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Heterogeneous ion exchange membranes with silver based additive

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Heterogeneous anion-exchange and cation-exchange membranes with the addition of antimicrobial additive Sanitized BC A 21-41 (silver in the glass matrix), reinforced with polyester fabric (AM-PES Sanitized or CM-PES Sanitized) were prepared on the pilot lamination line in our company. Basic physical and electrochemical properties of membranes, antimicrobial activity after long-term desalination in the electrodialysis unit were characterized. The release of silver from antimicrobial additive into the solutions was also determined when using atomic emission spectroscopy. Prepared membranes modified with antimicrobial additive have shown the improved antimicrobial properties over commercial membranes Ralex® in terms of the print on agar plates and the determination of inhibition zones for Escherichia coli and Staphylococcus aureus. Sanitized additive was not washed out from the membranes even after long-term electrodialysis tests. In addition, the prepared membranes have exhibited lower areal resistance due to the reduced thickness in the dry and swollen state, thus contributing to the reduction of energy needed for electrodialysis.

Keywords: Ion-exchange membrane; Antimicrobial activity; Plastic additives

Introduction

Plastic additives are a common part of plastic practice. They are represented by a wide spectrum of substances, such as antioxidants, stabilizers, pigments, lubricants, fillers, antistatic agents, plasticizers, blowing agents, flame retardants, antimicrobial additives, UV stabilizers, brighteners, etc. In principle, there are three basic criteria for using the additives [1] being necessary for the production/processing of plastics,

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improvement of the properties of the final product(s) or for compensating the problems caused by another additive. Antimicrobial additives to polymers provide a desirable resistance to biodegradation, the protection against staining, and degradation caused by fungi, algae, and other microorganisms. These microorganisms can reduce the overall life of the polymer or change its mechanical or electrical properties. Antimicrobial additives have a relatively high efficacy when used at low concentrations without side effects on physical properties or light resistance [2–4]. When antimicrobial additives are used in a matrix of heterogeneous ion exchange membranes (IM), such separation systems can then be applied in food applications; e.g., for dairy (whey, with pH adjustment), water treatment (various wastewater) or, in general, where there is a risk of microbial degradation of an organic material given or in some special applications (separation and treatment of sugar solutions, mucosa hydrolysates).

Most antimicrobial additives are suitable for the use in humid environments, medical devices, when may come into contact with food. The only problem is being their washing out from the polymer matrix of IM during test electrodialysis (ED) due to a migration towards the surface. In the best case, a protective film will be formed on the surface.

Previous work has dealt with the use of antimicrobial additives more extensively [5–6]. The influence of two additives (Sanitized BC A 21–41 and Sanafor PO 5) on properties of IM was studied. From these initial tests, Sanitized BC A 21–41 additive was selected as more suitable with respect to its higher antimicrobial activity, better IM properties, and a resistance during ED test. The IM production in larger scale has been realized on the continuous lamination line, when the testing took place in the ED pilot unit.

Sanitized BC A 21–41 contains the encapsulated silver as an active ingredient in a glass ceramic matrix. The active ingredient content is 1.6–1.8 wt. %, the recommended dosage by the manufacturer to the matrix then 0.2–0.6 wt. %; the additive being applicable up to 500 °C. The additive is supplied in the powdered form, allowing one easy dispensing into the mixture with the milled ion-exchange resin.

As a part of the work, heterogeneous anion-exchange and cation-exchange membranes (AM and CM, respectively) with the addition of Sanitized BC A 21–41, reinforced with polyester fabric (AM-PES Sanitized or CM-PES Sanitized) were prepared on the lamination line in MemBrain; see affiliation. Basic electrochemical properties and antimicrobial activity of IM were characterized after long-term desalination in the ED pilot unit. Solutions from the ED tests were analyzed by atomic emission spectroscopy.

Materials and methods

Heterogeneous CM-PES Sanitized and AM-PES Sanitized were prepared from a strong acidic cation-exchange resin (Purolite, Ústí nad Labem, Czech Republic) and a strong basic anion-exchange resin (Purolite), respectively, and from a low-density polyethylene (LDPE 605BA, manufactured by ExxonMobile Chemical, Prague, Czech Republic) acting as a matrix. The membranes were reinforced with polyester reinforcing fabric (Silk & Progress, Moravská Chrastová, Czech Republic), which provided sufficient mechanical resistance. The resin was washed, dried and milled to the desired particle size distribution. Subsequently, it was homogenized with the polymer matrix. The additive Sanitized BC A 21-41 (manufactured by Sanitized AG, HSH Chemie – a supplier for Czech Republic, Burgdorf, Switzerland) was added to the IM mixture during the homogenization of the ion-exchanger with matrix. The dosage of additive was 0.15 wt. % at the expense of polyethylene, the additive was metered into the pre-milled ion-exchange resin. The prepared granulate was then extruded into a flat membrane and laminated with reinforcing fabric on a three-cylinder arrangement. A detailed description of IM preparation is given elsewhere [7–9].

Electrochemical characteristics of IM (areal and specific resistance, R_a and R_s, respectively, and permselectivity, P), their physicochemical properties (thickness of dry IM, th_d, dimensional changes after swelling in demineralized water, Δth, Δw and Δl; relative water content, Δm), and ion-exchange capacity (IEC) were also tested in the electrodialysis cell (ED), where they had undergone a long-term testing. During such tests, the concentration of silver (as Ag^+) in the solutions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The surfaces of IM were characterized by imaging with scanning electron microscopy (SEM). Microbial activity, studied at the Technical University of Liberec, was measured using IM prints on agar plate (impression: 1 hour, print cultivation: 48 hours at 22 °C and evaluation of colony counting KTJ), followed by the determination of inhibition zones for *Escherichia coli* and *Staphylococcus aureus* (AATCC Method 147 for 4 lines of different concentrations of bacteria, 48-hours cultivation with IM at 37 °C and evaluation of inhibition zones). The exact measurement conditions for the individual IM parameters are available in literature [5–9].

To compare the results, samples of standard Ralex® IM-PES (a product by MEGA Co., Stráž pod Ralskem, Czech Republic), with the IM parameters given by manufacturer's datasheet [10], were also included and analyzed.

Results and discussion

The prepared IMs, broken in liquid nitrogen, were characterized by SEM with backscattered electrons to achieve the desirable material contrast; see Fig. 1. There are well distinguished dark gray regions of polyethylene and lighter gray ones belonging to the finely milled ion-exchange resin. The scans show the pores that result from swelling of IM in demineralized water (black areas). The light objects inhomogeneously distributed in the matrix are the particles of the Sanitized additive. Their unconsolidated distribution might be caused by the low additive concentration or insufficient homogenization in the polymer matrix. SEM images have been taken from a small sample area whereas, in real applications, tens of m^2 of IM are used and the effect of the additive is more complex. Local inhomogeneous distribution can only play a role in the characterization of IMs.

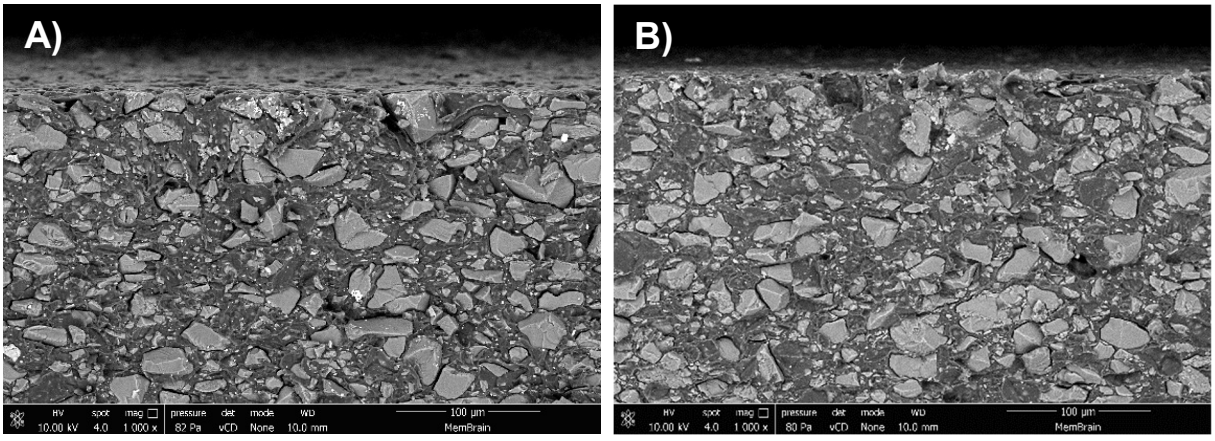

Fig. 1 SEM scans of A) AM-PES Sanitized and B) CM-PES Sanitized

Next, physical properties of IMs after swelling in demineralized water were tested (Table 1). The reinforcing fabric influences the swelling of IM. IM-PES Sanitized have contained the same reinforcing fabric as the commercially manufactured IM-PES Ralex®, and for this reason, IM-PES Sanitized changes are comparable to that of IM-PES Ralex®.

The only exception was the thickness of dry IM-PES Sanitized. This material was made with a lower thickness to reduce the IM areal resistances involved in the energy consumption of the entire ED technology. Thickness is one of the parameters by which the IM areal resistance can be reduced and the required energy savings thus achieved. This has also been confirmed and IM-PES Sanitized exhibited lower areal resistances (Table 2) than those of the commercial IM-PES Ralex® limit. The observed decrease could also be due to the additive, which contains metal in its structure. Another option is to increase the number of pores in the structure, which negatively affects the permselectivity. From the

table, it is also seen that the permselectivity of IM-PES Sanitized is at the limit of commercial IM-PES Ralex®. Ion-exchange capacity (IEC) should not be affected by the additive because this substance has been added to the IM at the expense of the polymer matrix. The assumption has been confirmed and the IEC values for IM-PES Sanitized are comparable to those for IM-PES Ralex®.

Table 1 Physical properties of IM-PES Sanitized compared to Ralex® IM-PES

IM-PES	th_d [mm]	Δth [%]	Δl [%]	Δw [%]	Δm [%]
AM-PES Sanitized	0.33 ± 0.03	48 ± 4	1.3 ± 0.5	3.3 ± 1.1	50 ± 3
Ralex® AM-PES	<0.45	<60	<3.0	<4.0	<65
CM-PES Sanitized	0.35 ± 0.04	62 ± 2	1.5 ± 0.1	2.8 ± 0.5	60 ± 1
Ralex® CM-PES	<0.45	<65	<3.0	<4.0	<65

Table 2 Electrochemical properties of IEC IM-PES Sanitized compared to Ralex® IM-PES

IM-PES	IEC [meq g^{-1}]	R_A [Ω cm^2]	R_S [Ω cm]	P [%]
AM-PES Sanitized	1.8 ± 0.1	6.3 ± 1.4	125 ± 21	90.8 ± 0.6
Ralex® AM-PES	>1.8	<7.5	<120	>90.0
CM-PES Sanitized	2.4 ± 0.1	5.7 ± 0.3	100 ± 6	89.7 ± 0.9
Ralex® CM-PES	>2.0	<8.0	<120	>90.0

The results of prints on the agar plate and on inhibition zones are shown in Table 3 and Fig. 2 for AM-PES Sanitized; prints being similar to CM-PES Sanitized. Any inhibition zones were observed for IM-PES Sanitized samples. The increase in bacterial colonies around the IM was observed, but there was no undergrowth of bacterial colonies under the IM indicating the antimicrobial properties of IM. If the zones of inhibition were measured, the result could be interpreted as a diffusion of the additive from the IM. It is evident from the IM prints on the agar plate that there has been the significant improvement in the antimicrobial properties of IM-PES Sanitized compared to the commercial IM-PES Ralex®, in which the colonies (on the agar plate) were unreadable, i.e. over 300 growth colony forming unit (KTJ). The only exception was AM-PES Sanitized from centre of ED, which also had a high KTJ value. This could be due to inhomogeneous distribution of the additive in the sample, as stated when discussing the SEM scans. Another possibility is to wash the additive from the IM into the solutions.

Table 3 IM prints on agar plate and inhibition zones for *E. coli* and *S. aureus*

IM-PES	IM print [KTJ]	Zone of *E. coli* [mm]	Zone of *S. aureus* [mm]
AM-PES Sanitized pristine	9	0	0
AM-PES Sanitized from centre of ED	>300	0	0
AM-PES Sanitized next to electrode	56	0	0
Ralex® AM-PES	>300	0	0
CM-PES Sanitized pristine	3	0	0
CM-PES Sanitized from centre of ED	39	0	0
CM-PES Sanitized next to electrode	27	0	0
Ralex® CM-PES	>300	0	0

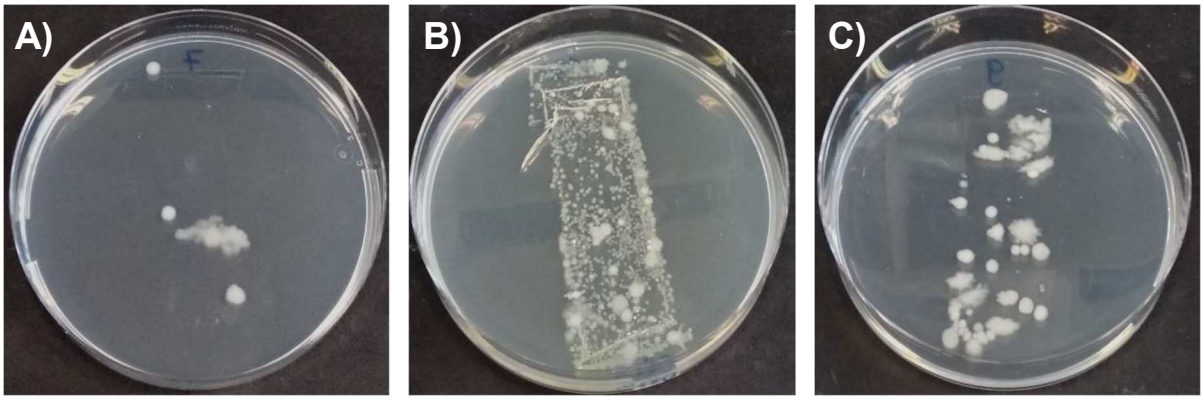

Fig. 2 AM-PES Sanitized prints on agar plate for A) pristine IM; B) IM from centre of ED and C) IM next to electrode

The concentrations of Ag determined in the ED solutions are surveyed in Table 4. After initial swelling of IM-PES Sanitized in demineralized water, the concentration of Ag was determined, followed by 1st batch test, after long-term continuous test and 2nd batch test. It can be seen from the respective values that the determined content of Ag moved around the limit of determination for the ICP-OES technique. These results clearly document that, in the tests, there is no measurable washout of the IM-PES Sanitized matrix. The remaining question is the long-term effectiveness in real food medium operation. Therefore, further tests will be directed to this area. The disadvantages include, of course, an increase of the IM-PES production expenses.

Table 4 Determination of Ag in tested solutions using ICP-OES

Solution / specification	Concentration of Ag [mg L^{-1}]
Solution from swelling of IEM Sanitized	<0.020
Mixed solution after 1st batch test	<0.019
Mixed solution after continuous test	<0.020
Mixed solution after 2nd batch test	<0.020

Conclusions

The prepared IM-PES Sanitized modified with antimicrobial additive has exhibited the improved antimicrobial properties over IM-PES Ralex® when tested on an agar plate and inhibition zones. Furthermore, it is necessary to test IM in real conditions of long-term operation and to define their benefits not only in terms of antimicrobial activity, but also because of reduced areal resistance.

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