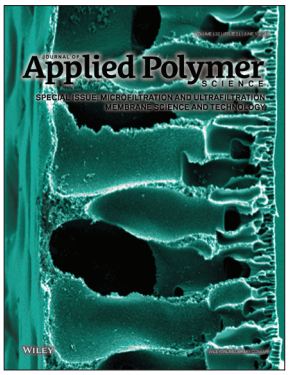
JOURNAL OF Applied Polymer SCIENCE

Special Issue: Microfiltration and Ultrafiltration Membrane Science and Technology

Guest Editors: Prof. Isabel C. Escobar (University of Toledo) and Prof. Bart Van der Bruggen (University of Leuven)



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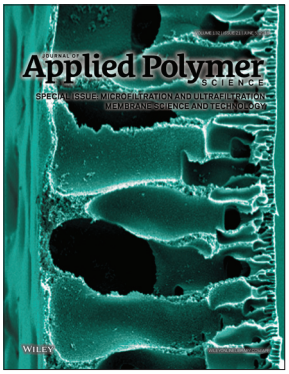

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Journal of Applied Polymer Science

Elucidating membrane surface properties for preventing fouling of bioreactor membranes by surfactin

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ABSTRACT: The large scale production of bacterial surfactin-an anionic lipopeptide is restricted by its high cost of production. Surface sorption of surfactin causes membrane fouling, decreasing air permeation, or filtration efficiency of membranes used in bioreactors. The aim of this study was to elucidate surface properties leading to reduction or even the prevention of surfactin sorption on fibrous membranes. Surface modification of fibrous polyethylene terephthalate (PET) nonwoven membranes using cationic and/or anionic biopolymers, or an antiadhesive fluorinated polymer, with or without a prior air plasma treatment, resulted in membranes with varying surface properties. Membranes with superhydrophilic to superhydrophobic behavior with varying surface charges (positive, nul, and negative) were produced. Water contact angle (WCA), capillary uptake, as well as Zeta potential of each modified membrane, were quantified. Sorption tests using surfactin, were carried during 5, 24, and 48 h, at pH 7. The amphiphilic anionic lipopeptide sorbed on positively charged membranes as well as on negatively charged hydrophobic, hydrophilic, or superhydrophobic membranes. PET membrane functionalized with alternate deposition of chitosan and alginate presented surface properties (zeta potential of −20 mV and WCA = 80°), which was effective in rejecting 100% of the anionic surfactin both at an initial stage and at a late stage (after 48 h). Discussion is proposed to explain possible interactions between the anionic lipopeptide and the functionalized nonwovens.
 J. Appl. Polym. Sci. **2015**, *132*, 41622.

KEYWORDS: adsorption; fibers; membranes; porous materials; surfaces and interfaces

Received 29 July 2014; accepted 2 October 2014
DOI: 10.1002/app.41622

INTRODUCTION

Bacterial biosurfactants are amphiphilic, which in addition to their emulsifying, foaming, dispersing, and wetting properties, have other important properties such as pharmacological, antifungal, and antiviral capabilities.[1–3] Their low toxicity, biodegradability, environmentally friendly nature, and the wide range of potential industrial applications in bioremediation, health care, oil, and food processing industries makes them particularly interesting.

Their large scale production and application are, however, currently restricted by the high cost of production and by the limited understanding of their interactions with cells and with the environment. In membrane based bioreactors used for production of biosurfactants by bacterial growth, fouling of biosurfactants on membranes reduce their production. Sorption of biosurfactants on ultrafiltration membranes used for aeration of bacterial cell culture, blocks membrane pores, which impedes oxygen transfer, and hence reduces bacterial growth.[4] Moreover, biosurfactant recovery is not cost effective because of the high sorption of surfactants on the microfilter membrane used for separation of the biosurfactants from bacterial cell culture medium (or from cell-free culture).[5] Biosurfactants tend to form micelles causing fouling of porous separation membrane, which then does not allow their easy diffusion through the micropores.

The aim of this work was to elucidate surface properties for prevention of fibrous membrane fouling by an anionic bacterial lipopeptide biosurfactant-surfactin. Indeed, past research works mainly deal with surface sorption prevention of anionic surfactants such as sodium dodecyl sulfate (SDS) and ammonium perfluoroalkyl carboxylate on membranes.[6–8] However, while both surfactants and biosurfactants may possess a hydrophobic tail made up of lipid (or of saturated or unsaturated fatty acids), bacterial biosurfactants do differ from synthetic surfactants because their hydrophilic head is mainly an organic part composed of amino acids or peptide anions or cations or mono/disaccharides or polysaccharides.[9–11] A recent article[12] deals with the prevention of membrane sorption by a bacterial

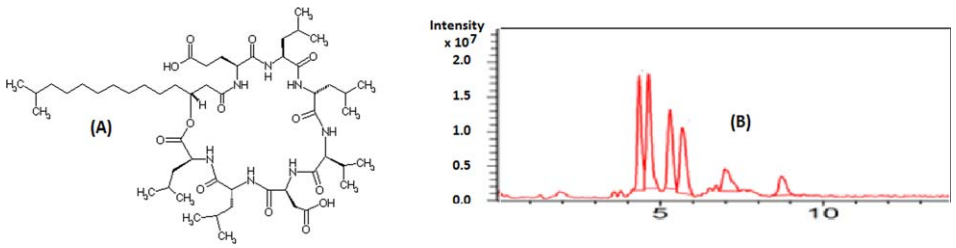

Figure 1. Chemical structure of surfactin, an anionic lipopeptide biosurfactant produced by *Bacillus subtillis* (A). A natural diversity occurs, differing from each other by the length and the ramification of the fatty acid chain, which explain the various peaks appearing in the HPLC chromatograph (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

rhamnolipid, which is an anionic glycolipid biosurfactant. However, the surfactin lipopeptide used in our study differs from the rhamnolipid as it is composed of a ring of amino acids (peptide) with two carboxylic groups (see Figure 1). Surface sorption of the anionic lipopeptide should be similar to that of proteins.

On the overall, a few review articles detail the different surface functionalization methods used for antifouling surfaces[13,14] to prevent sorption of specific proteins. Membrane surface morphology, charge, and hydrophilicity can affect membrane fouling by organic compounds.[15,16] Increasing the hydrophilicity of a membrane surface has been widely accepted as a useful way to improve organic antifouling properties[17–20] and to prevent sorption of rhamnolipids.[12] Different methods have been used to incorporate hydrophilic surface chemistry onto different polymer substrates such as PES(polyethersulfone) or PP(polypropylene) hollow fiber or microfiltration fibrous membranes.[21–26] Polymer surface grafting with hydrophilic molecules (acrylamide[22]) or hydrophilic polymers [polyvinyl alcohol,[23] polyethylene glycol (PEG),[24] and polysaccharides[25,26]] has been used without or with surface preactivation using plasma or UV-irradiation, to produce antifouling membranes.

Surface grafting of a zwitterionic polymer on membranes,[27] has also been used to produce antifouling surfaces. It has also been suggested by some authors that superhydrophobic surfaces could reduce the extent of protein adsorption due to Lotus effect.[28] While some studies show that proteins dissolved in water adhere to superhydrophobic surfaces less rapidly than on flat surfaces[29,30]; other studies do show that minimal adsorption of protein occurs on superhydrophobic fluorosiloxane coatings.[31]

The bacterial lipopeptide-surfactin considered in our study occurs naturally in various lengths, with the hydrophobic fatty acid chain varying between 13 and 15 carbons, without or with ramification. Thus, it is worthwhile elucidating surface properties, which can reduce surface fouling by the different homologs of the anionic lipopeptide surfactin biosurfactant.

In this work, fibrous polyester-PET (polyethylene terephthalate) nonwovens were functionalized with various polymer coatings to produce membranes with varying surface properties in terms of wettability and surface charges. Nonwovens are increasingly studied for their potential use as aeration membranes because of the availability of various pore sizes and pore connectivity. Already, our previous article showed that polyester (PET) nonwovens functionalized with hydrophobic and positively charged chitosan yielded very strong sorption of an anionic lipopeptide biosurfactant.[32] In this study, different strategies were adopted to prevent sorption of the biosurfactant. Superhydrophilic to superhydrophobic nonwovens were produced. Two methods were adopted to enhance the hydrophilicity: (1) by increasing air plasma treatment power (TP) to yield maximum negative surface charges and maximum hydrophilicity and (2) by using a hydrophilic polyanionic alginate on a plasma treated PET nonwoven or on a polycation-coated PET. The nonwoven PET was equally functionalized with an antiadhesive fluorinated polymer to produce a superhydrophobic nonwoven.

The modified PET nonwovens were characterized by water contact angle (WCA) measurements, capillary uptake, zeta potential and air permeability measurements. In the second part of the article, sorption studies of the anionic lipopeptide biosurfactant–surfactin on the different functionalized nonwovens were carried out.

MATERIALS AND METHODS

Materials

A nonwoven membrane composed of cylindrical-shaped PET (polyethyelene terephthalate) fibers (average diameter 28.2 μm) formed by carding and hydroentanglement was used. The membrane specific fiber surface area for adsorption is 25 m^2 per m^2 of nonwoven membrane. The membrane was cleaned to remove all surface impurities and spinning oil before surface functionalization.

Low molecular weight sodium alginate polymer (with a viscosity of 250 mPa s at 2 wt % aqueous alginate) was purchased from Sigma Aldrich [see Figure 2(A)]. A 65% deacetylated low molecular weight chitosan (purchased from Sigma Aldrich) was used as polycationic polymer.[32] A fluorinated water and oil repellent polymer–Unidyne [see Figure 2(B)] was purchased from DAIKIN Industries. Naturally occurring anionic lipopeptide biosurfactant-surfactin [see Figure 1(A)] produced from the strain *Bacillus subtilis BBG131* at the Probiogem laboratory (France) was used. The negatively charged polar part of this biosurfactant is made of a heptapeptidic moiety (with L-asparagine, L-leucine, glutamic acid, L-leucine, L-valine, and two D-leucines). The nonpolar part is a fatty acid chain, which varies in length, between 13 and 15 carbons. Thus, a natural diversity of the lipopeptide-biosurfactant-surfactin occurs, which explain

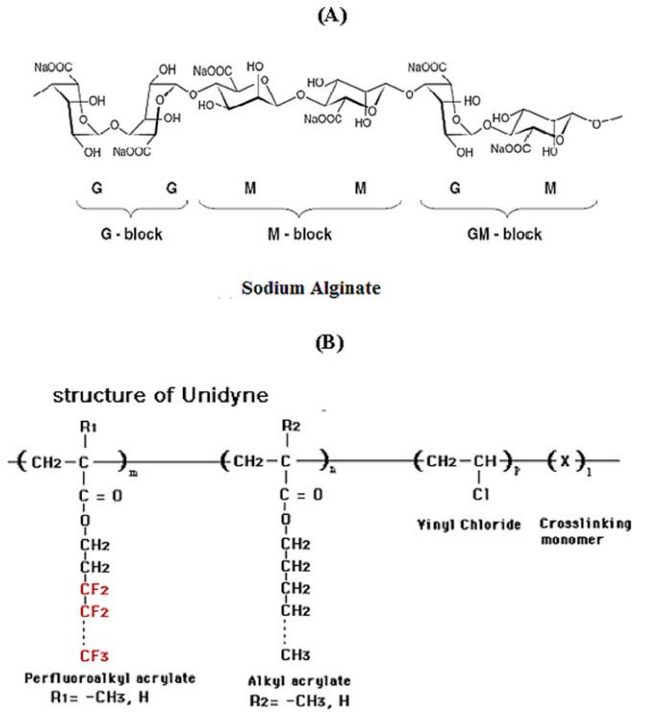

Figure 2. Schematic diagram showing the chemical structure of (A) sodium alginate and (B) unidyne fluorocarbon polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the various peaks appearing in the HPLC chromatograph [see Figure 1(B)] when a sample of bacterial biosurfactants is analyzed.

Nonwoven Surface Functionalization Methods

Plasma Treatment. Air atmospheric plasma treatment of the PET nonwoven was carried out using a plasma machine called "Coating Star" manufactured by Ahlbrandt System (Germany).[33] The nonwoven was subjected to a "dielectric barrier discharge," at a frequency of 26 kHz, interelectrode distance of 1.5 mm, using atmospheric air. The nonwoven was treated on one side, and on both sides using increasing plasma TP from 0 to 60 KJ/m^2. After plasma treatment, each plasma treated sample was separated from waste fabric and kept in aluminum foil away from light.

Immobilising Polymers on PET Nonwoven Fiber Surface. Padding procedure was used to deposit polymers (alginate or chitosan or fluorinated polymer) on untreated or plasma treated PET nonwoven membranes (Figure 3). Padding consists in soaking the nonwoven in the aqueous solution of polymer, followed by removal of excess solution by squeezing of the membrane through two pressurized rolling cylinders. Indeed padding allows a dynamic coating of the membrane inner and outer fiber surfaces in the nonwoven.

Deposition of Sodium Alginate Polymer on PET Nonwoven Pretreated with Air-Plasma or Precoated with Chitosan

In this work, PET nonwoven with or without plasma treatment was padded with an aqueous 3 g/L solution of sodium alginate. At a squeezing pressure of 3 bars, 0.3 g of sodium alginate was deposited onto 100 g of nonwoven PET. The nonwovens were then dried at room temperature for 24 h, and then characterized.

The alginate polymer was also deposited on PET nonwoven precoated with chitosan. Indeed PET nonwoven with or without plasma treatment (60 KJ/m^2) was first padded in an aqueous solution made up of 3 g/L of 65% deacetylated chitosan at pH 5. The padded sample was washed to remove unfixed chitosan. The nonwoven with fixed chitosan was then padded in an aqueous solution made up of 3 g/L of sodium alginate, and then washed to remove unfixed alginate and then subjected to drying at RTP. Release of excess sodium alginate was monitored by conductivity measurements.

Deposition of the Antiadhesive Fluorinated Polymer (Unidyne)

PET nonwoven without plasma treatment was padded in an aqueous solution made up of 10 g/L commercial fluorinated polymer (Unidyne) in presence of acetic acid (pH 5). Squeezing was carried out at a pressure of 2 bars, and the nonwoven was then dried in a stenter dryer at 110°C for 2 min and then subjected to a temperature of 150°C during 3 min to allow the crosslinking of the fluorocarbon polymer. At a squeezing pressure of 2 bars, ~1 g of Unidyne was deposited onto 100 g of nonwoven PET.

Characterisation of Functionalized Nonwoven PET Membrane Air Permeability Measurements. Indeed polymer deposition onto nonwoven fiber surface using squeezing rollers (during padding method-see Figure 3) can cause clogging of interstices (voids) in between fibers reducing the pore size. Drastic reduction of membrane permeability can be a drawback for its use for bioprocesses.

Therefore, air permeability measurements of the functionalized fibrous PET nonwovens were carried to characterize the extent

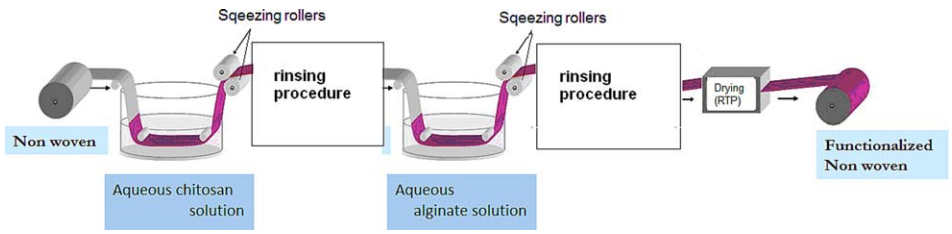

Figure 3. Stepwise deposition of chitosan followed by sodium alginate onto PET nonwoven. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of pore reduction due to the surface functionalization method used. This test was performed on ten samples for each functionalized PET nonwoven, according to the standard test ISO 9237 using a Textest FX 3300 instrument at a fixed pressure drop of 200 Pa.

WCA Measurements and Capillary Uptake Measurements. For measuring WCA >90°, sessile drop method using "Digidrop" from GBX Instrument (France) was used. However for lower contact angles (<90°), the water drop was absorbed by the nonwoven porous structure. Therefore, a more precise method, developed in several of our previous works[33] called the wicking test, was performed to calculate the WCA as well as the capillary uptake of various nonwovens. A rectangular nonwoven connected to a tensiometer at the weighing position, was brought into contact with water placed in a container. On immediate contact, a Meniscus weight (W_m) was measured. The WCA of the outer nonwoven membrane surface was calculated using eq. (1).

$$W_m \times g = \gamma_L \times \cos\theta \times p \quad (1)$$

where

W_m Meniscus weight (g).
p sample perimeter in contact with the liquid (mm).
g 9.81 g s^{-2}.
γ_L Surface tension of water.
θ WCA.

Capillary uptake due to water inflow inside the nonwoven by capillarity was also measured. Whereas, the WCA is a measure of hydrophilicity of the outer membrane, capillary uptake is an indicator of hydrophilicity of inner nonwoven fiber surfaces. At the end of 3 min, the nonwoven sample was separated from the water surface, and the weight of water entrapped inside the nonwoven structure by capillarity (W_c) read directly on the screen of the tensiometer. Experiments were repeated five times for each sample. More details are described in our previous article.[32–34]

Zeta Potential. The surface zeta potential was measured by streaming potential measurement using a Zetacad equipment (France) at 25°C. A 0.001 mol L^{-1} of KCl electrolyte solution was used; 1 g of nonwoven fibrous PET was maintained in a cell while the electrolyte was forced to flow through the membrane at varying pressures. Before any zeta potential measurement, the sample was maintained in the electrolyte solution for 24 h to reach equilibrium before making the measurement itself. Five measurements were carried out on each sample for pH values of the electrolyte solution varying from 3 to 10.

Evaluation of the Adsorbed Anionic Lipopeptides

The quantities of the anionic surfactin lipopeptide, which sorbed on various functionalized PET nonwoven membrane after 5 and 24 h, respectively, were determined by measuring the quantities of residual lipopeptides after each adsorption experiment; 4 ml of the aqueous biosurfactant solution (120 mg/L) at pH 7 was put in contact with 120 mg of nonwoven membrane, at 30°C, at pH 7 with ultrapure water in a 20 mL glass recipient under 160 rpm agitation.

In a second experiment, the quantities of residual biosurfactant were also measured when varying amounts of functionalized nonwoven were used for the sorption experiments during 48 h, using the same conditions described previously.

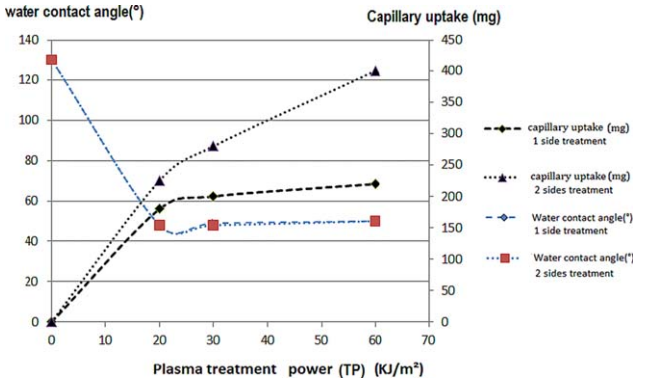

Figure 4. Variation of WCA and capillary uptake (mg) of PET nonwoven as a function of plasma TP used. Plasma treatment was applied on one side or both sides of the nonwoven. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Our work showed that out of 120 mg/L of anionic biosurfactant, 40 mg/l sorbed on the glass recipient even after a few hours, in all cases. This data was taken into account before calculating the quantity of biosurfactant that sorbed on the nonwovens.

The samples were filtered through 0.2 μm cellulose filters before analysis and the residual, nonsorbed surfactin lipopeptides were quantified using HPLC (Waters Corporation, Milford, MA) with water/ACN/TFA mixture as eluent and a C18 column as described by Gancel *et al.*[35]

RESULTS

Characterization of the Functionalized PET Nonwovens

Optimizing Plasma Treatment of PET Nonwoven Membrane. Indeed the WCA measured for the untreated PET nonwoven membrane is rather high (WCA = 132°). Minimum WCA of 41° is easily reached at low plasma TP of 20 kJ/m^2 when the nonwoven PET is treated on one side only, and this value does not vary with further increase in plasma TP or when the nonwoven is plasma treated on both sides. However, the capillary uptake of the nonwoven membrane increases as the TP is increased. Capillary uptake reaches 170 and 220 mg at 20 and 60 kJ/m^2, respectively, for plasma treatment on one side only. This capillary uptake reaches a maximum of 400 mg when the nonwoven is plasma treated on both sides at 60 kJ/m^2 (see Figure 4).

The zeta potential values of the plasma treated PET nonwovens are more negative than those of the untreated PET nonwoven. Indeed, at a constant pH of 7, the zeta potential of PET nonwoven decreased from −60 to −65 mV for a plasma TP of 30 kJ/m^2, and to −70 mV for a plasma TP of 60 kJ/m^2 (see Table I)

The increase in the proportion of polar groups, in particular carboxyl —O—C=O groups as described in a previous article,[33] would explain the reduction in zeta potential and in WCA values. The results show that small plasma TP treats the outer nonwoven surface but higher plasma TP is needed to treat fiber

Table I. Characteristics of Functionalized Nonwovens

	Air permeability ($L/m^2/s$)	Zeta potential (mV; at pH 7)	WCA	Capillary uptake (mg; 3 min)
PET	1490 ± 35	−60	132° ± 5*	/
PET Plasma (TP = 30 kJ/m^2)	1480 ± 44	−65	41° ± 6	280 ± 15
PET Plasma (TP = 60 kJ/m^2)	1480 ± 40	−70	41° ± 5	400 ± 14
PET/chitosan	1485 ± 37	+42	140° ± 5*	/
PETplasma/Chitosan	1421 ± 59	+20	65° ± 6	500 ± 20
PET/Chitosan/alginate	1034 ± 29	−20	80° ± 5	100 ± 20
PET Plasma/chitosan/alginate	1010 ± 51	−30	65° ± 5	650 ± 11
PET+ fluoropolymers (unidyne)	1480 ± 40		150° ± 5*	/

All WCAs were determined by tensiometry except those indicated by (*), which were determined by digidrop.

surface inside the PET nonwoven membrane. Whatever the conditions, there is nearly no change in membrane air permeability value after plasma treatment (see Table I).

Thus for the biosurfactant sorption test, only the most hydrophilic and the most negatively charged that is, the nonwoven PET treated on both sides at 60 kJ/m^2 by air atmospheric plasma was selected. Water durability test of the plasma treated PET nonwoven carried out during 24 h at RTP confirmed that the plasma treatment was resistant to conditions of the biosurfactant sorption experiment.

Nonwoven Membrane Functionalized with Sodium Alginate. ***PET functionalized by padding with alginate solution of plasma activated PET nonwoven.*** When membranes functionalized with sodium alginate after plasma activation were characterized, great irregularities in the measured membrane WCA values were recorded. This is explained by the release or desorption of alginate polymer deposited at the PET nonwoven membrane surface. This result is contrary to that observed in our previous works, which showed increased adhesion between PET and a hydrophilic PEG polymer,[34] and between PET and a polycationic polymer.[32] Indeed, electronic repulsion between the negatively charged alginate polymer and the negatively charged plasma treated PET would explain the nonadhesion of the hydrophilic alginate on the hydrophilic plasma treated PET.

Thus, the PET membranes (with or without plasma treatment) were first functionalized with a polycationic chitosan polymer before deposition of the anionic sodium alginate polymer (see Figure 3). PET membranes were first functionalized with 3 g/L of 65% deacetylated chitosan at pH 5, using the padding process (impregnation of the nonwoven with the aqueous chitosan solution followed by squeezing at 3 bars). This pH ensured that the chitosan was fully protonated. Approximately 0.39 g of chitosan was deposited onto 100 g of nonwoven PET, that is, 0.035 g/m^2 of fiber surface. The chitosan coated fibrous nonwovens were successively washed with distilled water until all unfixed chitosan were released. Chitosan deposited on PET membrane yielded a hydrophobic membrane (WCA = 140°) with zeta potential of +60 mV at pH 5. Chitosan deposited on plasma treated PET nonwoven yielded a more hydrophilic membrane (WCA = 65°) with zeta potential of +38 mV at pH 5 (see Figures 5 and 6 and Ref. [32]).

The positively charged membranes functionalized with chitosan were then padded at pH 5 with 3 g/L of low molecular weight sodium alginate solution. This pH ensured that the alginate was fully deprotonated. Rinsing procedure was again used to remove unfixed sodium alginate, before characterising the functionalized membranes. Release of unfixed chitosan or alginate was monitored using conductivity measurements of the washing waters.

The PET functionalized with chitosan and alginate was referred as PET/chitosan/alginate and the plasma treated PET functionalized with this method referred as PETplasma/chitosan/alginate. Application of the polyanionic sodium alginate on the chitosan coated PET, produced a nonwoven membrane (PET/chitosan/alginate) with zeta potential varying from +10 mV at pH 3 to −25 mV at pH 10 (see Figure 6). For the PETplasma/chitosan/alginate functionalized nonwovens, zeta potential values are more negative and vary from −5 mV at pH 3 to −40 mV at pH 10 (see Figure 6).

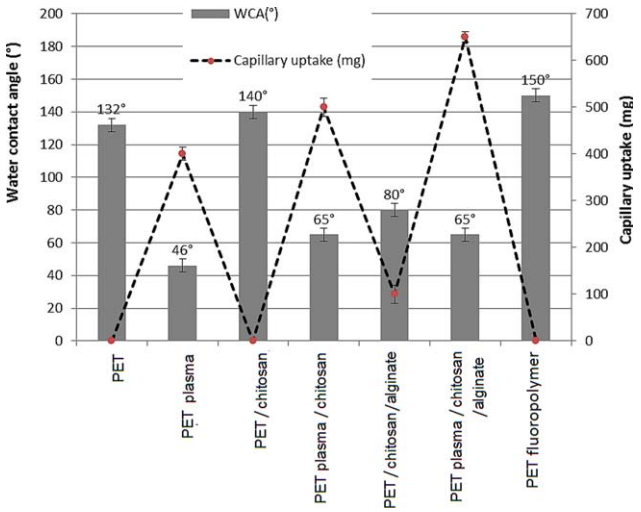

Figure 5. WCA and capillary uptake (mg) of various functionalized PET nonwoven membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

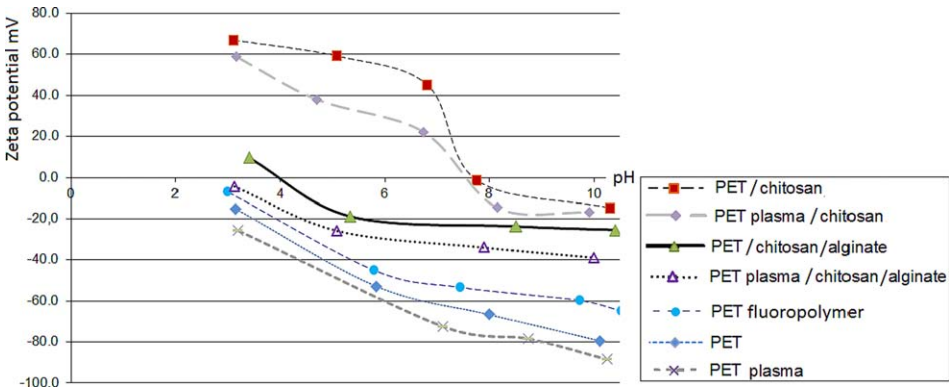

Figure 6. Zeta potential (mV) variations as a function of pH, for various functionalized PET nonwoven membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Without a prior plasma treatment, the PET/chitosan/alginate nonwoven is less hydrophilic (WCA =80°; capillary uptake = 100 mg) and approaches quasi nul charge (−20 mV) at pH 7. The PETplasma/chitosan/alginate nonwoven, which has a slightly more negative zeta potential (−30 mV) at pH 7, is very hydrophilic especially in terms of capillary uptake (WCA = 65°; capillary uptake = 600 mg).

There is a decrease (of 30%) in the functionalized nonwoven membrane air permeability (see Figure 7) after successive deposition of alginate on chitosan coated PET. This would suggest that more than a monolayer of hydrophilic alginate biopolymer should be deposited on the fiber surface, thus decreasing the pore size between fibers. However, the decrease in air permeability is similar for both the untreated or plasma treated PET after the chitosan/alginate deposition. Therefore, similar quantity of alginate should be deposited on the chitosan coated PET (with or without a prior plasma treatment). However, these data does not correlate with capillary uptake results: the PETplasma/chitosan/alginate seems more hydrophilic especially in terms of capillary uptake (650 mg), than the PET/chitosan/alginate nonwoven membrane (capillary uptake = 100 mg). This can be explained by the difference in alginate chain arrangement as well as the number of free carboxylic groups available at the extreme outer surface of these two functionalized nonwovens.

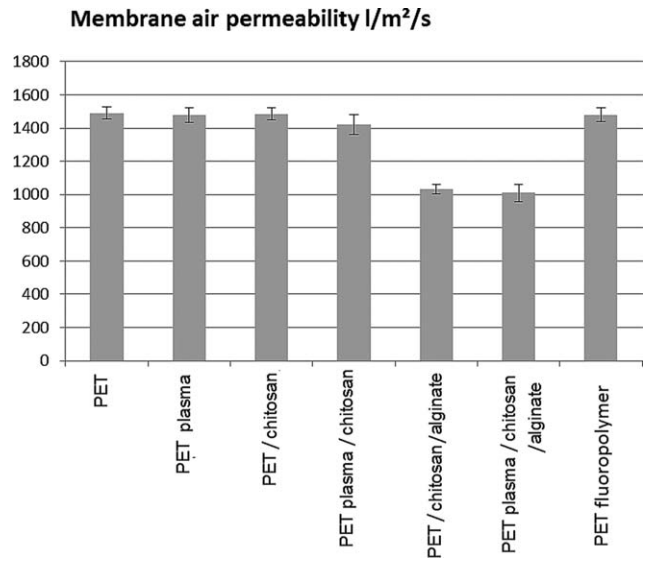

Figure 7. Air permeability (L/m²/s) of various functionalized PET nonwoven membranes.

Indeed when only chitosan is deposited on PET nonwoven, ionic (electrostatic) $-NH_3^+ \ldots {}^-OOC-$ interactions exist between the protonated amino group($-NH_3^+$) of the chitosan and the carboxylate groups ($-COO^-$ group) of the untreated or plasma treated PET, as it is confirmed by XPS measurements.[32] There is a however a smaller number of these ionic interactions for the untreated PET compared with the plasma treated PET, which has a higher number of $-COO^-$ groups, as confirmed by XPS measurements, too. Thus, the higher zeta potential value (+60 mV at pH 5) of the PET/chitosan membrane is indicative of a higher charge density of free protonated amino acids at the surface. The higher number of free protonated amino groups can interact with a higher number of carboxylate ($-COO^-$) groups of the alginate chains deposited at the final step. This would reduce the number of free $-COO^-$ groups of alginate chains at the top layer of the PET/chitosan/alginate, which can interact with water molecules, resulting in lower capillary uptake and reduced negative zeta potential (−20 mV at pH 7) as compared with the PETplasma/chitosan/alginate functionalized nonwoven (−30 mV at pH 7).

Nonwoven Membrane Functionalized with the Fluorinated Polymer. The fluorinated polymer showed very good adhesion to the PET nonwoven. Very thin coating of the fluoropolymer was deposited as confirmed by the air permeability of the functionalized nonwovens. Surface functionalization of the PET nonwoven lead to a very hydrophobic nonwoven membrane (WCA = 150°), a value, which approaches that of superhydrophobic behavior. At pH 7, the zeta potential value of this membrane was −50 mV, which is a bit less negative than that of untreated PET (−60 mV), see Figure 6. The value measured is however slightly more negative than that measured on solid PTFE surface (−30 mV at pH 7) by Lappan *et al.*[36]

Sorption of the Anionic Lipopeptide Biosurfactants on Functionalized Nonwovens

Figure 8 shows the % (Wt) of anionic biosurfactant which sorbed on 120 mg of functionalized nonwoven membranes at

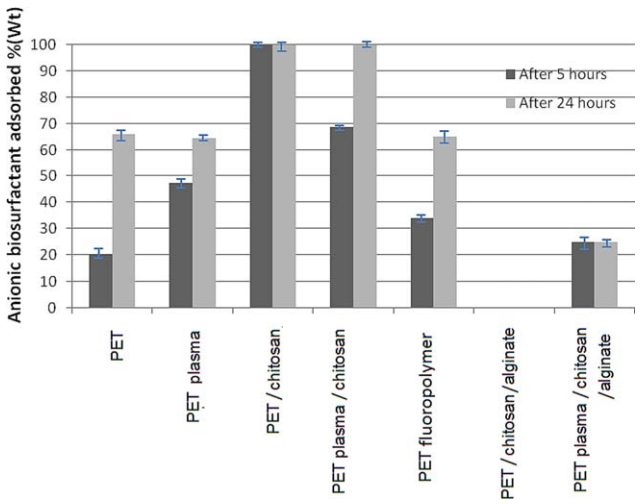

Figure 8. % (Wt) of anionic biosurfactant sorbed after 5 and 24 h at 30°C and at pH 7, on 120 mg of functionalized nonwoven membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

30°C, and at pH 7, after 5 and 24 h. With the highly positively charged PET/chitosan membrane, 100% of surfactin sorbed immediately (5 h). A prior plasma activation of the PET nonwovens before chitosan application, retards the sorption of all surfactin. Thus, 100% of surfactin is sorbed only after 24 h for the PET/plasma/chitosan membrane. Decreased zeta potential (+22 mV instead of +45 mV at pH 7) of the PET/plasma/chitosan membrane would explain the less rapid sorption of surfactin, as compared with the PET/chitosan nonwoven.[32]

For the untreated PET nonwoven, only 20% (Wt) of the total biosurfactants sorbed on the membrane, after 5 h, but after 24 h, the quantity of sorbed biosurfactant increased three folds (~65%). The anionic biosurfactant tends to sorb more rapidly on the plasma treated PET (after 5 h) than on the untreated PET. However, similar quantity of surfactin sorbed after 24 h on plasma treated and untreated PET membrane. On the nonwoven functionalized with antiadhesive fluorinated polymer, no reduction in biosurfactant sorption (after 24 h) could be perceived when compared with PET membrane without or with plasma treatment.

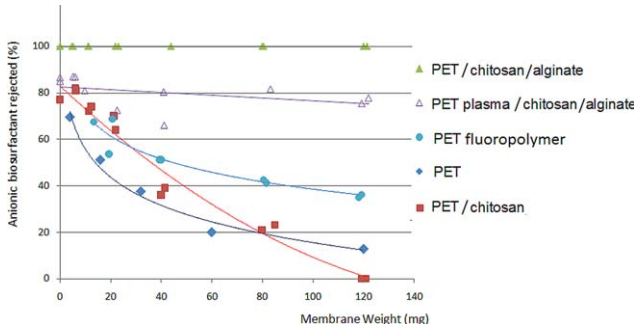

Figure 9. % (Wt) of anionic biosurfactant rejected after contact with varying mass of functionalized nonwoven membranes for 48 h, 30°C, at pH 7. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The quantity of the biosurfactants, which sorbed on the PET/chitosan/alginate membrane was null even after 24 h. Very small quantity, ~25% of the biosurfactant sorbed on the PET/plasma/chitosan/alginate membrane, and no further increase in biosurfactant sorption was measured after 24 h. Further experiments were carried out to investigate the effects of varying the functionalized PET membrane weight, on the anionic biosurfactant sorption. The residual amounts of the biosurfactant after sorption experiment during 48 h are shown in Figure 9. Whereas residual biosurfactant concentration decreases with the amount of nonwoven PET in contact, practically no lipopeptide sorbed on the PET/chitosan/alginate functionalized nonwoven whatever the weight of the nonwoven membrane used (from 5 to 120 mg).

For PET functionalized with anti-adhesive fluoropolymer, significant amount of the lipopeptide surfactin sorbed on it. Only very slight reduction in the biosurfactant sorption compared with nonwoven PET was measured. Strong physicochemical interaction between the biosurfactant hydrophobic tail and the hydrophobic fluoropolymer deposited at the PET surface, would take place.

DISCUSSION

The nonwoven PET functionalized with chitosan/alginate polymers yielded the highest resistance (100%) against fouling by the anionic lipopeptide biosurfactant. A pre-activation with plasma treatment followed by deposition of chitosan/alginate also reduces sorption of the anionic biosurfactant-80% of biosurfactant was rejected. The very hydrophilic and the most negatively charged plasma treated PET is not efficient at all in preventing the anionic lipopeptide sorption.

Indeed literature work shows that the nonfouling ability of superhydrophilic materials is correlated with a hydration layer near the surface,[37] because a tightly bound water layer forms a physical and energetic barrier to prevent protein adsorption on the surface. However, in addition to surface hydration, chain flexibility of hydrophilic polymers at a surface plays an important role in inducing steric repulsion of a protein molecule.[38] Indeed increased softness of a surface coating has shown to reduce protein sorption[39] whereas surface roughness scale also seems to influence protein adsorption.[40]

Therefore, the lack of hydrophilic flexible chains at the plasma treated PET surface would explain its inability in preventing the sorption of the anionic biosurfactant. It is also probable the hardness and nanoroughness of plasma treated fiber surface as shown by the AFM analysis in a previous work[41] should favor sorption of this biosurfactant.

Chain flexibility of the hydrophilic alginate chains may explain the efficiency of nonwovens functionalized with alginate (i.e., PETplasma/chitosan/alginate and PET/chitosan/alginate) in preventing the anionic lipopeptide sorption. However, the very hydrophilic plasma/chitosan/alginate coating is less efficient in preventing the biosurfactant sorption (only 80% rejected) while the less hydrophilic PET/chitosan/alginate nonwoven having the highest surface charge neutrality (−20 mV at pH 7), is the most efficient 100% of the anionic biosurfactant is rejected.

Indeed, while for the rhamnolipid (anionic glycolipid), a hydrophilic membrane was shown to be the most effective in prevention of surface sorption,[12] in our study we show that highest surface charge neutrality is a major surface parameter involved in sorption prevention of the anionic surfactin lipopeptide.

It is possible that the alternate positively (chitosan) and negatively charged(alginate) film would indeed create a material similar to zwitterionic materials where ions can bind water molecules even more strongly and stably via electrostatically induced hydration, as compared with hydrophilic materials which achieve surface hydration via hydrogen bonding. Strong ionic bonding between water and the chitosan/alginate (or the plasma/chitosan/alginate) coating surface would render the expulsion of water more difficult and would prevent the biosurfactant sorption. Electronic repulsion mechanism should not be the most important parameter in rejecting the anionic surfactant.

While chain flexibility and hydration layer may explain the efficiency of these two last nonwovens, some hypotheses may be made to explain why the PETplasma/chitosan/alginate nonwoven is a bit less efficient. Indeed in the plasma/chitosan/alginate coating, longer loops or free chains of alginate chains may be present at the utmost surface because very few —COO— groups of the alginate chains interact with the reduced number of free —NH_3+ groups present in the chitosan layer underneath (as explained in "Nonwoven membrane functionalized with sodium alginate"). As a consequence, hydrophilic alginate loops (at the extreme nonwoven surface) bearing free carboxylic groups can interact more easily with the hydrophilic part of the biosurfactant. This phenomenon would explain the reduced antifouling properties of the plasma/chitosan/alginate nonwoven membrane, but also its very hydrophilic behavior in terms of capillarity.

With the chitosan/alginate coating, the alginate loops or chains should be shorter with very few number of free —COO— available for interaction with the biosurfactant, since most of these groups interact with the higher number of free —NH_3^+ groups from the chitosan layer underneath. This phenomenon would also lead to a more neutral surface.

Our study also shows that the anionc lipopeptide biosurfactant does sorb on the superhydrophobic membrane. These results are contrary to the results of Stallard *et al.*,[31] either because this biosurfactant does not behave as proteins (Bovine Serum albumin or bovine fibrinogen) used in those studies, or because the fluorinated PET nonwoven is not superhydrophobic enough to prevent the biosurfactant sorption.

The main contributions to the superhydrophobic properties are the chemical nature of the fluorinated groups but also surface roughness scale. In the case of the nonwoven PET, surface microroughness is essentially due to the presence of microscale fibers (diameter 28 μm). This nonwoven does not bear any nanoscale roughness, which is more effective in conferring antifouling properties.[28,42]

CONCLUSIONS

Surface functionalization of PET nonwovens has been carried with and without plasma treatment using polymers or biopolymers yielding superhydrophobic to superhydrophilic properties, and variable zeta potential values, in order elucidate surface properties which reduce or suppress sorption of an anionic biosurfactant–surfactin on nonwoven fibrous PET membranes.

Both the very hydrophilic plasma treated nonwoven, and the superhydrophobic fluorinated polymer coated nonwoven are ineffective in preventing sorption of the amphiphilic negatively charged biosurfactant. Only the PET nonwoven modified with successive coating of chitosan and alginate and having surface charge closest to zero (−20 mV at pH = 7), is very effective in preventing the anionic biosurfactant sorption. This membrane is effective in preventing 100% of biosurfactant sorption both at an initial stage (5 h) and at a late stage (after 48 h).

Electrostatic repulsion is not enough to prevent fouling by the anionic biosurfactant. Steric repulsion seems to be the most important parameter controlling the anionic biosurfactant sorption. Further studies should be carried to test the membranes in real bioreactor working conditions, but the results are encouraging for future use in other bioprocesses.

Moreover, in this study an efficient padding method was used for functionalizing porous nonwovens with a complex cationic/anionic layer with little reduction in pore size. This can be a very rapid and cost effective method for surface modification of the fibrous nonwoven membrane for use as antifouling membrane.

ACKNOWLEDGMENTS

The authors acknowledge The Nord Pas De Calais Region for financing and the realization of this work in the frame work of ARCIR 4 project. They also thank Dr. Philippe Vroman for providing them with nonwoven membranes. They thank Mr. A. Louart, Mr. C. Catel and W. Sriwichai for their precious help.

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