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Compaction and its effect on retention of ultrafiltration membranes at different temperatures

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ABSTRACT

Compaction of a polymeric membrane results in a denser membrane structure with increased hydrodynamic resistance, which may positively affect the retention factor. This raises the question of whether membrane compaction could be a cheap and simple way to enhance membrane performance. In this study, compaction and retention data of four different commercial polyethersulphone and regenerated cellulose membranes were examined to gain insight into how membrane retentions could be improved with compaction at different temperatures. Although there was enormous variation in both the reversible and irreversible compaction of the membranes tested, retention in all membranes clearly increased after compression under 7 bar and 50 or 70 °C conditions. For instance, polyethylene glycol (PEG) (8 kg/mol) retention of a 30 kg/mol membrane increased even by 22 percentage points, up to 97%. This study demonstrates that it is possible to easily modify retention values of commercially available membranes, thereby increasing their usability in different applications.

1. Introduction

Application of pressure is known to cause compaction in polymeric membranes, which decreases the membrane permeability. Compaction affects the membrane porosity, average pore size, tortuosity and thickness [1]. In the compaction of an asymmetric membrane, the thickness of the backing layer, support layer and skin layer decreases according to the structural and material strength of each [1,2]. The skin layer of the membrane resists permeation the most [3]. The resulting denser skin layer increases membrane hydrodynamic resistance and may also affect retention [4–6]. The increased hydrodynamic resistance does raise the operation costs of the membrane process; however, compaction may be beneficial if it results in lower molecular weight cut-off membranes and does not decrease the filtration capacity too greatly. Thus, controlled compaction could be an attractive option to modify selectivity of commercially available membranes at mill sites.

The membrane compaction phenomena have been studied with offline and online methods. The offline methods are based on static mechanical compression and the online methods in real-time monitoring of the hydrodynamic compression process. In static compression the pressure is divided evenly through the membrane but in the hydrodynamic compression pressure gradually increases through the membrane and the bottom of the membrane is affected by the highest pressure. According to Persson et al. [7] at corresponding pressures, the mechanical treatment decreased the flux much more than the hydrostatic treatment.

In several studies the compaction of a membrane is estimated based on the changes in pure water fluxes [5,6,8]. The pure water flux can be measured offline before and after the compression or online simultaneously as pressure is increased. For instance, Hussain et al. [5,6] analysed and modelled the compaction behaviour of commercial thin film composite nanofiltration membranes. They proposed that the active layer of the membrane has two different compaction patterns: instantaneous and gradual. The drawback in the compaction evaluation based on the difference in pure water fluxes is that the pure water flux measurement is an indirect method. It will not separate the compaction from fouling or other changes in membrane structure or skin layer, for example swelling.

Ultrasonic time-domain reflectometry (UTDR) has been used to measure membrane compaction online [9]. Aerts et al. [10] measured mechanical compression of the Zirfon® organo-mineral membranes structure simultaneously with water permeability during ultrafiltration. The UTDR enabled to measure the effect of filler concentration on elastic and viscoelastic properties of the membranes. Higher filler concentration reduced the elastic

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deformation while time-dependent viscoelastic deformation increased. As most UTDR studies, this was also performed in a constant temperature as sonic velocity used to determine the distance to the membrane changes with temperature. This technical difficulty was overcome later by Stade et al. [4] when they presented the reference transducer for UTDR studies which can measure the sonic velocity in real-time.

Most membrane compaction studies have been made in a constant temperature with mechanical off-line methods or by assuming the permeability changes at an increased pressure to be caused by compaction. There are also studies and models which describe mechanical behaviour of polymers in different conditions [11,12]. However, the results achieved in those studies were gathered mostly with a single homogeneous polymeric film. Thereby they do not justify the deep understanding of the compaction phenomena of an asymmetric porous membrane which consists of multiple different polymeric layers and chemical additives.

It is also known that the membrane compaction occurs easier at elevated temperatures due to changes in the viscoelastic properties of the polymeric layers. Mehdizadeh et al. [3] studied temperature effects on the performance of polyamide reverse osmosis (RO) membranes. From the pure water flux results they expected that the compaction was apparent at all temperatures and it increased with temperature (5–60 °C) and pressure (350–7000 kPa). However, they did not measure the compaction but it was an assumption based on the pure water flux data.

The temperature effect on the membrane performance from the compaction point of view has not yet been studied thoroughly. Furthermore, the controlled compaction at an elevated temperature has not been used to modify the retention properties of a hydrophilic UF membrane. Therefore, the aim of this study was (1) to investigate how increased temperature influences reversible and irreversible compaction of polyethersulphone (PES) and regenerated cellulose (RC) UF membranes. The compaction is monitored online with the UTDR method. Moreover, the goal was (2) to discover how compaction affects membrane performance in terms of retention, and (3) to confirm whether or not it is possible to modify membranes with compaction. The overall goal was to modify the cut-off value of a hydrophilic 30 kDa UF membrane to lower than 10 kDa. This kind of a membrane could be used e.g. in wood-based biorefineries to fractionate wood polymers. As Koivula et al. [13] and Kallioinen et al. [14] showed the permeate flux of a hydrophilic cellulose membrane was superior compared to a more hydrophobic polysulphone membrane in the filtration of wood hydrolysates. Unfortunately very hydrophilic membranes having cut-off values about several thousands are not commercially available to be used in high-shear-rate modules. Therefore, the controlled compaction of high cut-off UF membranes presented in this study could open new possibilities for membrane based fractionation processes in future biorefineries.

2. Experimental

2.1. Ultrafiltration membranes, filtration modules and the UTDR measurement system

The following four commercial membranes were used in this study: regenerated cellulose (RC) membrane UC030, polyethersulphone (PES) membrane UP020, hydrophilic PES membrane UH030, and RC membrane C30V. The first three were manufactured by Microdyn-Nadir, and the fourth by JSC STC Vladipor. The membrane properties are presented in Table 1.

The molecular weight cut-off (MWCO) value of the C30V RC membrane manufactured by Vladipor was reported by Kallioinen [15] to be in the same range as the UC030 RC membrane manufactured by Microdyn-Nadir (the UC030 membrane was referred to in the study as "C30FM" and the C30V one as "C2"). MWCO values of the C30V membrane and the UC030 membrane were reported to be 15 kg/mol and 10 kg/mol, respectively (PEG concentration was 150–180 mg/L, at 0.25 bar, at 40 °C; cross-flow velocity was 0.85 m/s; UC030 permeate flux was $1.25 \cdot 10^{-5}$ m/s; and C30V permeate flux was $1.00 \cdot 10^{-5}$ m/s).

The UTDR ultrafiltration cross-flow membrane module used in this study for compaction experiments consisted of two 10 MHz ultrasound transducers mounted inside the module. The measurement system accuracy has been determined to be micrometer-level [16]. The filtration channel size was 0.31 m long, 0.018 m high and 0.018 m wide. More specific details of the UTDR theory, membrane module, equipment, filtration system and benefits of mounting transducers inside the module have been recounted by Stade et al. [4,16].

The retention measurements were performed with a 3-cell filter, which is another type of cross-flow filtration equipment. It has three parallel membrane cells which can be used simultaneously in the same filtration conditions. The membrane filtration area of one cell was 0.0045 m^2, and the filtration channel dimensions were 0.23 m long, 0.02 m wide and 0.001 m high.

2.2. Experimental methods

In this study, the non-invasive UTDR measurement system was used to monitor how temperature and pressure affect membrane compaction and a cross-flow type of membrane filter having three flat sheet cells in parallel was used to indicate how exposure to high temperature and pressure affect the membrane retention values. After the compaction experiments were conducted, Scanning Electron Microscopy (SEM) was used to study the structural changes in the membranes. The Shimadzu Total Organic Carbon (TOC) 5050A Analyser was used to analyse the organic content of the samples (i.e. the Polyethylene Glycol (PEG) concentration from the retention experiments) to subsequently calculate membrane retention and to ascertain possible changes in the membranes. Our experimental procedure is presented in Fig. 1.

All the experiments started with the pre-treatment of the membranes. The membrane samples were immersed in alkaline solution (pH ≈ 12) for 20 min and rinsed with RO treated water to wet the membranes and to remove the preservatives from them. After the pre-treatment the membranes were stored in RO treated water. Both the compaction and the retention experiments were repeated three times.

Compaction experiments with UTDR were performed with RO purified water, and a new pre-treated membrane was used for each experiment. Experiments were made by increasing the pressure stepwise from 1–3–5 to 7 bar. Each step lasted 75 min. After the 7 bar filtration, pressure was released, and the membrane was allowed to recover from compaction for 10 min before the final UTDR value was read. Pressure was at 0.15 bar when the "before and after" values were read in order to keep the membrane immobile against the support metal (and prevent it from floating, as this would cause an error in the UTDR measurements). No changes in membrane thickness attributed to a short time at 0.15 bar have been observed when the "before and after" values have been read [4]. Processing of the data of the UTDR experiment results has been explained in detail by Stade et al. [4]. Experiments were done at 30, 50 and 70 °C temperatures, each experiment being repeated three times. Cross-flow velocity over the membrane was kept in laminar regime (Re ≈ 1100), and retentate and permeate streams were recycled back to the feed tank. After compaction experiments, the used membranes were dried for SEM studies.

The retention experiments were performed with the 3-cell filter. One hour of pre-compaction before measurements was done