Polymeric Membranes With Sufficient Thermo-Mechanical Stability to Deploy Temperature Enhanced Backwash

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The alternative membrane cleaning method Temperature Enhanced Backwash exploits elevated temperatures of typically 125 °C to realize high shear rate. This exceeds usual operating temperatures by far. Therefore, the thermo-mechanical properties of polymeric membranes were investigated. A repeated load cycle testing was suited and sensitive to detect the failure of membrane material and potting. All tested PES membranes showed to be stable during the repeated load cycle testing. The potting adhesive may be decisive, thus, a tensile test at 125 °C is proposed.

Keywords: Alternative membrane cleaning, Material investigation and characterization, Repeated load cycle, Temperature enhanced backwash, Tensile testing

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1 Introduction

The Temperature Enhanced Backwash (TEB) is a cleaning method for porous membranes alternative to mechanical backwashing and chemical enhanced backwashing [1]. The TEB enables the elimination of the backwash pump and is supposed to prevent microbial recontamination in the membrane module and the permeate tank by autoclaving (steam sterilization and boiling). Thus, it is particularly suited to increase the resilience of purification systems towards climate change due to its flexible and robust operation. The mode of operation resembles the operation of an Italian coffeemaker, a so-called moka, and it was described in detail by Aumeier et al. [1]. TEB showed to be competitive with mechanical backwashing demonstrating its basic feasibility by exposing ceramic ultrafiltration membranes to model solutions and real river water for self-sustaining, decentralized drinking water purification [1, 2]. In order to reduce the investment cost of the filtration systems, the use of polymeric membranes instead of ceramic membranes may be advantageous. The recurrent thermo-mechanical stress (TEB at 115–141 °C and corresponding vapor pressure) can be related to an increased probability of loss of separation performance, i.e., changes in hydraulic resistance and compound retention, or even fiber breakage [3, 4].

Therefore, the objective of this study was to investigate the thermo-mechanical properties of polymeric membrane fibers and flat sheets and to determine their performance changes during recurrent TEB exposure. In addition, the secondary objective was to identify the most relevant key performance indicators to assess these properties.

2 Material and Methods

Investigated membrane materials included PES, PVDF, PTFE and PEEK. Tab. 1 shows various polymer transition temperatures, i.e., glass transition temperature $T_G$, melting point $T_M$, heat deflection temperatures at 1.8 MPa (HDT-A) and 0.46 MPa (HDT-B), respectively. Tab. 2 depicts the selected ultrafiltration and microfiltration membranes that were used in this study.

Samples of these membranes were examined with the following methods to assess their thermo-mechanical properties:

1) Thermogravimetric analysis (TGA) under a synthetic air atmosphere with a heating rate of 10 K min$^{-1}$. Membrane sample mass was approx. 10 mg.

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2) Field-emission scanning electron microscopy (FeSEM) before and after exposure to TEB (1 h backwashing at $T = 125^\circ C$, $Dp = 1.35\) bar).

3) Repeated load cycles consisting of five steps (a–e) conducted with the following membranes: inge0.9, UFC, HFS, UP150 (all PES), and Y948.1 (PTFE). The hollow-fiber membranes were potted with the epoxy adhesive UHU Endfest into custom-made sockets made of stainless steel (V4A). Surface areas $A$ of hollow-fiber and flat-sheet membrane samples ranged from 15 to 20 cm$^2$. Sockets and flat-sheet membranes, respectively, were sealed with EPDM O-rings into a three-way, stainless-steel module.

a) Membrane pretreatment: PTFE membranes were submerged in isopropanol for 30 min prior to use. HFS membranes were submerged in a 18-wt % ethanol solution for 24 h prior to use. Other membranes were used as received.

b) Pure water permeation (PWP) in dead-end configuration at $Dp = 0.5$ bar and $T_\infty \approx 20^\circ C$ with deionized (DI) water until a constant mass flux was recorded.

c) Filtration of a model solute dissolved in a 20 mM phosphate buffer solution (pH = 8). The model solute was gelatin$^1$ ($c_0 = 20\) mg L$^{-1}$, $MW \approx 100–330\) kDa, Sigma-Aldrich, gelatin from bovine skin, type B powder). The retention test was performed in turbulent (Reynolds number $> 3600$) cross-flow configuration with recycled retentate, at transmembrane pressure $Dp = 0.5$ bar and $T_\infty$ until a volume abort criterion $V_{\text{final}}$ was reached.

d) Temperature Enhanced Backwash (0.5 h backwashing at $T = 125^\circ C$, $Dp = 1.35$ bar) in an adapted autoclave (CertoClav CV-EL 18L) using DI water.

e) Repeated PWP as step (b).

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$^1$ In case of membrane HFS, the model solute bovine serum albumin (BSA, $c_0 = 100\) mg L$^{-1}$, $MW = 66\) kDa, Carl Roth, albumin fraction $V, \geq 98\) %) was used instead of gelatin due to the lower MWCO of the membrane.
The steps (a, b) were conducted once, steps (c) and (d) were conducted alternatingly at least 10 times each before final step (e) was conducted. The key performance indicators (KPI) here were the hydraulic resistance \( R_{\text{hydr}} \) (Eq. (1)) as well as the retention \( R_{\text{gelatin}} \) (Eq. (2)) during each step. Furthermore, virgin membrane samples as well as samples treated with this repeated load cycle were examined using FeSEM.

4) Tensile testing at 125 °C under normal atmosphere at a rate of 10 mm min\(^{-1}\) for hollow-fiber membranes (free length \( l_0 = 3 \) cm) potted with UHU Endfest into custom-made sockets made of stainless steel (V4A).

Darcy’s law was used to account for temperature-dependent viscosity:

\[
R_{\text{hydr}} = \frac{\Delta p A}{\nu m}
\]

(1)

with the hydraulic resistance \( R_{\text{hydr}} \) being derived from transmembrane pressure \( \Delta p \), membrane surface area \( A \), kinematic viscosity \( \nu \) and mass flowrate \( m \). The retention for the model solute gelatin \( R_{\text{gelatin}} \) was defined as followed:

\[
R_{\text{gelatin}} = 1 - \frac{c_{\text{gelatin,permeate}}}{c_{\text{gelatin,feed}}}
\]

(2)

with the gelatin concentrations \( c_{\text{gelatin,feed}} \) and \( c_{\text{gelatin,permeate}} \) in the feed and permeate, respectively.

3 Results and Discussion

3.1 Thermogravimetric Analysis

Fig. 1 shows the thermogravimetric analyses of two PES and one PTFE membranes. PTFE seemed to be stable until approx. 500 °C coinciding with its decomposition temperature of 514 °C [10]. There was a mass loss of 1 % (HFS) and 2 % (UP150) for the PES membranes, respectively, at 100 °C. Since the membrane samples underwent no pretreatment prior to TGA, this mass loss is attributed to evaporation of pore water, which was previously stabilized by glycerol. The mass loss above 160 °C in case of UP150 is associated with the decomposition of PE and PP in the support layer as well as of glycerol. Regarding the conditions during TEB at 125 °C, one can state that PTFE is stable and PES is expected to be stable. In general, the TGA can only give an initial impression about membrane composition. However, a distinct statement about thermal stability under TEB conditions was not possible without testing the performance during permeation and retention.

3.2 Repeated Load Cycles: Hydraulic Resistance and Solute Retention

To evaluate the practical performance during permeation and retention, a repeated load cycle testing was conducted. Figs. 2 and 3 each depict the results of two individual replicates of UFC (PES) and Y948.1 (PTFE) membranes, respectively. In the case of UFC 1, there is a pronounced and sharp drop in performance in the fifth retention cycle (decrease in hydraulic resistance and gelatin retention). On the contrary, UFC 2 demonstrated constant retention throughout and only slightly rising hydraulic resistance during PWP. In order to differentiate between membrane and potting failure, the membrane fibers from UFC 1 were cut, repotted and another cycle was conducted (semi-filled circle symbols). The recovered performance (increase in hydraulic resistance and retention) provided strong evidence that the potting had failed previously and the membrane itself has remained functional at all times. The other PES membranes showed similar behavior like the UFC membranes. No more failure of membrane or potting was observed in other experiments.

Regarding PTFE, the results were more difficult to interpret (Fig. 3). First, both replicates showed very similar and reproducible results. Second, the hydraulic resistance during PWP increased during the repeated load cycle testing. This may be interpreted as irreversible fouling or thermo-mechanically induced pore closure due to material creep alike.

![Figure 1. TGA of two PES and one PTFE membranes: (a) HFS, (b) UP150, and (c) Y948.1.](image-url)
Third, the consistently low gelatin retention (always < 40 %) suggests fouling rather than pore closure due to material creep. However, it has to be kept in mind that such low retentions are less sensitive to changes. The pore diameter of 0.05 μm has thus to be considered too large to be assessed with gelatin as model solute (d_{hydr} ≈ 12–15 nm, according to [11]). The observed retention is more likely to result from depth filtration rather than surface filtration.

Apart from that, the FeSEM imaging did not reveal any clear structural change in any membrane or material, neither conducted before and after 1 h TEB (method 2), nor before and after the repeated load cycle (method 3 with ≥ 5 h TEB).

### 3.3 Tensile Testing at Elevated Temperature

Since the repeated load cycle testing revealed that the potting of hollow fibers can be crucial for the performance with respect to permeation and retention, we expanded the study onto the potting itself. The results of the tensile tests at 125°C are shown in Fig. 4 in the form of a force-strain diagram. In one case, the fiber broke representing the normal failure mode, whereas in the other case, the potting adhesive was detached. The stress differed because the corresponding cross-sectional area and lateral area varied, respectively. The corresponding maximum tensile stress \(\sigma_{\text{max}}\) and shear stress \(\tau_{\text{max}}\) amounted to \(\sigma_{\text{max}} \approx 1.62\)–1.68 MPa (Inge0.9 3) and \(\tau_{\text{max}} \approx 1.30\) MPa (Inge0.9 4). The maximum tensile stresses reported for individual hollow fibers range from \(\sigma_{\text{max}} \approx 4.6\) to 9.4 MPa [12]. Childress and coworkers [12] reported higher tensile stresses than the ones in this study. However, it was expected that material strength at ambient temperature would be higher than at 125°C. In general, tensile testing is well suited to investigate the mechanical stability of membrane fiber and potting also under elevated temperatures.

Moreover, there is little scientific literature about the membrane potting process and its properties [12, 13]. However, there is even more limited experimental evidence...
of the effect of (operational) temperature on membrane integrity and potting stability. Most of the knowledge on potting adhesives is proprietary knowhow of membrane manufacturers.

4 Conclusion and Implications

In this study, we were able to identify suitable key performance indicators (KPI) to assess hollow-fiber and flat-sheet membranes as well as hollow-fiber potting at elevated temperatures up to 125°C. These elevated temperatures are of interest when employing Temperature Enhanced Backwash (TEB) for membrane cleaning. The following KPIs are proposed: First, hydraulic resistance combined with model solute retention, e.g., gelatin for UF membranes of approx. 100 kDa MWCO, using a repeated load cycle testing. Second, to assess the durability of hollow-fiber potting, a tensile testing at elevated temperature, e.g., 125 °C, is suggested. This is important because membrane potting is a significant factor in determining long-term module integrity and process performance.

Most importantly, the combination of hydraulic resistance and model solute retention during the repeated load cycle testing was sensitive to detect the failure of membrane material and potting. Thus, this combination of KPIs was the most sensitive and relevant in detecting failures and vice versa, demonstrating continued membrane integrity. All PES membranes showed to be stable during the repeated load cycle testing. However, the potting adhesive showed to be decisive for the thermo-mechanical stability in individual cases. Moreover, it was not possible to derive the thermomechanical stability of membrane material from FeSEM and TGA directly. With this knowledge, it is now possible to develop modules based on polymeric membranes in order to cut down investment costs while deploying TEB.

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### Symbols used

- $A$ [m$^2$] area
- $c$ [mg L$^{-1}$] concentration
- $d_{\text{hydr}}$ [m] hydrodynamic diameter
- $F$ [N] force
- $\dot{m}$ [kg s$^{-1}$] mass flowrate
- $\Delta p$ [Pa] gauge pressure, transmembrane pressure
- $R_{\text{hydr}}$ [m$^{-1}$] hydraulic resistance
- $R_{\text{gelatin}}$ [–] retention for gelatin
- $T_G$ [°C] glass transition temperature
- $T_M$ [°C] melting point
- $V_{\text{final}}$ [L] volume abort criterion

### Greek letters

- $\varepsilon$ [%] strain
- $\nu$ [m$^2$s$^{-1}$] kinematic viscosity
- $\sigma$ [MPa] tensile stress
- $\tau$ [MPa] shear stress
Abbreviations

BSA bovine serum albumin
DI deionized
FS flat sheet
FeSEM field-emission scanning electron microscopy
HDT heat deflection temperature
HF hollow fiber
KPI key performance indicator
MW molecular weight
MWCO molecular weight cut-off
PE polyethylene
PEEK polyether ether ketone
PES polyethersulfone
PP polypropylene
PTFE polytetrafluoroethylene
PVDF polyvinylidene fluoride
PWP pure water permeation
TEB Temperature Enhanced Backwash
TGA thermogravimetric analysis
UF ultrafiltration

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Research Article: The thermo-mechanical stability of polymeric membranes is investigated using the methodology of a repeated load cycle testing. The key performance indicators consist of a combination of hydraulic resistance $R_{\text{hydr}}$ and model solute (gelatin) retention $R_{\text{gelatin}}$. 