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The effect of initial moisture content of cation-exchange resin on the preparation and properties of heterogeneous cation-exchange membranes

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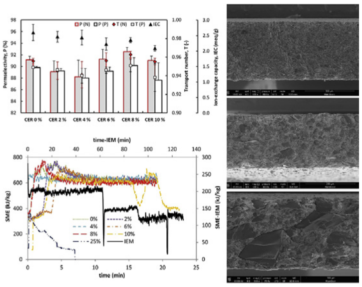
HIGHLIGHTS

- CEMs were prepared of resin varying in moisture content.
- The moisture's effect on resin grinding and CEM blending/extrusion are discussed.
- The influence of moisture on electrochemical and mechanical properties is studied.
- CEM resistance increases when increasing initial resin moisture content.
- IEC decreases while permselectivity varies with resin moisture content.

GRAPHICAL ABSTRACT



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ABSTRACT

This work deals with the influence of moisture content of cation-exchange resin (CER) on the properties of prepared cation-exchange membranes (CEMs). CER was dried and moistened to 2, 4, 6, 8, 10 and 25% and then milled using a vibratory mill. The CER was then mixed with low density polyethylene and extruded to prepare CEMs. Some of the samples were further hot-pressed. The CEMs were then characterized in terms of their mechanical and electrochemical properties, including specific and areal resistance, ion-exchange capacity (IEC), permselectivity and transport number. The results showed that resistance increases with increasing moisture content. IEC decreases with increasing moisture while permselectivity strongly varies with moisture content.

1. Introduction

Ion-exchange membranes (IEMs) are essential in electro-separation processes such as electrodialysis (ED) [1–3], electro-deionization [2,4,5], membrane electrolysis [6,7], and in power storage and generation (fuel cells and redox flow batteries) [8–10]. Recently, reverse ED has also become of greater interest [11–15]. IEMs are basically divided into, either cation and anion exchange membranes according to the ions they transfer/retain, or homogeneous and heterogeneous according to the IEM's composition [3]. Homogeneous IEMs are mostly comprised of a foil made of pure

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ion-exchange resin (IER) material, and therefore have supreme electrochemical properties but mostly poor mechanical properties. Conversely, a heterogeneous IEM is a functional composite made of a finely milled IER, a polymeric binder and a reinforcing fabric [1,3,16]. Together, these components ensure the required electrochemical properties (though lower than homogeneous IEMs) and also necessary mechanical properties for the aforementioned processes. The IER has the most influence on electrochemical/transport properties of an IEM, i.e. ion-exchange capacity (IEC), electrical conductivity and permselectivity. Moreover, these properties determine the other characteristics of the electro separation process, including separation efficiency and energy consumption, hence the cost of the overall process and applicability for larger industrial scales.

Many IERs are based on a copolymer of styrene and divinylbenzene, with bonded ion-exchange groups usually in the form of spherical beads or ground particles, which ensure the exchange of a selected ionic species [17]. To ensure an adequate surface area and blending with the polymer matrix without detrimental structural defects, IER is most often ground to particle sizes ranging from 1 to 50 μm [18]. Therefore, the particle-size distribution of IER is very important. The particle-size distribution is mainly influenced by the type of milling equipment, milling time and properties of the material to be milled (IER), the latter of which is related to the material moisture content. A higher IER moisture content or direct contact with water not only causes IER particles to swell, but also reduces their grindability, bulk properties and thus the complete preparation of IEMs. Moreover, moisture content affects the transport properties of the IEMs [19–21] and influences the morphology of ion-exchange polymers [22].

In practice, many manufacturers supply IERs in a fully swollen state, containing about 45–60% of water depending on type. This water must be removed before use for IEM preparation, which is done using a fluidized bed dryer to a theoretical value of 0%, even though there is always some moisture remaining. The IER moisture must be lower than 4% to be used in IEM production. Several studies have analysed the influence of IEM water content/transport either on a purely theoretical [23–25] or practical level by considering the IEM structure itself [26–28] or IEM-involved processes such as electrodialysis [29–31]. These works studied the influence of the overall water uptake of prepared IEMs and/or the influence of different humidity levels on transport properties. However, the influence of initial moisture of an IER on IEM preparation itself and its properties has not yet been studied. Therefore, this work aimed to determine the influence of IER (cation-exchange resin – CER) moisture on milling, CER/polymer matrix blending, extrusion and IEM hot pressing in relation to their final transport and mechanical properties. Transport properties were evaluated in terms of electrical resistance, IEC and permselectivity (transport number). These parameters were further compared between IEMs prepared by extrusion with subsequent hot pressing as well as non-pressed IEMs.

2. Experimental

2.1. Preparation of IER varying in moisture content

CER from Suqing (Jiangsu Suqing Water Treatment Engineering Group Co. Ltd., China) in bead form was used (Table 1). It has an optimal ion-exchange capacity/swelling capacity ratio. The CER is based on cross-linked polystyrene-co-divinylbenzene (PS-DVB) with sulfonic (CER) ion-exchange groups and is often used for production of heterogeneous IEMs. The CER was first washed and then dried at 130 °C using a fluidized-bed dryer to a minimum moisture content of about 0.5%. This value was considered referential, i.e. 0% of moisture. The CER was modified to 2%, 4%, 6%, 8%, 10% and 25% moisture content as follows. Water content φ of the IER was calculated as follows:

Table 1
Properties of CER used.

Type	Suqing 001x7Na, gel, strong acid
IEC[a] (meq g^{-1})	4.50
IEC[b] (meq g^{-1})	5.33
Swelling capacity[b] (cm^3 g^{-1})	2.52
Water content[a] (%)	45–50
Water content[b] (%)	49.9

[a] Product data sheet [32].
[b] Measured.

$$\varphi = \frac{m_w - m_d}{m_d} 100 \qquad (1)$$

where m_w and m_d are weights of wet and dry IER, respectively. The modified CER was milled using a Vibrom 42S vibrational mill filled with steel cylinders with dimensions of 12 × 12 mm and a weight of 170 kg. The CER was milled for 15 min at a vibrations frequency of 50 Hz and discharged for 20 + 2 min at 35 + 25 Hz. The particle-size distribution of the milled resin was measured using a Malvern Mastersizer 2000 laser diffraction analyzer.

2.2. Membrane preparation

The milled CER samples with varying moisture content were blended with low density polyethylene (LDPE) in a mixer at 140 °C to prepare pellets. The amount of CER was 62% per weight of LDPE. The pellets were extruded to prepare membranes. Some membranes were further hot-pressed at 135 °C for 5 min at 25 bars and cooled down to 60 °C to compare against the properties of non-pressed membranes. Both homogenization and extrusion were performed in a HAAKE PolyLab OS Rheo Drive 16 machine (ThermoScientific). A PTW 24/28 twin screw (diameter and length/diameter ratio were 24 and 28, respectively) was used for homogenization and a Rheomex 19/25 single screw for extrusion, both with a compression ratio of 2:1. The materials to be blended were dosed to the mixer using Congrav® OP1T CB Plus feeders (Brabender Technologie GmbH & Co. KG) with a twin screw and a single screw for CER and LDPE, respectively, with a frequency of 60 rpm. The parameters of extrusion were recorded in software, including the revolution speed, torque, pressure on the extrusion head, and pressure in front of the extrusion head. The extruder response was expressed using the specific mechanical energy calculated as follows [33–35]:

$$SME(\mathrm{kJ/kg}) = \frac{2\pi \cdot n \cdot T}{MFR} \qquad (2)$$

where n is the screw revolution speed (min^{-1}), T is the screw (motor) torque (N·m) and MFR is the mass flow rate (g/min) given by the dosing speed of CER and LDPE, which is 43.86 g/min. SME reflects the work input from the motor into the material during the blending/extrusion i.e. the shearing energy exerted to the composite [35].

2.3. Membrane characterization

2.3.1. Ion-exchange capacity (IEC)

IEC is the number of equivalents of bound dissociated groups in IEM related to the weight of dry matter [36]. The method to determine IEC is described elsewhere [37]. Briefly, the sample