UNIVERSITY OF
BATH

University of Bath

Title:

Towards continuous wine making: the optimization of mixed matrix membranes for wine fining

Authors & affiliations:

Darrell A. Patterson[a], Mark Bowstead[b], Anh Tran[b] and Bryony James[b]*

[a] *Nanostructured and Tuneable Materials Laboratory, Department of Chemical Engineering, University of Bath, Bath, United Kingdom.*
[b] *Department of Chemical and Materials Engineering, University of Auckland, Auckland, New Zealand.*

*: d.patterson@bath.ac.uk

Abstract: (Your abstract must use **Normal style** and must fit in this box. The abstract should be written in English and should be around 1000 words long, i.e., 2 pages excluding title, authors & affiliations, keywords and references. Authors are encouraged to show important figures/tables etc in the abstract so as to make a full presentation.)

Proteins (from grapes and yeast) are present in wine. They are only present in low concentrations and add no nutritional value; however, their presence can adversely affect the clarity and stability of wines. An important step in wine production is the removal of proteins by "fining". Generally conducted as part of a batch process, fining agents need to be handled with care in terms of concentration and processing time. "Over-fining" can strip a wine of flavour and colour and generate excess lees. Large scale fining of quality white wines is almost invariably conducted using sodium bentonite. This is added as a slurry which settles over time to create "lees". The fined wine is then "racked" off the lees (run from the tank above the sediment). This incurs costs by creating a waste product (the lees) and resulting in losses of wine of up to 10%. Cost is also incurred by lower wine quality if wine is recovered from the lees. The process can be improved if the fining agent can be immobilised, accompanied with optimisation of the fining process to make it continuous. Therefore, there is potential to remove the haze forming proteins from wine in a continuous system by filtering with mixed matrix membranes (MMMs). MMM's combine the principles of adsorption (and chromatography when in series) and membrane filtration in a single separation step that harness particles with an active surface on which the protein adsorbs as the wine is filtered. The ideal MMM must show specificity onto the encapsulated particles while maintaining an open matrix with well attached particles that have most of their active surface available for adsorption.

This work quantifies and characterises MMMs fabricated using phase inversion by immersion precipitation. Ten weight percent (wt%) polyethersulfone (PES) and polyvinylidene fluoride (PVDF) were combined with 0, 15, 30 and 40 wt% montmorillonite (MMT – the active component of sodium bentonite) or zirconia (Zr). A Sterlitech HP4750 dead-end cell was used to filter a model wine solution consisting of 300mg L^{-1} Bovine Serum Albumin (BSA), 12% w/w ethanol with the remainder water through thirteen fabricated membranes. These membranes were also subjected to weight-loss analysis, different feed pHs and morphology characterisation via scanning electron microscopy (SEM, Philips XL30S Field Emission Gun).

Results showed that there were differing membrane morphologies with increasing particle loading for MMT and Zr. Increased MMT loading increased porosity (and therefore flux) as shown in Figure 1. This is what is desired – a high immobilisation of

MMT in a porous polymer matrix, so that proteins can be selectively adsorbed, whilst similar size molecules that are need for the wine flavour and texture pass through the membrane. X-ray photoelectron spectroscopy of used membranes confirmed this, showing that the more porous MMMs remove proteins via particle adsorption whilst the denser membranes work via a top layer rejection and adsorption mechanism. Increased Zr loading gave smoother, denser and more symmetrical, lower flux membranes; as such, increased Zr loading produced membranes with less desirable characteristics. Due to these morphologies, the membranes with a higher MMT loading and lower Zr loading gave the best rejection whilst maintaining an operationally acceptable permeance (Figure 2), with the optimal being the 10wt% PES membranes with 30 and 40 wt% MMT.
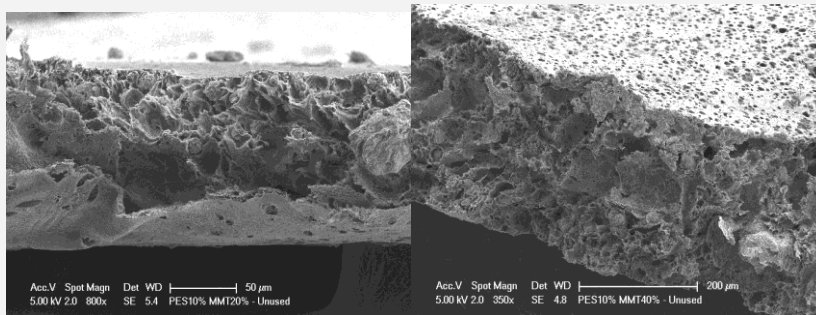

Figure 1: Cross-sections of PES MMMs, showing the effect of increasing MMT loading on the morphology. (a) 20wt% MMT, (b) 40wt% MMT.
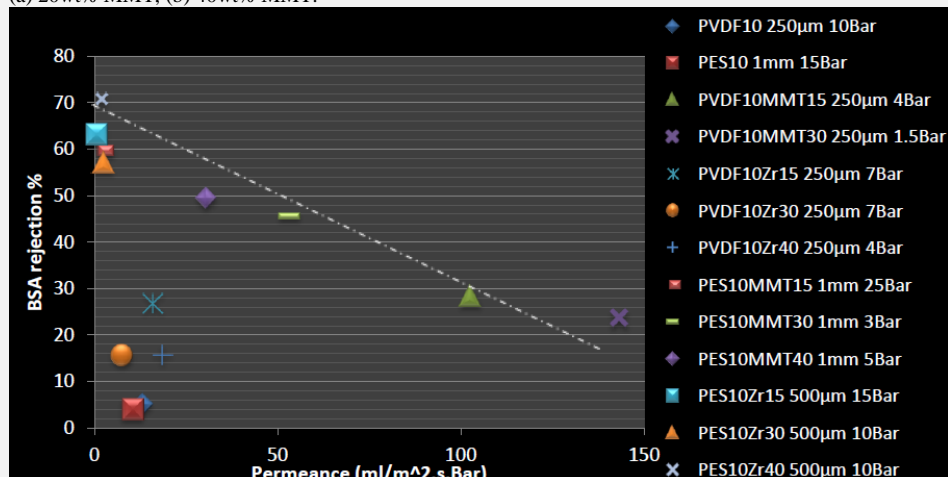

Figure 2: Rejection of BSA versus permeance for the MMMs tested. The legend describes the different membrane types and testing pressure, as follows: [Polymer name][polymer wt%][particle name][particle wt%][cast thickness][filtration pressure].

MMMs also need to be operationally stable. Therefore, particle loss during filtration was evaluated by conducting multiple solvent runs and evaporating the permeate using a rotary evaporator, then weighing the released particles. This showed that the more porous membranes exhibited greater particle loss (in particular the aforementioned 10wt% PES, 30 and 40 wt% MMT membranes) indicating that greater porosity (and flux) needs to be compromised with particle retention. Based on this, the optimal MMM was the 10wt% PVDF 15wt% MMT or Zr membranes, which have a higher particle retention and moderate rejection and permeance. In general Zr particles were better retained in both polymers compared with MMT, perhaps indicating a stronger

membrane-particle interaction. This also reflects the contrasting porosity versus particle trends seen in the SEM results (Figure 1).

Overall this study shows that it is possible to remove proteins from a model wine solution with MMT and Zr mixed matrix membranes. With some refinement of the membrane recipe and further testing (including desorption and longer term cross-flow testing) these membranes will open up the possibility of continuous wine fining operations. This will therefore take the wine industry one step closer towards continuous wine making operations.