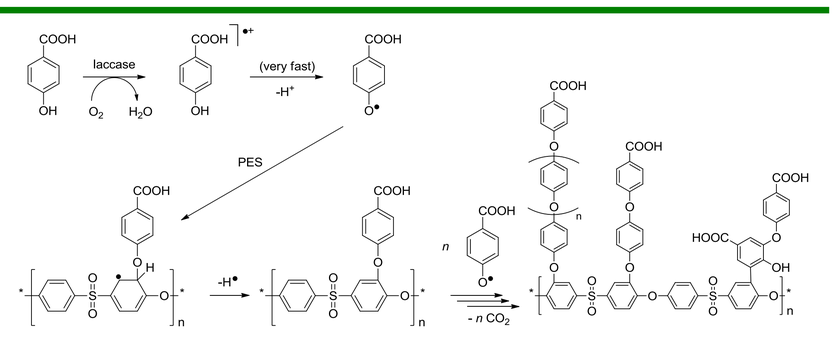

Figure 2b. Tentative mechanism for the formation of reactive 4-hydroxybenzoic acid radicals by laccase and grafting of the radicals to PES membranes.

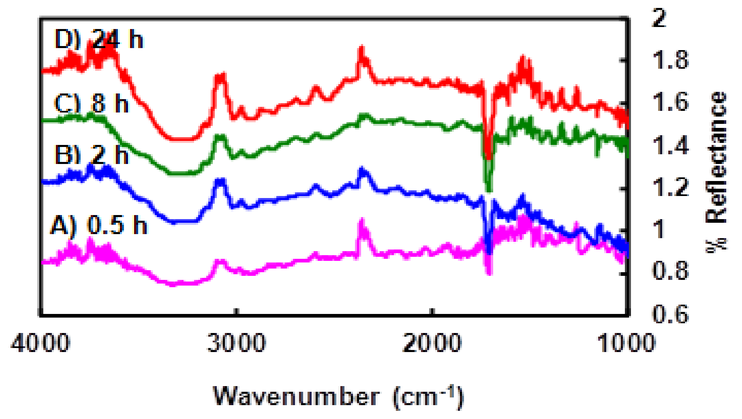

Figure 3b. IRRAS Spectra for 4-hydroxybenzoic acid-grafted membranes at 0.5 (A), 2 (B), 8 ©, and 24 h (D) modification time, reflectance is relative to an unmodified membrane.

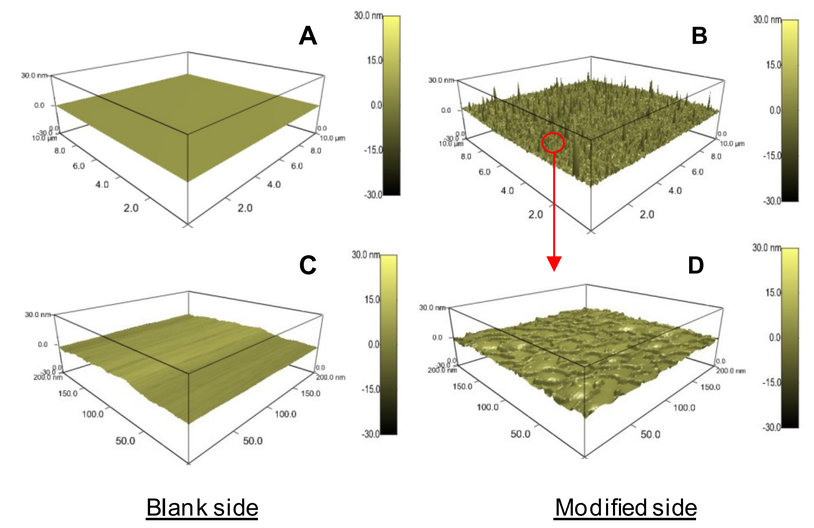

Figure 4b. AFM images of half-modified model PES membrane: blank side [10 µm (A) and 200 nm (C)], 4-hydroxybenzoic acid modified side [10 µm (B) and 200 nm (D)]. Modification conditions: 28.8 mM 4-hydroxybenzoic acid, 2 h modification time, 0.5 U·ml^{-1} laccase, 25 °C, and pH 5.

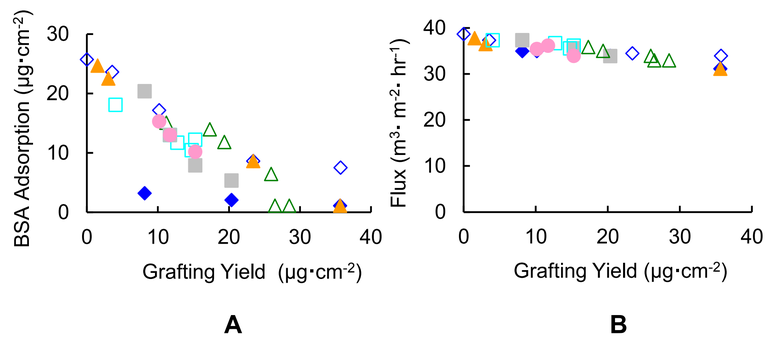

Figure 5b. A) BSA adsorption and **B)** Clean water flux, as function of grafting yield for different reaction conditions using 4-hydroxybenzoic acid modifier.

Conclusions

Enzyme-catalyzed modification

of PES membranes
can be carried under **eco-friendly** conditions
and is suited for the preparation of

high flux

low protein fouling

membranes

Grafting of Poly(arylsulfone) and a Process of Grafted Poly(arylsulfone), Norhan Nady, Karin Schroën, Maurice Franssen, Remko Boom, and Han Zuilhof, European Patent No. 10169842.1-1214, (2010)
Applicant: Pentair X-flow

ISPT Project FO-00-01, Mild fractionation of suspensions and emulsions