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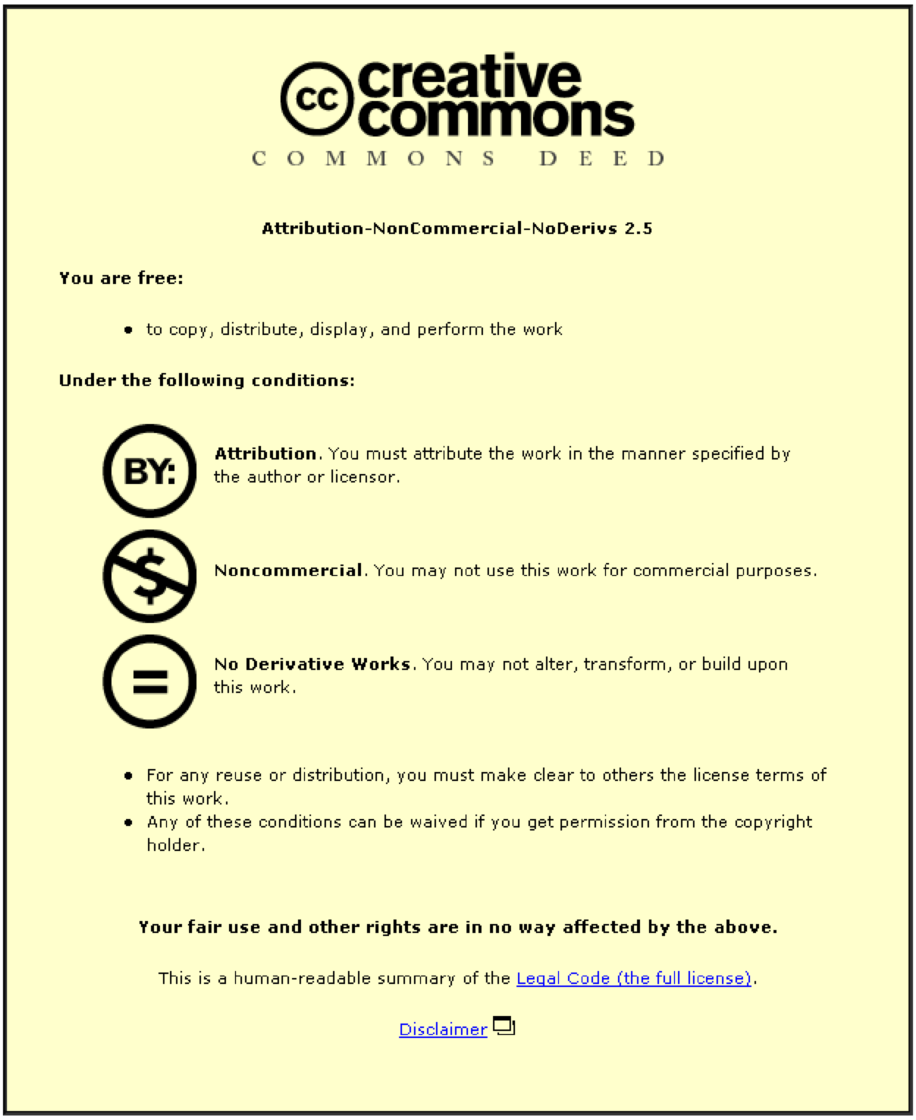

CATALYST CROSSLINKED MEMBRANES FOR USE IN SOLVENT RESISTANT NANOFILTRATION

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ABSTRACT

This paper details the characterisation (e.g. stiffness, swelling) of catalyst crosslinked polydimthylsiloxane (PDMS) and its subsequent performance as the selective layer in polyacylonitrile (PAN)/PDMS composite nanofiltration membranes. The latter is illustrated by way of the representative filtration performance of 9,10-diphenylanthracene solute from n-heptane solvent. It was found that altering the composition of the PDMS polymer has a relatively large effect on the rigidity of the material but little effect on the extent of solvent induced swelling. Additionally, when used as part of a membrane, increasing the catalyst amount has the dual effect of increasing solute rejection and lowering solvent flux. In this way a modicum of tailoring can be introduced to the membrane manufacture process to suit specific process needs.

KEYWORDS

PDMS; Solvent resistant membranes; Nanofiltration; Catalyst; Solvent.

INTRODUCTION

The use of solvent resistant nanofiltration (SRNF) membranes to filter solutions of solvents and dissolved species is a newly emerging industrial process. The majority of membranes feature a polymer based selective layer and a typical way to impart stability is to initiate and control the extent of crosslinking by thermal means or free radical initiation. Irradiation induced crosslinking does not always provide a uniform crosslinking density in the final membrane. For example, a striped pattern of high and low crosslinking where the intensity has not been uniform can be produced[1]. However, it is possible to crosslink the polymer by dispersion of a catalyst in the base mixture which should provide a more uniform crosslinking density.

This paper presents initial data regarding the production of PDMS with catalyst induced crosslinking, the characterisation of PDMS slabs and finally its application as the active layer in composite nanofiltration membranes. The reported data is intended to be a precursor to further filtration work with the manufactured membranes that will examine solute/solvent transport mechanisms and compliment and help interpret the work already published by an author[2-7].

METHOD

Two different experimental apparatus were used during the work – a cantilever rig for determinations of polymer/membrane swelling, Figure 1 (*left*), and a crossflow filtration rig, Figure 1 (*right*). The cantilever rig consisted of a sealed test cell, the top of which contained a sliding plunger. The polymer slab/membrane sample to be tested was placed beneath the plunger and subsequently immersed in one of eight chosen solvents that was injected via a port in the top of the cell. As the sample swelled so it acted upon the plunger which in turn activated a digital measurement probe placed either directly in contact with the plunger or in contact with a cantilever bar which rested upon the plunger. Although a pressure could be applied to a sample by hanging

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weights from the cantilever, all the tests reported here were obtained with no additional pressure. Further details of the technique are available elsewhere for the interested reader[4,5].

Figure 1 (*right*), shows a schematic of the crossflow rig used to determine solvent flux and solute rejection characteristics for the manufactured membranes. The apparatus comprised a single reservoir from which the process fluid was pumped through a coarse filter to the crossflow module containing the membrane. The retentate stream from the module was fed back to the reservoir via a cooler which utilised the exhaust stream from the air driven pump as the cooling fluid. The permeate from the module was collected to determine the flux and rejection (as compared to a sample of the process feed solution) of the chosen representative n-heptane solvent and 9,10-diphenylanthracene solute.

The PDMS used in the study was obtained from Techsil Ltd as a two part kit comprising a silicon containing pre-polymer and a dibutyl catalyst (DBT). Following discussions with Techsil, the catalyst was incorporated with the pre-polymer in amounts ranging from 0.1 to 0.5 wt%. The initial characterisation tests to be conducted on the PDMS necessitated a certain level of structural integrity so thick films (‘slabs’) of *circa* 2 mm thick were manufactured.

The polymer slabs were produced in batches of twelve at a time in order to reduce the variance in any individual piece and provide some allowance for failed samples. By preparing sufficient polymer/catalyst mixture to cast twelve slabs at once the amount of catalyst required increased to a more manageable amount, *circa* 0.1 g. It is noted that the liquid catalyst is quite viscous and introducing amounts less than 0.1 g proved unreliable in terms of final catalyst quantity. Producing the polymer slabs in batches of twelve ensured a sufficient quantity so that each of the eight solvents used for swelling determinations could be tested against the same composition of polymer. This is important because although catalyst amounts are referred to as 0.1%, 0.2% etc. in the paper, in practice the actual amount was subject to some variance so values such as 0.104%, 0.099%, 0.206% etc. could occur. If each polymer sample was made individually the bulk variance in the tests would have introduced a small, but ultimately unnecessary, error into the experimental procedure.

After blending the pre-polymer and catalyst, the resultant mixture was evenly distributed into twelve 30 mm square casting trays and left standing for at least 48 hours at ambient conditions to allow polymerisation to occur. Each PDMS slab was then shaped into a cylinder 26 mm in diameter and *circa* 2.25 mm in height; these dimensions were dictated by the internal space of the available membrane swelling test cell (Figure 1 (*left*)). The exact height of the cylinder was measured and a plan view of each sample was photographed so that computer image analysis could subsequently be used to calculate the initial size. To determine the extent of solvent induced swelling, a sample was secured in the test cell and 30 ml of solvent introduced. As previously noted, the cell was sealed to prevent loss of solvent through evaporation and the digital probe recorded the movement of the plunger which rested upon the sample. Once an equilibrium expansion was attained (in some cases after 22+ hours) the final swelled thickness was recorded, the cell was opened and a second photograph taken. The mass of the polymer cylinder before and after an experiment was also measured. From the data the relative change of two parameters, volume and weight, could be calculated and used to assess the extent of swelling (see, for example, Figure 2 (*left*)).

The membranes used in this study were created by coating the surface of a restrained commercial PAN support layer with a solution consisting of the polymer mixture detailed above and n-hexane to aid coating. The membrane was left to stand for at least 20 hours at ambient conditions before being used. A total of three different grades of membranes were produced only differing by catalyst amount.

RESULTS AND DISCUSSION

The first results presented make comparisons between the catalyst derived PDMS slabs and a commercially manufactured PDMS/PAN nanofiltration membrane that is crosslinked predominantly by radiation at an intensity of 80 kGy. Figures 2 and 3 show the relative changes in mass and volume upon immersing *circa* 0.3 wt% DBT PDMS slabs in eight different solvents (Figure 2 (*left*)), the effect of catalyst amount on the changes in slab thickness with three of the solvents (Figure 3 (*left*)) and the effect of catalyst amount on polymer rigidity (Figure 3 (*right*)). Some comparable data for swelling of two commercial membranes, a 10 µm PDMS selective layer thickness membrane and a double stacked 2 µm PDMS selective layer thickness membrane, are shown in Figure 2 (*right*). These data, taken from[5], show a similar trend to the data in Figure 2 (*left*) which in turn implies that a correlation should exist between the performance of the commercially available membrane and a membrane manufactured using the catalyst derived PDMS.

Figure 2 (*left*) shows the extent of swelling recorded with the cantilever rig for immersion of PDMS slabs in pure solvents for a period exceeding 22 h. The graph shows a curved relationship with maximum swelling noted for solvents exhibiting a solubility parameter ~15 MPa$^{0.5}$ and progressively smaller swelling for solvents with higher solubility parameters; the maximum swelling coincides with the typically quoted solubility parameter for PDMS. Relative change in this case assumes that a value of 100% corresponds to no change in the parameter, a value of 200% corresponds to a doubling of the parameter, and so on. Measurements for change in weight are based on the mass of PDMS sample before and after immersion in a solvent. Because of the thick films being used, the evaporation rate was not high enough to cause a problem – separate tests found that the time required for evaporation to alter the result by 1% was more than a minute which was significantly longer than it took to record the mass of a sample. The relative change by volume was calculated by using the change in height (the standard swelling measurement for membranes) and multiplying it by the change in plan area. The latter was determined by computer analysis of photographs taken immediately prior to and after immersion and relating to a calibration grid. It is evident that there are differences between the two measurement methods as the results obtained by weight don't dip below the 100% mark. A value of less than 100% for weight would be the result of experimental error arising from some of the polymer not being recovered for weighing. However, it is believed that shrinkage of PDMS in alcohols (which exhibit solubility parameters in the range 24-30 MPa$^{0.5}$) is a real effect as similar results have previously been obtained with swelling measurements using commercial PDMS membranes[4,5].

A sequence of corresponding experiments to those shown in Figure 2 were performed with polymer slabs made using different amounts of catalyst. Figure 3 (*left*) shows how the extent of swelling was affected by three solvents. The relative magnitudes of swelling are similar to those in Figure 2 (*left*), i.e. heptane has the greatest effect, xylene is a close second with ethanol barely having any effect at all. However, with regard to the dependence on catalyst amount, any effects on swelling propensity are either non existent or show a slight negative trend whereby the result for the 0.5 wt% PDMS seems to be lower than for the 0.1 wt% PDMS. Whilst this result could be expected as more catalyst will tend to induce more crosslinking in the PDMS, the results lies within the bounds of experimental error and further work is required to confirm.

To further investigate the apparent lack of dependency between catalyst amount and the properties of PDMS, Young's modulus of the manufactured PDMS was determined. Square cross-section 'bars' of PDMS, 4 mm x 4 mm x 50 mm, were produced in five different catalyst compositions and suspended upon two knife edge supports spaced 45 mm apart. A series of weights between 2 g and 10 g were centrally loaded onto a bar and the maximum deflection from the horizontal was recorded in each case. The classical mechanics equation for a simply supported beam loaded with a concentrated force was used to calculate Young's modulus. A total of 16 bars were tested across the range and each combination was checked to see which produced the closest approximation to linearity, i.e. which set produced the largest value of Pearson's product moment correlation coefficient (PPMCC). Figure 3 (*right*) shows this data set.

The fact that Young's modulus more than doubles over the range of catalyst amount tested yet there was no discernable change in swelling for the same range is a curious result. It was expected that Young's modulus would be proportional to the amount of crosslinking within the PDMS, which is observed in Figure 3 (*right*) and borne out in the crossflow filtration experiments reported below. The fact that this proportionality did not result in significant changes in the observed swelling is the subject of current investigation.

With the characterisation tests completed, the behaviour of the produced PDMS was deemed to have been established. A fresh batch of PDMS was produced and used to form the selective layer of a composite membrane by coating a commercially available PAN support layer. The produced membranes spanned the available range of catalyst amount and were initially tested to ensure that defective membranes (uneven coating, pin hole defects etc.) were eliminated. The screening took the form of crossflow tests at a small number of pressures, with poor selectivity being the ruling criterion for pass/fail.

A total of three membranes were ultimately tested in the crossflow rig, one each of ~0.1 wt%, ~0.3 wt% and ~0.5 wt% catalyst amount. Typical results are shown in Figure 4. The test solution used in each case was ~30 ppm 9,10-diphenylanthracene in n-heptane with a stage cut between 5 and 10%. One test was conducted at each operating pressure with repeat runs only being completed for obviously anomalous results. n-heptane was chosen as the solvent as it elicited the greatest swelling response of those solvents tested during characterisation work and therefore alters a membrane to the greatest extent. 9,10-diphenylanthracene was chosen as the solute due to its high absorbance in UV-vis measurements, thus ensuring more accurate calculation of rejection values. Future work will include expanding upon the range of solvent/solute combinations.

Figure 4 (*left*) demonstrates two key trends. Each membrane shows a positive linear dependency between applied pressure and permeate flux. This trend is logical and in accordance with Darcy's law as an increase in pressure will increase the driving force and therefore improve transport rates. The second trend is that for any chosen pressure the flux of the 0.1 wt% membrane is higher than the flux of the 0.3 wt% membrane which in turn is higher than the 0.5 wt% membrane. This trend is in line with the result shown in Figure 3 (*right*). As the amount of catalyst is increased so the rigidity of the active layer increases which in turn could reasonably be expected to decrease transport across the PDMS layer. Focusing on individual data points, there seems to be a trend of increasing scatter at higher flux values. The 0.5 wt% membrane produced a good linear correlation which is in contrast to the more scattered results for the 0.1 wt% membrane. Here, points are seen to lie either side of a linear trend line. The scatter seems to increase with increasing pressure but available data are currently insufficient to assign any value to this phenomenon.

Figure 4 (*right*) shows rejection data for the same experimental parameters. The level of rejection was determined by measuring the absorbance of light at a wavelength of 392 nm for samples taken from the test fluid before an experiment and from the collection bottle filled with permeate during an experiment. Absorbance values were obtained using a UV-vis spectrophotometer and converted to a solution concentration by means of a calibration chart constructed from solutions of known concentration. Figure 4 (*right*) also shows two main trends. Firstly rejection increases with increasing applied pressure, although not linearly. Each of the tested membranes showed evidence of a plateau rejection forming toward higher pressures thereby implying a limit to the benefit to be gained from increasing pressure. Such results are in accordance with data obtained with commercially produced PDMS/PAN membranes and some of the authors previous works[2,3,7]. The second trend spans the different membranes, with increasing catalyst amount yielding an increased rejection. Again this result is in agreement with the trends noted previously as a more rigid selective PDMS layer would reasonably be expected to provide better filtration (i.e. less transmission of solute).

Combining all the trends observed it is deduced that as the catalyst amount increases so the extent of crosslinking increases, which in turn raises the rigidity of the PDMS. The increased rigidity tends to make the selective layer more dense and ultimately has the dual effect of lowering solvent flux and increasing solute rejection. In this way a SRNF membrane can be tailored to a given application during the manufacturing process by simply altering the degree of crosslinking.

CONCLUSIONS

It has been shown that by varying the catalyst amount during manufacture the rigidity of a PDMS slab can be altered over a significant range. However, this change does not seem to influence the extent of swelling that the polymer undergoes when immersed in a solvent. Catalyst derived PDMS has been shown to exhibit similar swelling properties to quoted literature values for PDMS/PAN membranes. Altering the composition of the PDMS when it is used as the selective layer in a composite membrane has also been shown to be beneficial. Raising the catalyst amount leads to increased rejection and lower flux when filtering a typical solute/solvent combination such as 9,10-diphenylanthracene and n-heptane. This allows for tailoring of a membrane to a given process, but more research will be required to fully utilise such a result.

NOMENCLATURE

DBT	Dibutyl catalyst
PAN	Polyacrylonitrile
PDMS	Polydimethylsiloxane
PPMCC	Pearson’s product moment correlation coefficient

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FIGURES AND TABLES

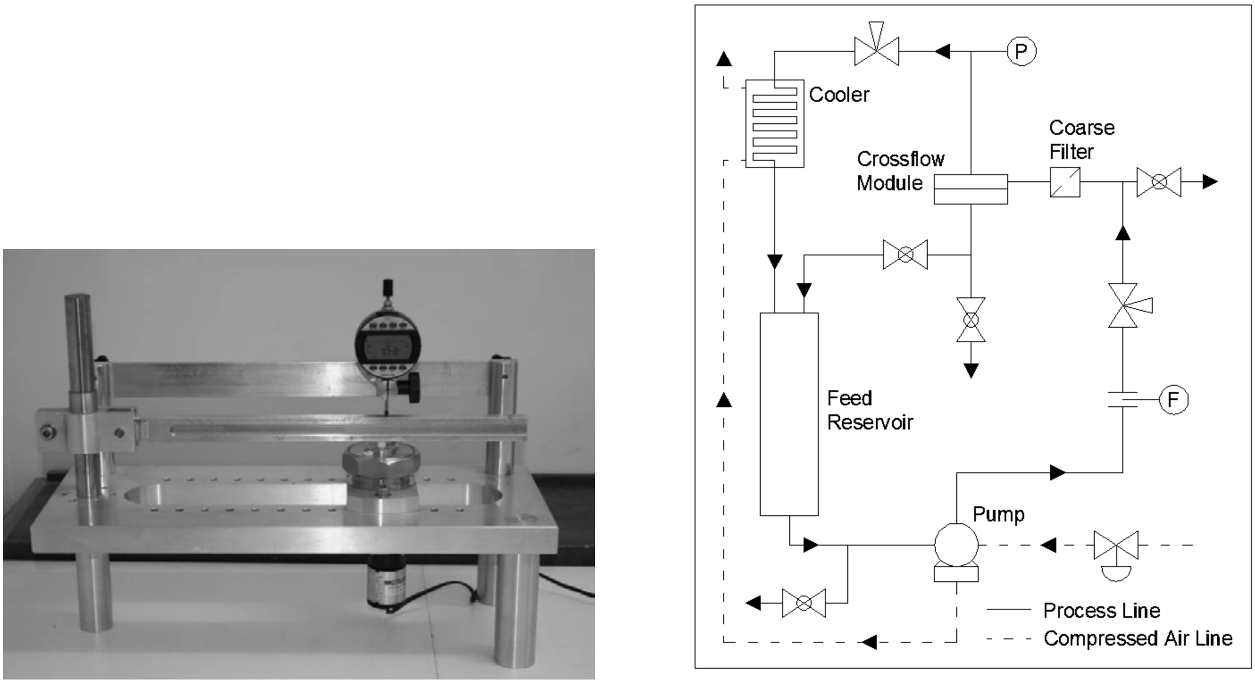

Figure 1: Photograph of the cantilever rig (*left*) and schematic of the crossflow rig (*right*).

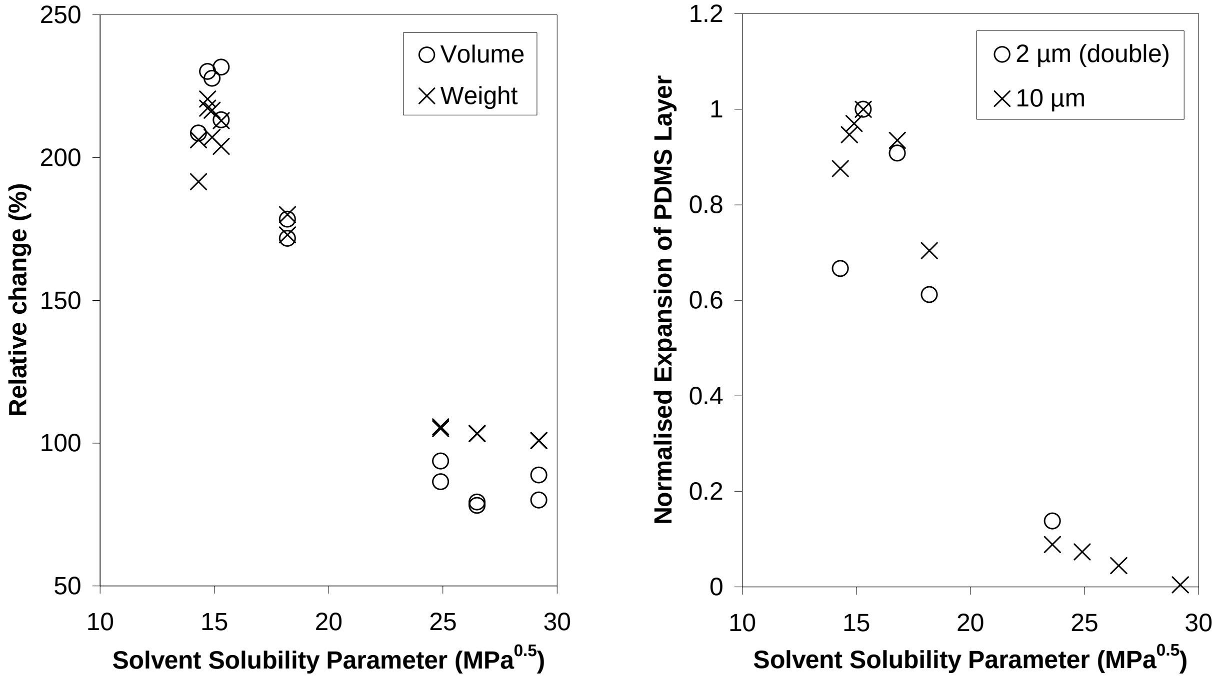

Figure 2: Effect of solvent type on 0.3 wt% catalyst derived PDMS slab swelling (*left*) and typical swelling data for commercial PDMS/PAN membranes[5] (*right*).

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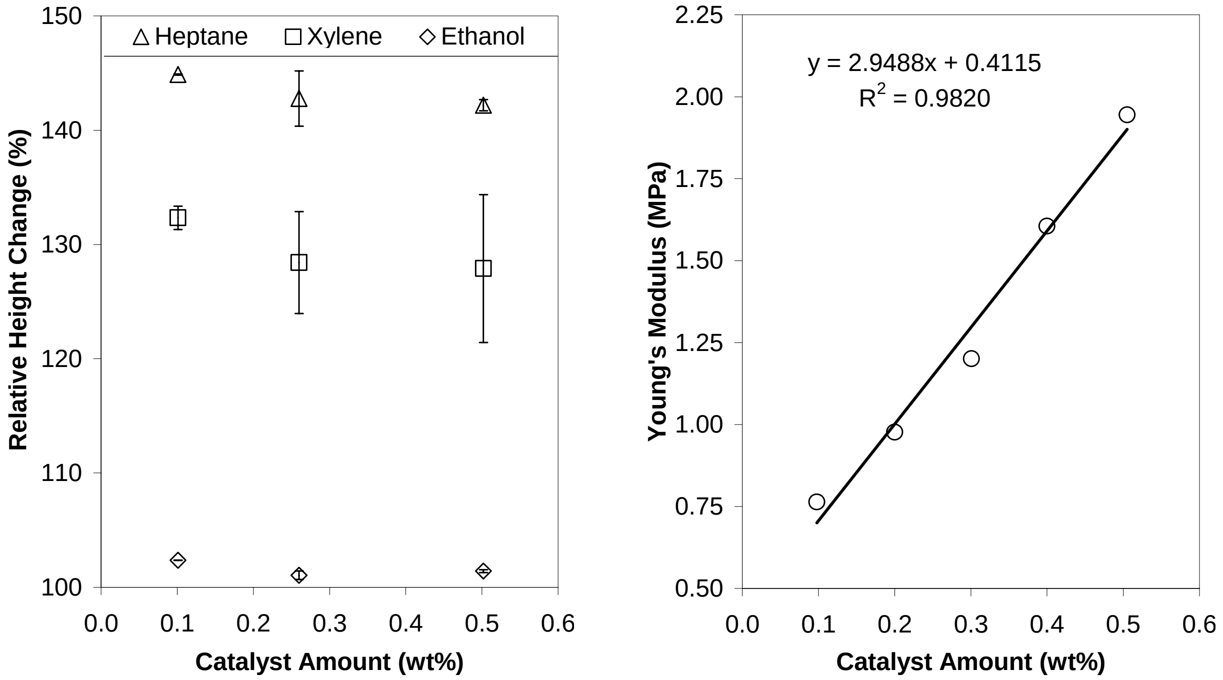

Figure 3: Effect of catalyst amount on PDMS swelling (*left*) and effect of catalyst amount on PDMS rigidity (*right*).

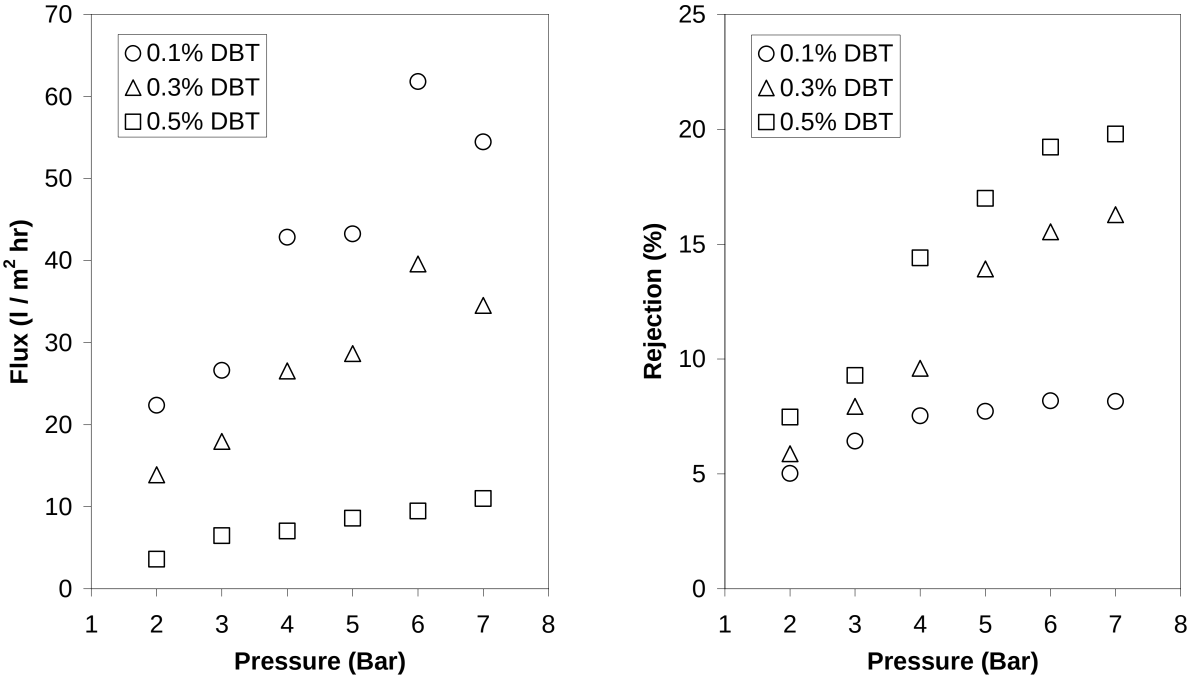

Figure 4: Flux data for several membranes made with different catalyst amounts (*left*) and corresponding rejection data (*right*).

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