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Multidentate polyzwitterion attachment to polydopamine modified ultrafiltration membranes for dairy processing: Characterization, performance and durability

Thomas G. Barclay[a,*,1], Hanaa M. Hegab[b,c], Andrew Michelmore[a,d], Michael Weeks[e], Milena Ginic-Markovic[a]

[a] Future Industries Institute, University of South Australia, Adelaide, South Australia 5095, Australia
[b] Natural & Built Environments Research Centre, University of South Australia, Adelaide, South Australia 5095, Australia
[c] Institute of Advanced Technology and New Materials, City of Scientific Research and Technological Applications, Borg El-Arab, Alexandria 21934, Egypt
[d] School of Engineering, University of South Australia, Mawson Lakes, South Australia 5095, Australia
[e] Dairy Innovation Australia Ltd., Werribee, Victoria 3030, Australia

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ABSTRACT

Filtration membrane technologies are used extensively in dairy processing and due to the high quantities of both organic and inorganic foulant, membrane fouling is a significant problem in the industry. To address this issue, a polyzwitterionic antifouling coating was applied to polyethersulfone ultrafiltration membranes for reduction of biofouling in skim milk filtration. The novel polyzwitterion was synthesised from a branched polyethyleneimine-based macroinitiator to allow multidentate binding to polydopamine coated membranes. Attachment of polyzwitterion to the polydopamine was confirmed using FTIR-ATR and XPS and the coating proved effective in increasing the wettability and smoothness of the membrane surface as well as reducing its charge. The reduced strength of binding between proteins and the membrane of the coated membrane compared to the control was demonstrated with its positive influence on fouling coefficient and recovery of the membranes while retaining skim milk flux and the rejection characteristics of the control membrane. The improved filtration characteristics of the coated membranes were generally retained through multiple cleaning cycles, though there was evidence of oxidative degradation after sanitation.

Introduction

Membrane filtration is employed extensively in the food industry, using as much as 30% of the current membrane production [1]. Much of this capacity is applied to dairy processing [1] that uses filtration variously to separate components such as fat, proteins, lactose and salts from milk and its intermediate products [2]. Due to the high levels of organic and/or inorganic foulant in each filtration step, membrane fouling is a significant issue in dairy processing [1,3,4]. For example, ultrafiltration is used to concentrate skim milk proteins for use in cheese making, for milk standardization and for spray dried powders as well as to separate out lactose [2,5–7]. The high protein concentrations in skim milk mean that a concentration polarization layer forms within seconds of commencing ultrafiltration processing [8,9]. Within that layer, the solubility limits of constituents are surpassed [10], and a loosely bound gel layer forms. Precipitation of proteins from that gel onto the membrane surface can be joined by components such as calcium phosphate and lactose to form a tightly bound fouling layer [8,11]. The significant fouling in skim milk ultrafiltration means processing can only run approximately 8 h [5] before clean-in-place (CIP) procedures are required. The CIP process comprises rinsing, which physically removes the loosely bound layer, followed by a series of alkaline, acid and oxidant cleaning cycles to remove organic, inorganic and microbiological

Abbreviations: CIP, clean-in-place; PEI, polyethyleneimine; PES, polyethersulfone; ZIC, zwitterionic compound; PEI-BiB, PEI-Bromoisobutyrl macroinitiator; PEI-pZIC, PEI terminated polyzwitterionic compound; ARGET ATRP, activators regenerated by electron transfer atom transfer radical polymerization; FTIR-ATR, Fourier transform infrared-attenuated total reflectance; VCF, volumetric concentration factor.

* Corresponding author.
E-mail address: tom.barclay@unisa.edu.au (T.G. Barclay).
[1] Current address: School of Pharmacy and Medical Sciences, University of South Australia, Adelaide, South Australia 5000, Australia.

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foulant respectively [3,5,9,12]. Consequently, any method to reduce fouling, extending the life of filtration membranes and reducing the costs of cleaning in terms of time and materials, will have enormous benefits to increasing efficiency in dairy processing.

Surface modification of bulk materials has been used extensively to reduce fouling. Despite the heavy use of membrane filtration in the dairy industry [1], research into antifouling coatings for membrane filtration is dominated by examples from water treatment [13,14]. Part of the reason for limited research on antifouling coatings for dairy is because of the high levels of foulant in dairy products means that concentration polarization often controls flux characteristics [1,8], and so improvements in reducing tightly bound fouling shows little or no immediate flux improvement. Nonetheless, despite CIP procedures, ultrafiltration flux is significantly reduced from the virgin membrane over months of commercial production (flux is halved in 10 months for ultrafiltration of whey) so mitigating fouling in dairy processing is important, if sometimes difficult to quantify in typical laboratory experiments [5].

Polydopamine based surface modification of bulk materials has exploded over the last 10 years [15], with significant use in membrane filtration [13]. While polydopamine-based modifications have reduced fouling and increased flux and rejection in waste water treatment for ultrafiltration membranes, the promising results in model systems could not be repeated in a system designed to mimic industrial conditions [16]. For this reason, we chose to evaluate the potential for use of polydopamine adhesive layers to attach zwitterionic compounds to ultrafiltration membranes [17–19] and evaluate filtration performance under conditions that mimic industrial dairy processing.

Experimental

Materials

Branched polyethyleneimine (PEI, average M_w ~800, M_n ~600), dichloromethane (anhydrous, 99.8%), 2-Bromoisobutyryl bromide (BiBBr, 98%), copper (II) bromide (99%), tris(2-pyridylmethyl)amine (TPMA, 98%), ascorbic acid (AR), dopamine hydrochloride, tris(hydroxymethyl)aminomethane (Tris, ACS), hydrochloric acid (ACS, 37%) cyclopentanone (99%) and polysulfone (average M_w ~35,000, M_n ~16,000) were all purchased from Sigma–Aldrich (Australia). Ecolab (Australia) membrane cleaning products (Ultrasil 67, Ultrasil 73, Ultrasil 75 Ultrasil 110 and Oxonia Active) were all obtained from the manufacturer. Chemsupply (Australia) was the source of methanol (AR) and Alpha Chemistry (China) supplied [3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl) ammonium hydroxide inner salt (3-SBMA, 98%). High purity nitrogen and medical grade oxygen were acquired from BOC (Australia) and pure water was obtained from a Barnstead NANOpure Diamond water purification system operating at a resistance of at least 18.0 MΩ/cm. Filtration membranes purchased from Nanostone water (USA) were Sepro polyethersulfone flat sheet ultrafiltration membranes with dextrin molecular weight cut-offs of 5 kDa, 10 kDa and 20 kDa (PES 5, PES 10 and PES 20 respectively) and dialysis was conducted using Pur-A-Lyzer Mega 1000 (MWCO 1 kDa) kits.

Synthesis

PEI-BiB initiator [20,21]

Polyethyleneimine (PEI, 1.85 g) was dissolved in dichloromethane (100 mL) under an atmosphere of nitrogen and then cooled in an ice bath. 2-Bromoisobutyryl bromide (BiB, 0.5 mL, 0.919 g, 4.0 mmol) dissolved in dichloromethane (50 mL) was added dropwise to the polyethyleneimine solution over 30 min at 0 °C. After the addition, the reaction temperature was increased to ~22 °C and left stirring for 24 h, resulting in the formation of a viscous precipitate. The reaction mixture was poured off the precipitate and the solvent was removed under vacuum (750 mBar at 50 °C). The product was then dissolved in methanol, which was removed under vacuum (280 mBar at 50 °C) twice to remove all traces of dichloromethane. Care was taken not to completely remove all the methanol as the product then becomes insoluble in the subsequent ARGET ATRP reaction mixture. The final yield was ~70%.

ARGET ATRP of PEI-pZIC [22]

[3-(Methacryloylamino)propyl]dimethyl(3-sulfopropyl) ammonium hydroxide inner salt (3.52 g, 12 mmol), copper(II) bromide (15.2 mg, 0.068 mmol) and tris(2-pyridylmethyl)amine (80 mg, 0.276 mmol) were dissolved in water (9.6 mL) and PEI-BiB (400 mg, ~1.36 mmol BiB) was dissolved in methanol (4.16 mL). The two solutions were added together and purged under nitrogen for 1 h. The mixture was stirred under inert conditions at 35 °C and an ascorbic acid solution (18.4 mg, 0.104 mmol in 2.8 mL water and 1.2 mL methanol) was slowly added over 5 h (2 mL) and then the rest (2 mL) added and the reaction was left to stir overnight. The product was purified using dialysis (MWCO 1 kDa) resulting in ~40% yield.

Coating procedures

Membrane coating

A custom membrane coating apparatus was made from acrylic sheet (180 mm × 120 mm internal area) to seal against the active side of the membrane with an expanded neoprene gasket. The membrane, gasket and coating apparatus were clamped onto a Ratek platform mixer using springs as shown in Fig. 1, creating a container to hold the coating mixture against the membrane surface. Prior to coating, the membranes (PES 10 or PES 20) were cut to size using the custom coating apparatus as a template and then soaked in isopropanol for 1 h, with the solvent exchanged at 30 min. The membranes were then rinsed thoroughly in deionised water before being coated.

The general coating procedure was as follows. In preparation for coating Tris(hydroxymethyl)aminomethane (3.634 g, 30 mmol) was dissolved in deionised water (2 L) and then acidified with hydrochloric acid (conc, ~1 mL) to make a buffer (15 mM, pH 8.5). If oxygenated coating was conducted, oxygen was bubbled into the buffer through a porous frit (2 LPM) for at least 1 h prior to coating. For these experiments oxygenation (2 LPM) continued in the custom-built apparatus during the coating reaction.

Membranes were installed into the custom coating apparatus and dopamine (1 g) was added to the tris(hydroxymethyl) aminomethane buffer solution (500 mL). This mixture was rapidly stirred and added to the coating apparatus as soon as the dopamine was dissolved. The coating reaction proceeded for 10 min–24 h with rocking at 4 rpm before the membranes were thoroughly rinsed in deionised water. Then the adlayer ingredient (PEI-pZIC [1–5 mg/mL]) was dissolved into Tris(hydroxymethyl) aminomethane buffer (~250 mL) and the pH adjusted back to pH 8.5 with hydrochloric acid before the solution was added to the membrane which was taped flat into a plastic container and rocked for at least 24 h. After this, the membranes were thoroughly rinsed in deionised water, cut to size for stirred cell or crossflow testing and stored in Ultrasil 73 solution (1.5% v/v) before samples were analyzed.

Silicon wafer coating

Polysulfone (3% w/v) was dissolved in cyclopentanone using sonication and filtered using a 0.2 μm filter. Silicon wafer coupons

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