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# Preparation of composite hollow fiber membranes: co-extrusion of hydrophilic coatings onto porous hydrophobic support structures

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# Abstract

Coating a layer onto a support membrane can serve as a means of surface functionalization of membranes. Frequently, this procedure is a two-step process. In this paper, we describe a concept of membrane preparation in which a coating layer forms in situ onto a support membrane in one step by a co-extrusion process. Our aim is to apply a thin ion exchange layer (sulfonated polyethersulfone, SPES) onto a polysulfone support. The mechanical stability and adhesion of the ion-exchange material to the hydrophobic support membrane (polysulfone) has been studied by a systematic approach of initial proof-of-principle experiments, followed by single layer and double-layer flat sheet casting. Critical parameters quantified by the latter experiments are translated into the co-extrusion spinning process. The composite hollow fiber membrane has low flux as a supported liquid membrane for the copper removal due to the low ion exchange capacity of the SPES. The coating layer of the composite membrane is porous as indicated by gas pair selectivity close to unity. However, our new composite membrane has good nanofiltration properties: it passes mono and bivalent inorganic salts but rejects larger charged organic molecules. The experimental work demonstrates that co-extrusion can be a viable process to continuously prepare surface tailored hollow fiber membranes in a one-step process, even if the support and coating material differ significantly in hydrophilicity. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Co-extrusion; Co-casting; Composite hollow fiber membranes; Salt retention; Adhesion

# 1. Introduction

Composite membranes emerged right after the discovery of asymmetric RO membranes [1]. This development opened the door for tailor-made membranes to a much wider range of applications. Several methods can be used to prepare composite membranes [2,3]: lamination of a pre-formed film, interfacial polymerisation, in situ polymerisation, dip coating, plasma deposition and dynamic membrane formation. In general, fabrication of such a composite membrane

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consists of at least two separate steps: manufacturing of the support and subsequent coating. The advantage of this sequential processing includes flexibility in adjusting a variety of parameters and immense knowledge is today available. However, such multi-step fabrication processes are more expensive and time consuming. In addition, the composite membranes produced by these processes can experience failure and poor performance due to an increasing risk of introducing defects in the substrate and separating layer with the increasing number of processing steps involved.

Co-extrusion is a fabrication method to make a multi-layer configuration in the form of film, sheet, or fiber by simultaneous extrusion of two or more

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polymers through a single die [4]. Co-extrusion avoids many of the manufacturing steps required by conventional lamination and coating processes, such as making and handling of individual films, application of coating primers, and solvent drying. Because of these economic and technical advantages, the application of co-extrusion is growing rapidly [5–10].

Co-extrusion in membrane technology is challenging, with only a few patents and publications [11-24]. Basically, co-extruded membranes include two types: dense and porous. Co-extruded dense membranes include dialysers [15] and gas separation membranes [11–14,17]. Most of the work published deals with the co-extrusion of similar polymers for both the coating and support membranes. Porous membranes, both for ultrafiltration and microfiltration, are made from the same polymers, i.e. polypropylene [20,21], polysulfone (PSf) [22,23] and polytetrafluoroethylene [24]. To our knowledge, there are only two patents describing the spinning of sulfonated polymers on PSf or polyethersulfone (PES) [18,19]. Sulfonated polysulfone (SPSf) with an ion exchange capacity of about 0.8 meq./g is coated on a PSf solution [18]; and this is used as an anti-fouling membrane in the separation of an emulsion solution. The other patent [19] describes the use of blends of SPSf and PSf or PES to hydrophilize the membrane surface.

In this paper, a systematic approach is described to prepare a co-extruded composite membrane with a coating layer of SPES onto a PSf support. The sulfonated polymer itself will be investigated in terms of mechanical properties as well as adhesion onto the PSf support. A concept of critical polymer concentration is introduced for preparation of an integral composite hollow fiber membrane of SPES on PSf (see Fig. 1). Initial screening and proof-of-principle experiments are carried out determining the critical process parameters in the co-extrusion process. The fiber integrity is characterized by scanning electron microscopy (SEM). Based on these experiments, detailed characterization of the coagulation behaviour of the coating material is performed and the obtained membranes are characterised by field emission scanning electron microscopy (FESEM). Co-casting of flat-sheet membranes addresses the critical issue of layer adhesion in order to identify recipes that can be further applied during co-extrusion. Finally, co-extruded membranes are tested with respect to their gas sepa-



Fig. 1. Working procedure for the preparation of a hydrophilic SPES coating onto a hydrophobic support by a co-extrusion spinning process.

ration, ion retention and liquid membrane extraction performances.

## 2. Experimental

### 2.1. Materials

Polysulfone (PSf, Udel P3500) is purchased from Amoco. Sulfonated polyethersulfone (SPES) is provided by AKZO Nobel. Solvents, *N*-methylpyrrolidone (NMP), diethylene glycol (DegOH), acetone are purchased from Merck. The solvents are of analytical grade and used without further purification. Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and copper sulfate (CuSO<sub>4</sub>) are purchased from Merck of analytical grade. Three dyes are used: procion blue ( $M_w$  840.12, negatively charged,  $\lambda_{max}$  607 nm, from Chimica), sunset yellow ( $M_w$  452.38, negatively charged,  $\lambda_{max}$  482 nm, from Aldrich) and methyl green ( $M_w$  472.51, positive charged,  $\lambda_{max}$  629 (423) nm from Merck).

#### 2.2. Characterization of SPES

The ion exchange capacity (IEC) is defined as the number of equivalents per gram of dried polymer. It is

Table 1			
Properties	of	sulfonated	poyle the rsul fone

Polymer	Ion exchange capacity (meq./g dry polymer)	Degree of swelling (DS, %)
PES	_	3.1
SPES	0.36	9.1

SD, substitution degree. Swelling is determined at  $250\,^\circ\mathrm{C}$  in pure water.

determined by elemental analysis. The water sorption is measured by soaking two pieces of SPES films in pure water at 25 °C for 7 days. The swollen films are weighed and then dried in vacuum oven at 30 °C for another 7 days. The degree of swelling (DS) is determined from the difference in weight (*W*) between dry and swollen films according to

$$\mathrm{DS} = \left(\frac{W_{\mathrm{swollen}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}}\right) 100$$

The degree of swelling and the IEC of SPES are listed in Table 1. The properties of PES are listed as well for comparison. SPES has an ion exchange capacity of 0.36 meq./g, which is low compared to other ion exchange materials. SPES shows a water uptake of 9.1 wt.%, which is significantly higher than that of PES (3.1 wt.%).

# 2.3. Single film casting

Before solution preparation, SPES is pre-dried in an oven at 80 °C for 1 week and in a vacuum oven at 30 °C for another week. SPES solutions are prepared by dissolving a certain amount of polymer in NMP or acetone and NMP mixtures at room temperature. After filtering by a 15  $\mu$ m metal filter, the solutions are allowed to degas for at least 24 h, and then cast onto pre-cleaned glass plates using a casting knife of a certain thickness (50  $\mu$ m). After 2 s of exposure to ambient air with a relative humidity of 45–55%, the initial films are immersed into an aqueous coagulation bath. The prepared films are stored in ultra-pure water (MilliQ, Millipore) to rinse residual solvent for 24 h at room temperature.

#### 2.4. Stress-tensile test

Mechanical stress-strain experiments are performed on a Zwick Tensile Machine (Materialprufung Z020)



Fig. 2. (a) Co-casting knife; (b) schematic description of casting knife for double layer membranes.

made in Germany. Pre-dried SPES films are initially cut into standard dumb-bell test pieces. And then two ends of the film are clasped onto the tensile machine. Because of film shrinkage, a certain force, 0.25 N, is pre-applied to avoid contribution of the force acting on flattening the crumbled films.

#### 2.5. Double layer casting

A special casting knife is used to co-cast double layer membranes as shown in Fig. 2. The settings of the casting knives are 200 and 250  $\mu$ m respectively, resulting in a coating thickness of 50  $\mu$ m and a sublayer thickness of 200  $\mu$ m. The polymer solutions are cast on a glass plate and the precipitation starts from the top side of the films. When the support solution contains additives, such as diethylene glycol, a nitrogen flushed box with a relative humidity between 10 and 15% is used for casting. The films are rinsed in tap water for at least 24 h before analysis. The adhesion of the top layer to sublayer is examined visually both in wet state and dry state.



Fig. 3. Schematic description of the spinning set-up and spinneret: (a) spinning set-up; (b) bottom view of a real spinneret; (c) schematic description of the spinneret. A, coating solution channel (1.1 mm); B, support solution channel (1.0 mm); C, bore liquid channel (0.6 mm).

#### 2.6. Co-extrusion hollow fiber spinning

Pre-dried PSf (1 week in  $120 \,^{\circ}$ C oven) is dissolved in a mixture of NMP and diethylene glycol (PSf/NMP/DegOH,  $17/52.4/30.6 \,$ wt.%). The polymer solution is filtered and degassed before spinning. The coating solutions are prepared as described above.

In order to prepare a composite hollow fiber, a spinneret with a tube and two orifices is used as shown in Fig. 3(b) and (c) [25]. The SPES coating solution is extruded through the outer orifice A, whereas the PSf solution is extruded simultaneously through channel B. Channel C is used for the bore liquid. Two gear pumps are used to control the flow velocity of both polymer solutions. After a short contact inside the spinneret, the solutions enter the air gap between the spinneret and coagulation bath followed by solidification in the coagulation bath. In the air gap, heat enhanced drying might be applied as well. A convective drying chimney or infra-red (IR) radiation are used as the drying techniques as seen in Fig. 3. The chimney is kept at constant temperature by a silicon oil bath. At the same time, pre-heated nitrogen gas flushed through the inside of the chimney with a laminar flow. A mixture of NMP and water with weight ratio of 3:1 is used as the bore liquid. The fibers are cut into pieces of 60 cm and rinsed with tap water for 48 h. The fibers are then immersed in 20 wt.% glycerol/water solution for another 24 h and then allowed to dry in the air.

## 2.7. Characterization of permeation properties

All permeation properties are measured for two membrane samples. For gas permeation characterisation, six co-extruded hollow fibers are dried in air and potted at the end with one side open at a length of 20 cm. Helium, nitrogen and carbon dioxide permeation is measured at room temperature  $(22 \,^{\circ}C)$  at a pressure of 0.4–1.0 bar gauge.

For ion retention permeation experiments, two wet fibers of 38 cm are potted into a glass housing. Test solutions are circulated through the lumen of the fiber and the permeation is collected from the outside. The solutions are sodium sulfate, copper sulfate, methyl green, sunset yellow, and procion blue at a concentration of 500 ppm, respectively.

To perform the supported liquid membrane experiment (set-up is described in detail in [26]), two dried hollow fibers of 38 cm are potted into a glass housing. LIX84-I diluted in dodecane at 20 vol.% is used as organic extractant. A 0.025 M CuSO<sub>4</sub> solution is used as the feed and a 2 M H<sub>2</sub>SO<sub>4</sub> solution as the strip. The total volume of both feed and strip is 200 ml. The aqueous phases flow parallel along the fiber with the strip solution at the shell side and the feed at the lumen side. The flow velocity of feed and strip is 1.86 and 0.094 m/s, respectively. The temperature is kept at 25 °C. The concentration of the feed and strip is determined by taking seven samples in 7 or 8 h interval and analysed by atomic absorption spectrometry

Table 2

Screening and	l proof-of	f-principle	experiments
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(Spectra 10, Varian, Houten, The Netherlands). The copper flux is calculated from the slope of the copper concentration versus time.

#### 2.8. Scanning electron microscopy

Samples for SEM (JEOL JSM-T220A) are prepared by cryogenic breaking of the fresh wet films or fibers. Samples are allowed to dry under vacuum at 30 °C for overnight and then coated with a thin gold layer. Samples for FESEM (Hitachi S800) are coated with an Au/Pd layer at a thickness of approximately 4 nm.

#### 3. Results and discussion

#### 3.1. Screening and proof-of-principle experiments

The initial concept of preparing the SPES coated PSf hollow fiber membrane was based on accelerated drying of a low concentration solution of SPES using a convective evaporation chimney or infra red light. During drying, the polymer concentration in the polymer solution increases, resulting in a thin coating layer. Table 2 summarises a variety of experiments performed based on this concept. Major problems are the integrity of the coating layer and the adhesion of the coating layer onto the support. Several conclusions can be drawn from these spinning experiments:

SPES (wt.%)	Drying method		Outside surface	Adhesion
	Process	Temperature (°C)		
4	IR radiation	(-)	Uneven surface, holes	Separated
		52	Numerous holes	Separated
6	Chimney	70	Cracks, dispersed holes	Separated
		90	Uneven, less cracks	Separated
	IR radiation	(-)	Uneven, less cracks	Separated
		(-) <sup>a</sup>	Big cracks and holes	Separated
	(-)	(-)	Numerous holes	Separated
10	IR radiation	(-)	Holes, small cracks	Small part attached
16	IR radiation	(–) <sup>b</sup>	Smooth with dispersed holes	Partly separated

(-) not available. Spinning parameters: coating solution, SPES/NMP/acetone; NMP/acetone ration, 50/50; coating solution flow rate, 1.3 ml/min; air gap, 200 mm; spinning rate, 6 m/min; chimney length, 200 mm; IR radiation, IR lamp.

<sup>a</sup> Without acetone.

without acetone.

<sup>b</sup> The membrane became brittle after drying. All other membranes showed brittleness of the coating layer but the hollow fibers were still tough.

- increasing the chimney temperature results in a coating layer with less mechanical defects;
- infra-red radiation results in an improved layer, but the surface smoothness is still insufficient;
- addition of volatile solvent (acetone) improves the surface integrity;
- increase of the SPES concentration improves adhesion and integrity of the coating layer, however, the fiber becomes brittle upon drying.

From these screening experiments, we encounter two major problems related to co-extrusion of SPES onto PSf solution: (a) the mechanical property and integrity of the SPES thin coating layer; and (b) the insufficient adhesion between the coating layer and the support. The first problem results in cracks and holes on the outer fiber surface (SPES). For the second problem, the thin layer tends to separate from the support layer in some cases. In the following parts, we address both problems separately: firstly, the mechanical properties of the SPES film is investigated to find a relationship between mechanical properties and casting solution composition; secondly, adhesion of SPES layer onto the PSf layer is investigated with a co-casting process. Finally, co-extrusion experiments are carried out based on the knowledge gained from the experimental series.

## 3.2. Mechanical stability of SPES films

In general, the hydrophilic SPES films coagulated in a water bath show mechanical instability upon drying. Initially, the films are soft because of the gel-like structure containing water. Upon drying, water slowly evaporates from the membrane resulting in a brittle structure. Visual observation of these films gives qualitative information (see Table 3). In the wet

Table 3 Observation of SPES films in wet and dry state

SPES concen- tration (wt.%)	Wet state	Dry state
10	Opalescent, soft	Clear, brittle
15	Opalescent, soft	Clear, brittle
20	Opalescent, flexible	Clear, brittle
25	Opaque, flexible	Clear with droplets, rigid
30	Opaque, tough	Clear with droplets, rigid
35	Opaque, tough	Clear with droplets, tough

state, the films cast from a solution with a concentration less than 20 wt.% are opalescent and extremely soft. It is rather difficult to remove these films from the glass plate without breaking. Upon drying in an ambient environment, these films become so brittle that they break into small pieces upon a gentle touch. By increasing the polymer content above 20 wt.%, tough and flexible films are obtained when the films remain wet. However, at dry state, a SPES concentration up to 35% is necessary to obtain a tough film. This information is significant for the spinning process: the coating is located on the outside of the fiber and therefore it should be strong enough to withstand the friction from conducting rollers and possible stretching. On the other hand, it is required that the composite fiber should be mechanically stable at dry state. As indicated by the initial experiments, the composite fibers become brittle when the coating layers are brittle and show good adhesion to the support. Therefore, the coating layer itself needs mechanical stability. These experimental considerations indicate that a high SPES content is required.

To quantify the mechanical properties, the single cast SPES films are dried in air and their stress-strain behaviour is tested. Fig. 4 shows the stress-strain behaviour of two SPES films with the concentration of 30 and 35 wt.%, respectively. It can be seen that a 5 wt.% increase of SPES concentration influences the mechanical failure behaviour significantly. Films from a 30 wt.% solution show a lower fracture stress, of about 24.1 MPa compared to 32.0 MPa for the films from a 35 wt.% solution. Moreover, the maximum



Fig. 4. Tensile test of SPES/NMP films made from SPES/NMP solutions coagulated in water.

strain before film rupture increases from 1.23 to 3.56%. The initial stress for the 30 wt.% film is higher than that of the 35 wt.% film because of difference in thickness. The significant change of mechanical properties indicates that concentration increase transforms an extremely brittle film to a more flexible one.

Fig. 5 shows the micro-structure in the middle part of SPES films coagulated in water with different SPES concentrations in the solution. Films from a 20 wt.% solution (Fig. 5(a)) show a nodular structure with only weak bridges between the nodules. The nodules are about 40-60 nm (including about 4 nm platinum coating). Films cast from a 30 wt.% solution have a similar structure with stronger interconnections between the nodules having the appearance of local melting upon contact. With a SPES concentration of 35 wt.%, an interconnected cellular structure is obtained which is completely different from the other two. A further proof of improved mechanical toughness is the bright and fluffy structure observed in the photo, probably caused by the plastic deformation of the cell walls upon breaking. We interpret the transition from the nodular to cellular structure to be responsible for the mechanical strength increase with the increase of polymer concentration. Unfortunately, the solutions with a concentration above 30 wt.% SPES cannot be used for double-film casting or co-extrusion spinning due to its high viscosity. With this in mind, we proceed to experiments with the highest SPES concentration of 30 wt.% in the coating solution since the 30 wt.% SPES solution can form a mechanically stable film at wet state with sufficient mechanical strength at dry state.

# 3.3. Adhesion of SPES layer onto PSf layer

The previous section discussed the first of the two problems encountered in the co-extrusion of hydrophilic materials onto porous hydrophobic support membranes. The second problem, interlayer adhesion, is addressed below by performing a systematic study in double-layer casting of flat membranes. The support membrane is based on a PSf/NMP solution of 25 wt.%. Furthermore, the influence of an additive (diethylene glycol) will be investigated as well. The additive acts as a non-solvent and results in a more rapid demixing of the support membrane [27], which may influence the adhesion.



Fig. 5. FESEM pictures of SPES films prepared from immersion of SPES/NMP: (A) 20 wt.%; (B) 30 wt.%; (C) 35 wt.%, solution in a tap water at room temperature. Casting thickness: 50 μm.



Fig. 6. Adhesion of SPES/NMP solutions and SPES/NMP/acetone solutions on PSf/NMP 25 wt.% solution. Arrow refers to the coating layer. (A, C, E), SPES/NMP solution at 20, 25, 30 wt.%; (B, D, F), SPES/NMP/acetone solution at 20, 25, 30 wt.%; NMP/acetone ratio: 50/50.

# 3.3.1. Effect of polymer concentration and volatile co-solvent in coating solution

Fig. 6 and Table 4 summarise the results of a systematic parameter study. At a low concentration of SPES in the coating solution, the coating layers completely separate from the PSf support. In fact, the coating layers are already separated even in the

wet state. Using coating solutions of 25 wt.% SPES, the adhesion improves considerably. The SPES film partly separates but the area with good adhesion is larger than the delaminated area. We attribute this to a lateral heterogeneity in the phase separation kinetics. With a further increase of SPES concentration to 30 wt.%, an excellent adhesion of SPES to PSf

Support	Coating solution	ution (wt.%)		Wet state	Dry state	
	SPES	NMP	Acetone			
A	20	80	(-)	Separated	Separated, SPES film brittle	
	25	75	(-)	Good adhesion	Good adhesion, brittle	
	30	70	(-)	Good adhesion	Not brittle, neither flexible	
	20	40	40	Separated	Separated	
	30	35	35	Good adhesion	Good adhesion, not brittle	
В	20	80	(-)	Separated	Separated, brittle	
	30	70	(-) <sup>a</sup>	Good adhesion	Good adhesion, not brittle	
	30	70	(-) <sup>b</sup>	Separated	Separated	
	20	40	40	Separated	Separated	
	30	35	35 <sup>a</sup>	Good adhesion	Partly separated	
	30	35	35 <sup>b</sup>	Separated	Separated	

Table 4 Adhesion and mechanical properties of double layer films cast from SPES solutions on PSf solutions

Support solution A: PSf/NMP 25/75 wt.%. Support solution B: PSf/NMP/DEG 17/52.4/30.6 wt.%.

<sup>a</sup> In a controlled condition with humidity of 15%; support solution was still clear.

<sup>b</sup> In the ambient condition; support solution was already demixed before casting the second layer.

is obtained. The phenomena can be qualitatively understood by a decrease of water diffusion into the interface between SPES and PSf solution. As listed in Table 5, a SPES 30 wt.% solution in NMP has viscosity at zero shear rate of 22000 cP; whereas the viscosity at 25% is 6300 cP, less than one third of the former: an extremely low viscosity of a 20 wt.% solution is found being 380 cP. For a simplified estimation, the Stokes-Einstein equation gives an inverse relationship between diffusion coefficient D and viscosity. Therefore, the approximate ratios of water diffusion coefficients in a 30 wt.% and a 25% solution are 1.7 and 6.0% of that in a 20 wt.% solution. We hypothesise that the polymer chains can diffuse freely resulting in a entangled "interdiffusion" layer as long as no water reaches the interface. This "interdiffusion" stops when the non-solvent (water) reaches the solution forming the porous support membrane. Hence, the longer time available given for the diffusion, the

Table 5

Viscosity and estimated diffusion coefficients of SPES solutions at zero shear rate

SPES concentration (wt.%)	Viscosity (cP)	Ratio of estimated diffusion coefficients
20	380	1.0
25	6300	0.06
30	22000	0.017

Solvent: NMP; temperature: 25 °C.

better the adhesion. SPES/NMP solution of 30 wt.% is the most viscous solution resulting in the slowest water inflow and the best adhesion for the final double layers. The authors are aware that the same argument of slow diffusion with increasing polymer concentration holds for the polymer interdiffusion. However, this extremely complex phenomenon is beyond the purpose of this paper and requires more work.

When acetone is added into the coating solution, only the 30% solution shows good adhesion to the support. The coating layer prepared from a 20 wt.% solution is brittle and damaged by sample preparation. For a coating solution of 25 wt.%, the coating layer delaminates from the support and thus, only the bottom side of the SPES layer is observable. Nevertheless, an increase of the SPES concentration results in a better adhesion.

#### 3.3.2. Effect of the solvent in the support solutions

A support solution of PSf/NMP forms a relatively dense layer indicated by finger structures and closed cells. Non-solvent additives can make the support open by decreasing the "solvent power" of the support solution [28]. However, this change in support solution may affect the adhesion between the coating layer and the support membrane.

A rapidly demixing PSf/NMP solution can be achieved by adding diethylene glycol up to 30.6 wt.%. Within less than 2 s, the solution becomes white only



Fig. 7. SEM photos of double layer films from (A) SPES/NMP, 30 wt.%; (B) SPES/NMP/acetone, 30/35/35 wt.%. Support solution: PSf/NMP/diethylene glycol, 17.0/52.4/30.6 wt.%. Arrow refers to the coating layer.

being in contact with ambient air having a humidity of about 55%. As seen in Table 4, after exposing this solution to air for 10 s, the coating solution of SPES/NMP 30 wt.% does not adhere to PSf. However, under controlled environment with a humidity less than 15%, this coating solution shows a good adhesion to the support layer. Quite similar results are shown for the adhesion property between the additive-doped support and the original PSf solution. Both SPES/NMP and SPES/NMP/acetone solutions at 30 wt.% show a very good adhesion to the PSf/NMP/ DegOH layers as can be seen in Fig. 7(A). Moreover, a much more porous support structure is obtained compared to the original solution without loss in adhesion property.

The double-layer casting of flat sheet membranes reveals that an increase of the SPES concentration results in a mechanically stable and good adhering coating layer. Adhesion is not influenced by the additive inside the support solution if the environmental humidity is at a low level. The next paragraph describes the co-extrusion of composite hollow fibers based on these observations. Diethylene glycol is added into the support dope to prepare an open support membrane.

#### 3.4. Spinning of double-layer membranes

As seen in Fig. 8, six membranes are prepared from a SPES/NMP and SPES/NMP/acetone solution respectively and a SPES concentration of 20, 25, 30 wt.%. With respect to the SPES/NMP coating solution, a concentration increase from 20 to 30 wt.% shows a large improvement in adhesion. With an air gap of 30 mm, the contact time between coating and support solutions is about 0.3 s at a spinning speed of 6 m/min. In such a short time interval, the concentration effect is a predominant factor. The lowest SPES concentration results in a separated coating layer as shown in Fig. 8(A). A SPES concentration of 25 and 30 wt.% results in composite membranes with good adhering layers. The coating solutions containing acetone give also very well adhesion. However, a concentration as low as 20 wt.% appears to be insufficient.

Composite hollow fiber membranes show high flexibility in both wet and dry state after immersion in glycerol. However, without any glycerol addition, the membranes become brittle upon drying when the coating concentration is lower than 25 wt.%. Mechanically stable composite membranes are obtained when the SPES concentration is 30 wt.% as shown in Table 6. In the dry state, the composite membrane shows the similar mechanical properties as the coating layer itself and the fiber no longer maintains the flexibility of the support structure. We, therefore, conclude a similarity in mechanical behaviour between the coating layer material (see single layer experiments) and the composite structure.

# 3.5. Separation performance of the composite hollow fibers

The composite fibers are used as supported liquid membranes for copper transport. We anticipate the co-extruded membrane to have improved life-time performance as a stabilised supported liquid membrane



Fig. 8. SEM photos of SPES/NMP and SPES/NMP/acetone coatings. (A, C, E), SPES/NMP coating layers with a polymer content of 20, 25, 30 wt.%, respectively; (B, D, F), SPES/NMP/acetone coating layers with a polymer content of 20, 25, 30 wt.%, respectively. Arrow refers to the coating layer, spinning speed: 6 m/min, air gap: 30 mm, flow rate: 0.43 ml/min, temperature:  $21 \pm 0.5$  °C.

as well as a relatively high flux. The PSf support membrane without the coating has a flux of  $5.1 \times 10^{-9}$  mol cm<sup>-2</sup> s<sup>-1</sup>, which is comparable to porous microfiltration membranes such as Accurel or Celgards [26]. However, an extremely low flux for Cu<sup>2+</sup> is obtained being  $0.15 \times 10^{-9}$  mol cm<sup>-2</sup> s<sup>-1</sup> for the

composite membrane made from a coating solution of 30 wt.% (with a coating layer thickness of 2  $\mu$ m). This low copper flux for the composite membrane is caused by the low ion exchange capacity of the SPES top layer, which exhibits a high resistance towards the transport of copper ions. Clussen

Table 6 Mechanical behaviour of the composite hollow fiber membranes Conting colution Wat Der

composition (wt.%)		wet	Diy	Olycelol	
SPES	NMP	Acetone			
(-)	100	(-)	Flexible	Flexible	Flexible
20	80	(-)	Flexible	Brittle	Flexible
25	75	(-)	Flexible	Brittle	Flexible
30	70	(-)	Flexible	Rigid	Flexible
20	40	40	Flexible	Brittle	Flexible
25	37.5	37.5	Flexible	Rigid	Flexible
30	35	35	Flexible	Rigid	Flexible

Support solution: PSf/NMP/DegOH, 17.0/52.4/30.6 wt.%. Wet state: stored in water; dry state: dried in air. Glycerol: immersed in 20 wt.% glycerol solution for 48 h, then dried in air. Spinning speed, 6 m/min; air gap: 30 mm; coating flow rate: 0.43 ml/min.

Gas permeation experiments are performed with the composite hollow fibers using helium, nitrogen and carbon dioxide (see Table 7). Because the experimentally observed selectivity is high compared to Knudsen selectivity, it is suggested that the SPES coating is a porous layer having pores similar to the free path length of the gases. This is in agreement with FESEM analysis performed on the single-cast SPES layers described earlier.

Finally, the membranes are characterised with respect to their retention and aqueous flux characteristics in pressure-driven applications. Table 8 summarises the permeation experiments for a variety of solutes. All experiments are carried out as single component experiments and the membranes remained in the wet state. HT-SPES-25 is a composite membrane made from a coating solution of SPES/NMP/acetone solution at 25 wt.%. It is more porous than HT-SPES-30, thus all retention values for this membrane are lower than those of the second membrane. Almost all copper

Table 7

Gas permeation results for SPES composite hollow fiber membranes

SPES concentration (wt.%)	Gas pair selectivity				
	$\alpha$ (N <sub>2</sub> /He)	α (CO <sub>2</sub> /He)	$\alpha$ (CO <sub>2</sub> /N <sub>2</sub> )		
	0.38 <sup>a</sup>	0.30 <sup>a</sup>	0.80 <sup>a</sup>		
25	0.85	0.78	0.91		
30	0.78	0.68	0.86		

Coating solutions: SPES/NMP/acetone, NMP/acetone 50/50 wt.%. <sup>a</sup> Knudsen selectivity.

Table 8							
Nanofiltration	results	of SPES	composite	hollow	fiber	membran	es

	-		
Membrane	HT-SPES-25	HT-SPES-30	
Coating solution composition (SPES/NMP/acetone, wt.%)	25.0/37.5/37.5	30.0/35.0/35.0	
Clean water flux $(l m^{-2} h^{-1} bar^{-1})$	8.9–12.9	0.5–0.8	
Solute retention (%)			
CuSO <sub>4</sub>	0.0	6.3	
$Na_2SO_4$	1.2	21	
Methyl green	10	34	
Sunset yellow	12	87	
Procion blue	28	92	

The hollow fiber membranes were kept wet by immersing in a 20 wt.% glycerol water solution.

sulfate and sodium sulfate pass through this membrane, however, retention of 6.3% for CuSO<sub>4</sub> and 20.7% for Na<sub>2</sub>SO<sub>4</sub> are obtained for HT-SPES-30. In addition, charged dye molecules are also used as model compounds. Methyl green is a positive charged dye with a molecule weight of 472.51 Da. Although it is large in size, its retention is low, 10 and 34% for both membranes respectively. For sunset yellow, a negatively charged dye of molecular weight 450.38, a higher retention is obtained, 12% for HT-SPES-25, but 87% for HT-SPES-30. Moreover, the retention for a negatively charged procion blue of  $M_w$  840.12 is even higher; 28% for the first membrane and 92% for the second membrane.

These results can be explained by two factors: steric (sieving) and Donnan effects [29-32]. SPES has sulfonic acid groups on the main chain, and therefore, it rejects solutes with the same charges, i.e. sunset yellow and procion blue. Moreover, it shows a low rejection for positive charged solute, i.e. methyl green. On the other hand, sieving effect contributes as well. HT-SPES-25 membrane is a rather porous membrane compared with HT-SPES-30. Hence, the retention is much higher for HT-SPES-30 than for HT-SPES-25 when the molecule has a comparable hydrodynamic size as the pore size of the coating layer.

#### 4. Conclusions

Integral SPES composite hollow fiber membranes are successfully prepared by co-extrusion of SPES solutions onto PSf solutions. In terms of mechanical and adhesion properties, the SPES concentration in the coating solution is of key importance to obtain a good composite membrane. A nodular to cellular structure is observed when the SPES concentration changes from 20 to 35 wt.% and this corresponds to an improvement in mechanical properties. Adhesion of the coating to the PSf support is also improved by increasing the SPES concentration of the coating solutions.

The composite hollow fiber shows an extremely low copper ion transport in supported liquid membrane system and no selectivity for He/N<sub>2</sub>, He/CO<sub>2</sub> and N<sub>2</sub>/CO<sub>2</sub> in gas separation. The membrane shows low inorganic salt retention and high retention for charged organic dye molecules. The concept of a co-extruded membrane with a ion exchange functionality in the coating layer shows potential to be used as a nanofil-tration membrane as well as a tight hydrophilic ultra-filtration membrane.

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