MODIFICATION OF PES MEMBRANES: AN ENVIRONMENTALLY FRIENDLY APPROACH

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Abstract

This study presents enzyme-catalyzed grafting of PES membranes as a first successful example of environmentally friendly modification of PES membranes. The modification is carried out at room temperature in aqueous medium. The resulting surfaces were amongst others investigated by colour, as an indicator for successful modification, and with IR-spectrometer connected to IR-microscope equipped with a grazing angle objective (IR-GIR) to elucidate the chemical bonds that are formed during modification. The obtained results are discussed in relation to membrane performance, and protein repellence as function of reaction conditions.

1. Introduction

Influencing surface properties is seen as one of the ways to improve membrane performance. Although the importance of surface hydrophilicity and surface structure for prevention of protein adsorption has been presented in literature [1-3], a clear relation is not available yet.

In this work we mainly use poly(arylsulfone) membranes, such as poly(ethersulfone) (PES), of which it is known that the intrinsic hydrophobic character can be reduced by incorporation of hydrophilic polymers through e.g. blending [4], coating [5], and radiation induced-grafting [6]. Although successful to some extent, these methods only offer random control over the resulting surface structure and may be environmentally adverse. Therefore, any method

that allows better control over the modification process is of relevance, and for this, we opted to use the enzyme laccase from *Trametes versicolor*.

2. Membrane Modification

Flat PES membranes purchased from Sartorius (0.2 µm pore size, 50 mm diameter, 150 µm thickness, water flow rate > 28 ml·min^{-1}·cm^2 at ΔP = 1 bar) were incubated in 0.1 M sodium acetate buffer (pH 5 and 25 ℃). The liquid contained different concentrations of 4-hydroxybenzoic acid (1-30 mM) and enzyme (0.25-1 U/ml), and air is bubbled through for supply of O_2 and gentle mixing. Although various substrates are accepted by the enzyme, here we only report on the results obtained with 4-hydroxybenzoic acid.

After a specific incubation time (0.5-24 hours), the modified membranes were washed by strong flushing with water, repeated dipping in Milli-Q water and subsequent decantation. Then, the modified membranes were washed by filtration of at least 1000 ml deionized water. The modified membranes were kept in glass-covered dishes in desiccators supplied with silica gel for 24 h before analysis.

BSA was used to evaluate protein adsorption; 1g/l BSA solution was prepared using 0.1 M sodium acetate buffer pH 7. The membranes were exposed to BSA solution while gently shaking (200 rpm) at 25 ℃ for 24 h. BSA concentration in the solution was measured using UV-Vis spectrometer (280 nm), and from this the adsorbed amount was calculated.

3. Results and Discussion

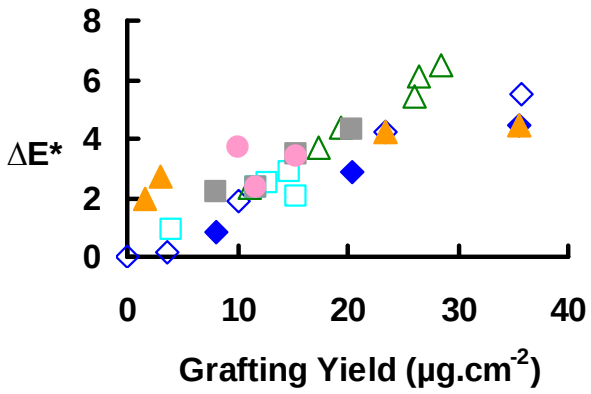

Figure 1: Total change of colour (ΔE*) as function of grafting yield for different reaction conditions. Different symbols signify different reaction parameter that were varied (substrate concentration, enzyme concentration, temperature, reaction time, buffer strength, pH) while keeping the other parameters constant.

Various reaction conditions were tested, and the total change of colour (ΔE*, see Figure 1) increased with increasing grafting yield. At much higher grafting yield (beyond the used scale), the total change in colour started to increase exponentially with grafting yield; this could be explained by the formation of dense layers that are more saturated in colour.

The IR-GIR spectra of the 4-hydroxybenzoic acid grafted membranes at different incubation times (0.5, 2, 8, and 24 h) are shown in Figure 2. A clear sharp C=O group peak at 1708 cm^{-1} indicates the presence of carboxylic acid. The intensity of this peak increases with increasing incubation time (*i.e.*, increased amount of grafting). The characteristic bands due to aromatic C-H stretch around 3030-3080 cm^{-1} (benzene ring) and the intense, broad band of OH around 3200-3500 cm^{-1} all refer to the newly attached phenolic compounds.

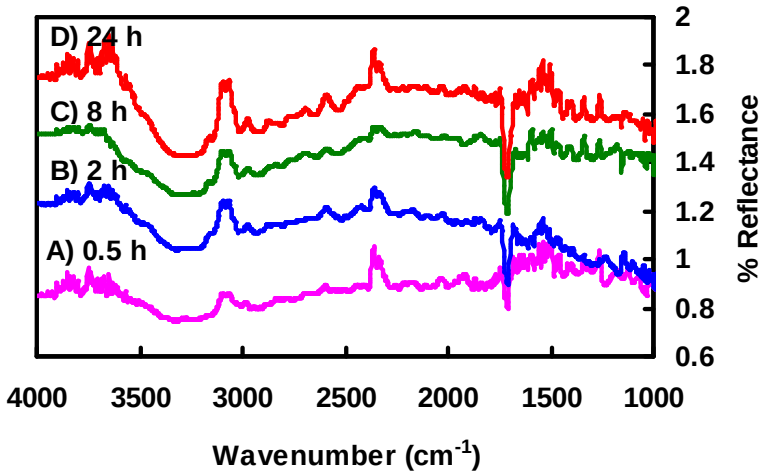

Figure 2: IR-GIR spectra for 4-hydroxybenzoic acid grafted membranes at 0.5 (A), 2 (B), 8 (C), and 24 h (D) incubation time. Reflectance is relative to unmodified membrane.

Although the grafting yields can be very different, this did not influence the membrane flux too much. A very modest (10%) linear flux decrease as function of grafting yield can be noted, as illustrated in Figure 3. The highest flux reduction was found to be 20%, but in most cases, the flux reduction was below 10%, and this implies that the original pores of the base membrane (0.2 μm) have not become constricted by the modification layer.

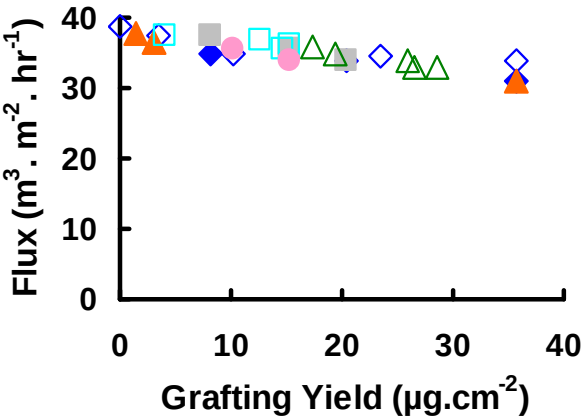

Figure 3: Flux as function of grafting yield for various reaction conditions. Symbols are the same as in Fig. 1.

Regarding protein adsorption, the general trend is that the adsorbed amount of bovine serum albumin (BSA, see Figure 4) decreases with increasing grafting yield. At some modification conditions and high grafting yield, BSA adsorption is even below the detection limit. This could be interpreted as an effect of increased surface hydrophilicity, however, at different grafting yields, the same adsorbed BSA amounts can be found, therefore, we propose that it is not 'just' hydrophilicity that determines whether protein can adsorb or not. What is the actual mechanism behind this is still under investigation.

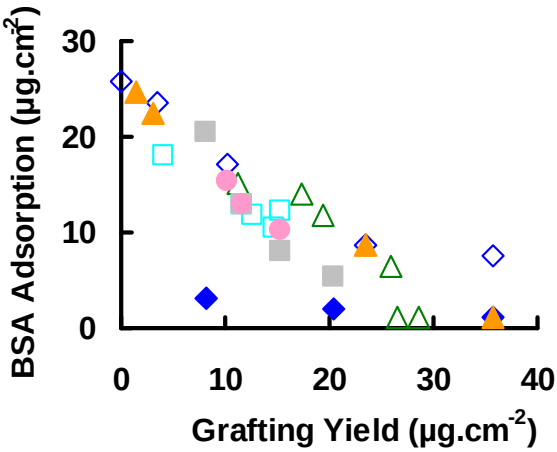

Figure 4: BSA adsorption as function of grafting yield for different reaction conditions.

4. Conclusions

In this paper, we have shown that it is possible to covalently link phenolic compounds to PES membranes with the enzyme laccase. The resulting modified membranes are still highly porous and in some cases possess excellent protein repellent properties. Since the reaction can be carried out in water at room temperature and does not require toxic components, we like to think that enzyme-catalyzed modification is an eco-friendly alternative for the current modification methods used for PES membranes.

Although not reported here, we have found that other polymers, for example poly(aryl ether ketones) such as poly(ether ketone) (PEK), poly(ether ether ketone) (PEEK), and poly(ether ketone ether ether ketone) (PEKEEK) [7,8], can be modified using the same procedure; also here, colour formation takes place, indicating covalent linkage of the phenolic acid to the polymer.

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