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Formation of Porous Bilayer Hollow Fibre Membranes

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Summary: Support membranes in bioartificial organs contact blood or plasma on one-side and adhesion dependent cells on the other side. Since membranes for biomedical applications, such as for haemodialysis, are optimised for blood contact and membranes for biotechnological applications for cell contact, there are no membranes available addressing the requirements of artificial organ technology. One approach is the preparation of porous bilayer membranes with a wall consisting of two chemical different polymer layers. Results of the preparation of such membrane types using triple spinnerets and a wet phase inversion process are shown here. It is demonstrated that one of the most important parameter is the structural integrity of the membrane wall at the interface between both layers. A new spinneret construction is presented where the membrane forming polymer solutions are layered in the spinneret before extrusion. As a result porous bilayer hollow fibre membranes with a high structural integrity could be manufactured using different composed polysulfone (PSu) polymer solutions for model investigation.

Introduction

Membranes with specific transport properties are widely used in different separation processes for technical, biotechnological and biomedical applications.[1] Particularly in the medical field, membranes are applied as hollow fibres for blood oxygenation and detoxification, such as artificial lung, haemodialysis, plasmapheresis etc.[2-4] The separation of toxins from human blood is a crucial tool for treatment of kidney diseases but also in cases of hepatic failure. However theses treatments replace only a part of the organ function for a short time.[5,6] As consequences side effects of treatments are observed.[7,8] Hence efforts were made to combine the passive function of membranes or particles in adsorbing or filtering of toxins with the active function of specific organ cells immobilised on membranes in bioartificial organs.[9,10] In contrast to traditional detoxification systems with membranes having only blood or plasma contact, the membranes in bioartificial organs are contacted by blood or plasma on one side and adhesion-dependent cells on the opposite side.[11] Besides suitable separation properties

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these requirements on substrata are main prerequisites for a good function of support membranes in bioartificial organs. Existing prototypes of bioartificial organs like artificial liver use mostly commercial membrane materials such as polycarbonate, polysulfone, polypropylene and other[12] that must be considered as one of the main reasons for the limited life time and the poor performance of already existing devices.[13] Hence new membrane types are required with a blood and a tissue compatible side.

One way to realise such membrane types is the preparation of porous bilayer membranes with a membrane wall composed of two different polymer layers. It is known that such membranes can be generated using so-called double tube in orifice spinnerets (triple spinnerets) which allow a separate transport of two different polymer solutions and the bore fluid in the spinneret. First investigations using such a technique are carried out to prepare bilayer Cuprophan membranes which layers consists of different cellulosic composition[14] including also adsorption materials in the outer membrane layer.[15] These membranes are successfully applied in adsorptive hemodialysis.[16,17] Further investigations showed that the outer slit of the spinneret can be used for a weak nonsolvent to form asymmetric gas separation[18] or ultrafiltration[19] membranes as well as for solvent to generate microfiltration membranes.[20] Moreover, such spinnerets are applied to prepare bilayer gas separation membranes[21,22] and composite membranes[23] for gas separation. However in all cases a dry-wet spinning process was applied at which the formed polymer solution will be extruded in an air gap especially at higher temperature initiating solvent evaporation before contacting the outer coagulation bath. Recently Li et al.[24-26] discussed the preparation of annular hollow fibre membranes, a "bilayer" hollow fibre membrane with separated layers like a fibre-in-fibre construct, prepared by wet spinning process and using double tube in orifice spinnerets. The separation of layers was initiated to use the annular space between the fibre layers as a compartment for encapsulation of liquid membranes or yeast.

However a high integrity of the bilayers in the membrane wall is essential for application of bilayer hollow fibre membranes as support membranes in bioartificial organs. In this study model investigations are carried out to prepare porous bilayer hollow fibre membranes with a high structural integrity using a wet spinning process.

Materials and Methods

Materials: For the preparation of porous bilayer hollow fibre membranes PSu (type: Ultrason S 3010 (BASF, Germany) was used as membrane-forming polymer. To vary the structure of the PSu membranes poly (vinyl pyrrolidone), type K25 (PVP) (Serva, Germany) was used as additive.[27,28]. The polymers were dried 2 h at 140°C under vacuum before used for the preparation of the polymer solutions. The solvent N,N-Dimethylacetamide (DMAc) obtained from Merck, Germany was applied as received. The polymer was solved by heating the composition 2 h at 80°C under stirring.

Preparation of porous bilayer hollow fibre membranes: The hollow fibre membranes were prepared from spinning solutions of different compositions using a wet spinning process. In figure 1 a drawing of the used experimental equipment is shown.

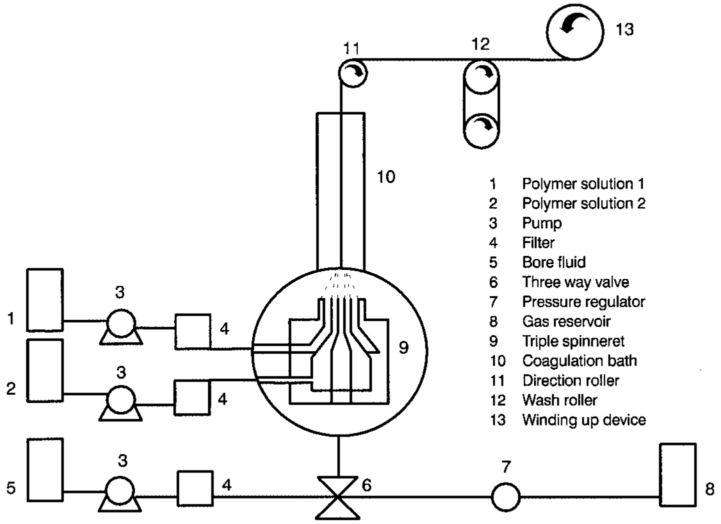

Figure 1. Drawing of the equipment for preparation of bilayer hollow fibre membranes.

The filtered and degassed polymer solutions were transported from the reservoirs (1, 2) with help of gear pumps (3) through a final filter (4) to the spinneret (9). In a similar transport line the bore fluid was conveyed to the spinneret (5, 3, 4, 6 to 9). All three fluids were separately piped in the spinneret (9) to thoses exit, directly extruded into the external coagulation bath (10) at the bath bottom. The nascent hollow fibre membrane was continuously drawn out on the top of the coagulation bath. Then the hollow fibres were washed (12) and reeled up on rolls (13). In a second step the collected fibres were kept in a storage tank filled with tap water for discontinuously washing and stabilising the structure during 12 h. Finally residual solvent were removed continuously by a short-time final washing step at 95°C, fixed to mats and dried at room temperature.

Two different constructed triple spinnerets were checked for preparation of porous bilayer hollow fibres, both fabricated by Wetzel Micro Products, Germany. The conventional spinneret had the dimensions 190 µm/360 µm/600 µm/860 µm/1060 µm (inner diameter of the hollow needle/ inner diameter of the inner space/ outer diameter of the inner space/inner diameter of the outer space/outer diameter of the outer space). The own developed triple spinneret had the dimension of 190 µm/360 µm/560 µm/760 µm (inner diameter of the hollow needle/ inner diameter of the space/diameter between the inner and outer space in the spinneret/ outer diameter of the space). Different spinning conditions were applied to vary the phase inversion process during the formation of the bilayer membranes.

The compositions of the polymer solutions applied in the experiments are summarised in table 1.

Table 1. Composition of the PSu polymer solutions forming the bilayer membranes.

Code	Location in the membrane wall	PSu [w.-%]	PVP [w.-%]	Solvent [w.-%]
1	inner layer	20	20	60
	outer layer	15	5	80
2	inner layer	18	12	70
	outer layer	15	0	85
3	inner layer	18	12	70
	outer layer	18	12	70
4	inner layer	18	12	70
	outer layer	15	5	80
5	inner layer	20	20	60
	outer layer	18	6	76

The codes of this table are identical with the numbers in the SEM micrographs.

Characterisation of the phase separation behaviour in solution: A qualitative evaluation of the miscibility of the applied polymer solution combination was carried out. Both polymer solutions were mixed in a weight ratio of 1:1 at 60°C for 2 h. Mixed polymer solutions were centrifuged and the phase behaviour visually estimated.

SEM characterisation of the membrane morphology: Morphology of the bilayer hollow fibre membranes was examined by scanning electron microscopy (SEM) (JSM 6400-F field emission SEM, Joel, Japan). The fibres were first immersed in liquid nitrogen, frozen, fractured, positioned on a metal holder and coated with gold/palladium (80/20) using sputtering in vacuum. The investigation was carried out at an acceleration voltage of 5 kV. The following codes are applied and integrated in the SEM pictures: a - cross section, b - cross section at a larger magnification, c - interface between both polymer layers of the membrane wall.

Results

Prerequisites for the preparation of bilayer hollow fibre membranes with a high structural integrity are a suitable triple spinneret and partial or complete compatible polymer solutions forming the membrane wall. A high structural integrity of the membrane wall can only be expected if the applied polymer solutions are partly or completely compatible in the solved state. However it is well known that different composed polymer solutions can form phase boundaries provided by a positive free energy of mixing.[29,30] The formation of phase boundaries is the usual situation if different kinds of polymers are mixed in a solved state. A better chance of miscibility is given by mixing of different composed polymer solutions containing the same basic polymer as investigated here. Hence the compatibility of the investigated polymer solution systems was experimentally estimated by mixing experiments. Phase boundaries were not observed which is a good prerequisite for manufacture of bilayer membranes with a high structural integrity.

Figure 2 shows a schematic drawing of a triple spinneret necessary for the preparation of a bilayer hollow fibre. Characteristic for such a spinneret is that besides the separate conveying lines of the bore fluid both polymer solutions can be separately transported inside of the spinneret to their exit. The different polymer solutions get together at the exit of the spinneret. At the same time the bore fluid contacts the inner polymer solution to stabilise the shaped solution composite or to initiate phase separation.

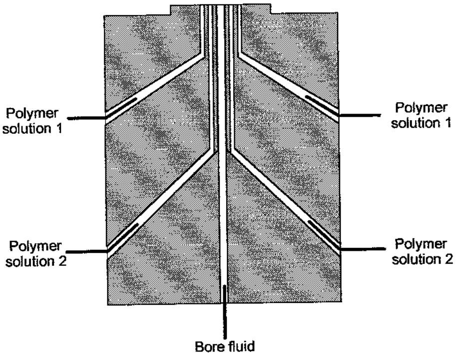

Figure 2. Build up principle of a conventional triple spinneret (schematically) applied for the preparation of bilayer membranes.

"Bilayer" hollow fibre membranes were prepared from PSu polymer solutions varying in the polymer concentration and the content of PVP using such a constructed spinneret. Typical SEM photographs of the membrane wall are depicted in figure 3.

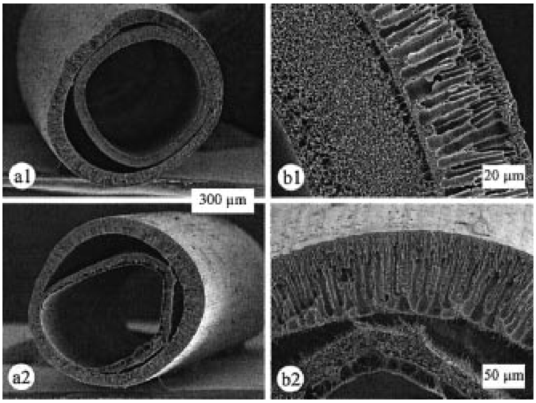

Figure 3. Typical SEM morphologies of "bilayer" membranes prepared using the triple spinneret of figure 2 and different composed PSu polymer solutions (numbers according table 1 and description in SEM characterisation).

Different polymer layers with different morphology were formed but between the layers an annular space like a fibre-in-fibre construct is generated at which the inner fibres adhere only at small areas to the outer fibre. Therefore the membrane wall does not show any structural integrity between the layers, the most important parameter characterising bilayer membranes.

In order to find out the reasons causing this unexpected behaviour further experiments were carried out. The membrane wall was prepared using polymer solutions of the same composition. Such conditions are principally identical with the situation during the formation of conventional "monolayer" hollow fibres using only one polymer solution. The results are depicted in figure 4 for hollow fibre membranes prepared by applying a solvent containing coagulation system (bore fluid: 80 w.-% solvent, coagulation bath 70 w.-% solvent) and a solvent-free coagulation system (bore fluid and coagulation bath: water).

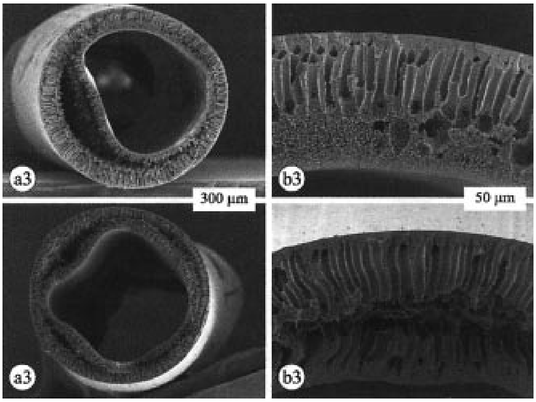

Figure 4. SEM morphology of "bilayer" hollow fibres prepared using polymer solutions of the same composition (top: solvent containing coagulation conditions; bottom: solvent-free coagulation conditions).

The pictures demonstrate that the resulting hollow fibres do not exhibit a complete adherence of both polymer layers. This can be clearly seen in the cross sections (a). It seems that the contact of both polymer solutions forming the membrane wall is not intensive enough before gelation of the shaped solutions.

During the preparation of bilayer membranes two different single processes have to be considered: the contact of polymer solutions forming the membrane wall and their phase inversion. If the contact is incomplete or too short a strong adherence of both layers can not be expected. The phase inversion of both polymer solutions solidifies the real state of contact, if there are no shrinking differences of both layers. The last aspect is practically realised in our investigated system. The decoupling of both single processes should permit a longer contacting time and, therefore a better contact of the polymer solution before phase inversion. One the other hand, the intensity of the contact should be increased if it is carried out under pressure. In realisation of both requirements a modified triple spinneret was developed. The construction principle is shown in figure 5. This spinneret realises the same separate conveying lines for bore fluid and both polymer solutions as the spinneret shown in figure 2. However the polymer solution streams are layered inside the spinneret side by side and are transported as polymer solution composite to the exit of the spinneret. During this transport an intensive contact of both solutions under pressure is possible. Furthermore, the contact of polymer solutions and the phase separation step are decoupled: The contact is realised before phase inversion and a stable polymer solution composite can form.

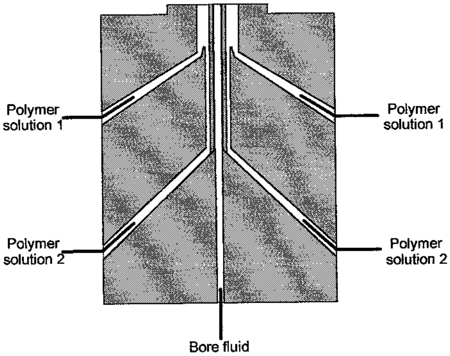

Figure 5. Construction principle of the modified triple spinneret (schematically).

PSu polymer solutions were applied to manufacture bilayer membranes under different coagulation conditions using the modified spinneret. Typical SEM morphologies of selected bilayer membranes are shown in figure 6.

In the upper part of figure 6 the "bilayer" hollow fibre membrane was prepared using the same polymer solution composition for both layers and water as bore fluid and coagulation bath. The micrographs prove the intense adherence between both layers. The membrane wall reveals a high structural integrity (a, b). Any structural differences in the morphology at the interface between both layers were not observed (c).

In the central part of figure 6 different composed PSU solutions are used which generate a more macrovoidal and a more sponge-like morphology if water is applied as coagulation bath and a solvent containing (80 w.-%) bore fluid. A bilayer hollow fibre membrane with a high structural integrity could be prepared under the applied spinning conditions (a,b). A strong difference in the morphology at the interface between both layers is documented in figure 6c.

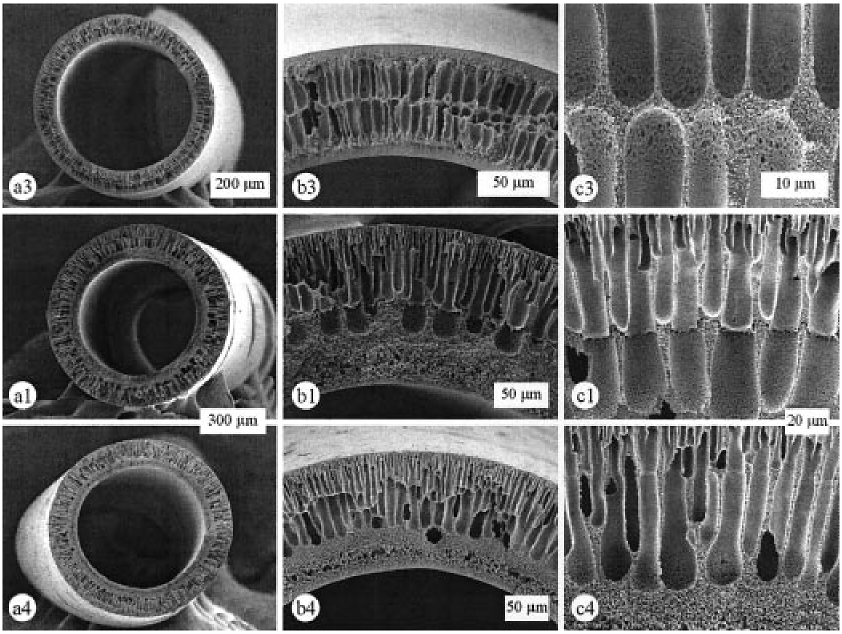

Figure 6. Typical SEM morphologies of bilayer membranes prepared using the modified triple spinneret of figure 5 and different composed PSu polymer solutions (numbers according table 1 and description in SEM characterisation).

A bilayer hollow fibre membrane, which was prepared using different composed PSU solutions with lower polymer concentration and coagulation conditions according to the middle part bilayer membrane is depicted in the bottom part of figure 6. Also under such conditions a high structural integrity of the bilayer hollow fibre (a,b) and a structural difference in the morphology at the interface (c) can be detected.

Summary and Outlook

Investigations were carried out to manufacture bilayer hollow fibre membranes by use of triple spinnerets and application of a wet spinning process. The bilayer membranes described in this paper possess a membrane wall composed of two different polymer layers. Bilayer membranes can be formed from two polymer solutions differing in the polymer concentration, the additive content and the solvent as well as the kind of polymer. In this work different composed PSu polymer solutions were applied differing in the polymer concentration and the additive content. The miscibility of the used polymer solution combinations without phase boundaries was shown qualitatively.

Therefore a successful manufacture of bilayer hollow fibre membranes with high structural integrity was expected. Despite suitable prerequisites with respect to the polymer solution properties, bilayer hollow fibre membranes with a strong structural integrity could not be prepared using a wet spinning process and conventional triple spinnerets. The same result was also obtained if both polymer solutions had the same composition. This unexpected behaviour was caused by the construction of the spinneret, which do not allow an intense and long-time contact of the different polymer solution before coagulation. Therefore a new spinneret was developed which realise an intensive contact of the polymer solutions by layering both solutions side by side inside the spinneret and their extrusion as a polymer solution composite out of the spinneret. In addition to the better contact of the different polymer solutions, solution contact and coagulation process were separated. Using the modified spinneret bilayer hollow fibre membranes with a high structural integrity from different polymer solution compositions could be successful prepared.

The manufacture of bilayer hollow fiber membranes described here offers many possibilities to design membranes with optimal structural and surface properties and therefore new fields of membrane application should be opened in future. One use discussed in the introduction is their application as support membrane for biohybrid organs. One the other hand such membrane types could be provided for application in technical and biotechnological fields where special membrane morphologies are necessary.

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