



High-performance and durable reverse osmosis (RO) membranes

with BASF's polysulfone (PSU) Ultrason® S

Processing guide



Contents

ULTRASON® S FOR REVERSE OSMOSIS MEMBRANES	04
REVERSE OSMOSIS MEMBRANE TECHNOLOGY	05
DESIGN AND MATERIAL SELECTION FOR HIGH-PERFORMANCE THIN FILM COMPOSITE REVERSE OSMOSIS MEMBRANES	06
THE INFLUENCE OF THE RAW MATERIAL PROPERTIES AND THE CASTING PARAMETERS ON THE PSU SUPPORT LAYER	08
Material properties of Ultrason® S	09
Preparation of PSU casting solution	11
Critical casting parameters of the PSU support layer influencing the reverse osmosis membrane performance	12
TROUBLESHOOTING FOR PROBLEMS IN REVERSE OSMOSIS MEMBRANE MANUFACTURING	16

Ultrason® S for reverse osmosis membranes

The polysulfone (PSU) Ultrason® S is one of BASF's polyarylethersulfone grades. The high purity material is established as a global benchmark for the production of a homogeneous and durable porous support layer in nanofiltration (NF) and reverse osmosis (RO) membranes while maintaining a stable and high throughput production output with less downtime for cleaning (Figure 1). Other applications for Ultrason® S include ultrafiltration (UF) and microfiltration (MF) membranes used in gas separation, food and beverage as well as water treatment in flat sheet or hollow fiber configurations.

Advantages of Ultrason® S:

- Low cyclic oligomer content and contamination level
- Suitable solution viscosity range for production of NF/ RO support layer
- High molecular weight with a narrow molecular weight distribution
- Strong adhesion with the selective (PA: polyamide) and backing layer (polyester) under low or high pressure

Key success factors:

- **Selection of PSU material:** purity, solution viscosity, molecular weight and molecular weight distribution, and oligomer content
- **Step-by-step preparation of the casting solution:** drying, formulation, and mixing
- **Control of casting parameters:** casting thickness, casting speed, coagulation bath temperature, ambient temperature and humidity level, and residual solvent in the coagulation bath



Fig. 1: Ultrason® S 6010

The interfacial polycondensation to form the polyamide layer has been widely discussed in scientific journals and patents. The non-woven backing layer is typically sourced from specialized external suppliers. However, the selection of a high-quality PSU material and substantial casting know-how to create the PSU layer on top of a (non-)woven substrate has not yet been reviewed systematically. This guide will give you an overview on how to manufacture high-quality RO membranes made of BASF's PSU Ultrason® S in a continuous production.



Ultrason® S

RO membrane technology

RO membrane technology, which uses pressure greater than the osmotic pressure in the opposite direction of feed water to remove salts, is one of the most well-known and economic separation technologies for a wide range of applications. These include:

- tap water and brackish water purification
- seawater desalination
- chemical processing
- food and beverage filtration
- waste water treatment

Feed solutions with a very low (below 50 mg/l) to a very high salinity (over 55,000 mg/l) can be treated with RO membranes as summarized in Table 1.

To date, thin film composite (TFC) RO membranes are widely used and more popular than cellulose acetate (CA) RO membranes due to their higher water flux and rejection as well as better chemical resistance. Due to variations in the feed water properties, RO membrane elements have to withstand not only high operating pressure but also adverse chemical conditions such as a wide operating pH range from 2 to 11, including an intermittent cleaning at pH 1 and pH 13.

The membrane material selection, membrane configuration, and module design are critical for a high performance RO system: high production rates of clean water with low energy consumption, low fouling, and long membrane lifetime.

Salinity Range	Type of Feed Water	Typical RO Operating Pressure (bar)
Very low ≤ 50 mg/l	High purity water (HPW) Ultrapure water (UPW)	2-3
Low salinity 50 - 500 mg/l	Tap water/household	2-4
Medium salinity 500 - 15,000 mg/l	Groundwater Brackish water Waste water/tertiary effluent	10-20
High salinity 35,000 mg/l or above	Seawater	50 and above

Table 1: RO operating pressures for various types of feed water

Ultrason® S

Design and material selection for high-performance thin film composite RO membranes

A typical structure of a TFC RO membrane consisting of three layers is shown in Figure 2. The layers can be tailored and optimized individually to achieve the targeted performance:

- dense polyamide selective skin layer, formed by interfacial polycondensation (IP)
- porous substrate layer, made of PSU material
- backing layer, typically made of polyester

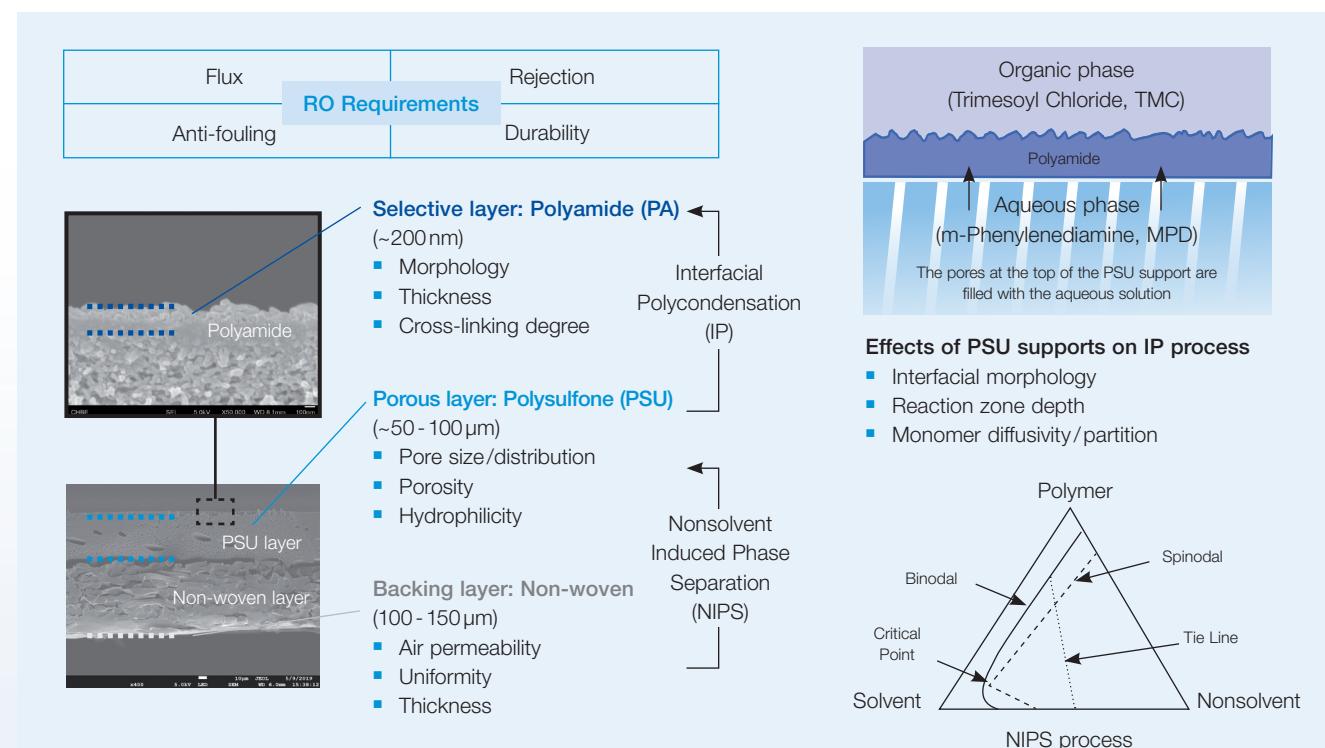


Fig. 2: Schematic diagram of a thin film composite (TFC) RO membrane

The polyamide thin film formed by an interfacial polycondensation reaction is the main functional layer that governs the overall RO performance including water flux and salt rejection. In terms of properties, a more hydrophilic and smoother polyamide surface is typically preferred in order to minimize the tendency toward fouling and to reduce the cleaning frequency.

The underneath supporting layer made of PSU is a critical part: its morphology and surface chemistry play an important role in the formation of the thin polyamide layer. Furthermore, while this layer should provide a good mechanical support for the RO membrane against pressure, it should not create an additional resistance to the water transport across the RO membrane.

Finally, the texture uniformity of the backing layer is important to form a defect-free RO membrane. A stable and good quality of the backing layer with minimum variations is very critical, particularly for high pressure applications such as seawater desalination. An inconsistent backing layer quality is not only leading to fluctuations in the properties of the polyamide and PSU layers but also reduces the durability and lifetime of RO membranes.

Ultrason® S

The influence of the raw material properties and the casting parameters on the PSU support layer

The porous PSU support layer is normally formed by a non-solvent induced phase separation (NIPS) process. The raw-material properties, formulation and casting parameters determine its main properties and performance, such as surface pore size and pore size distribution, porosity and hydrophilicity. The main influencing parameters in context of the PSU layer are described in Figure 3.

During the interfacial polycondensation process of the polyamide layer, the pores on the top surface of PSU layer are filled with m-phenylenediamine (MPD) in aqueous solution and covered with a solution of trimethylchloride (TMC) in an organic solvent (Figure 2). At the interface between aqueous and organic solution, the reaction to form the polyamide takes place.

As a result, the properties and structure of the PSU layer need to be precisely tailored to optimize the interfacial morphology, the reaction zone depth and the monomer diffusivity.

Raw Material	Processing Parameters	
<ul style="list-style-type: none">▪ Solution viscosity▪ Molecular weight▪ Molecular weight distribution▪ Low contamination level	<ul style="list-style-type: none">▪ Casting thickness and speed▪ Coagulation bath temperature▪ Ambient temperature▪ Humidity level	
Key Requirements for PSU Support Layer		
Structure	Surface Properties	Stability
<ul style="list-style-type: none">▪ Pore size▪ Pore distribution▪ Porosity▪ Thickness	<ul style="list-style-type: none">▪ Surface charge▪ Hydrophilicity▪ Interfacial tension▪ Smoothness	<ul style="list-style-type: none">▪ Thermal resistance▪ Mechanical resistance▪ Chemical resistance▪ Anti-fouling

Figure 3: Overview of raw material properties and processing parameters influencing the PSU support layer performance

Material properties of Ultrason® S

Physical properties

Ultrason® S 6010 is supplied as transparent round shaped pellets with very little color and low contamination level. The high purity material reduces the frequency of filter cleaning and downtime in the RO membrane production process, which results in a higher production output for RO membrane manufacturers.

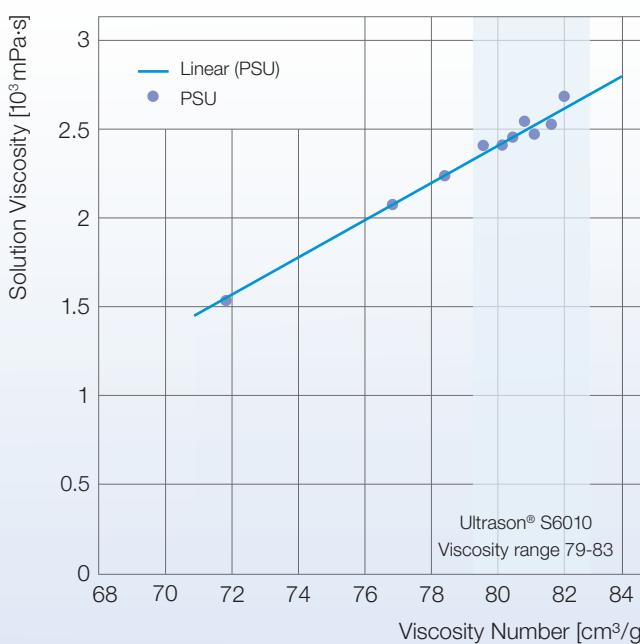


Fig. 4: Correlation between viscosity number (VN) and solution viscosity of Ultrason® S 6010

Solution viscosity

Ultrason® S 6010 (specified Viscosity Number range: 79 to 83 ml/g) corresponds to a solution viscosity of typically 2,500 mPa·s (tested with 25 wt% of PSU in Dimethylacetamide/DMAc solvent at 40 °C) as shown in Figure 4.

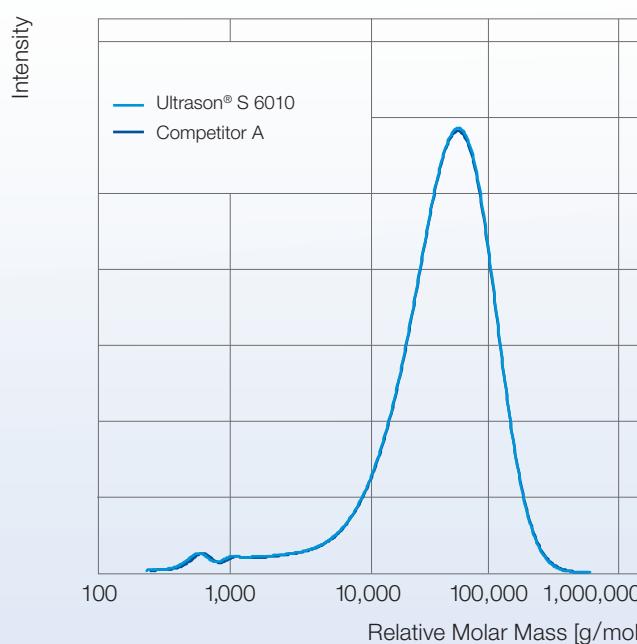


Fig. 5: Molecular weight and molecular weight distribution of PSU from Competitor A and of Ultrason® S 6010

Molecular weight distribution

High molecular weight PSU is preferred for the RO support layer in order to provide sufficient mechanical strength against pressure. A narrow molecular weight distribution of the PSU material is also important to ensure more uniform pore size and porosity in the support layer leading to a homogeneous and defect-free polyamide layer. The molecular weight and molecular weight distribution of Ultrason® S is about 62,000 Da with a narrow dispersity of 4.3 (Figure 5).

PSU Material	Mn (g/mol)	Mw (g/mol)	Dispersity (Mw/Mn)
Ultrason® S 6010	14,400	62,000	4.3
Competitor A	14,700	62,500	4.3



Oligomer content and stability of PSU solution

Ultrason® S 6010 is optimized for a low cyclic oligomer content. Cyclic oligomers show a strong tendency to form crystals in the spinning/casting solution. This is detrimental to the membrane manufacturing process and the performance of the membrane. A reduced cyclic oligomer content improves therefore

- the stability of the casting solution (restarts of production after interruptions possible)
- the stability of the membrane production process (less process disruption and lower frequency of filter and piping cleaning)
- a defect-free formation of the membrane surface

The stability of the polymer solution during storage is influenced by the content of oligomers. Figure 6a shows the turbidity of a 25wt% PSU polymer solution dissolved in dimethylformamide (DMF) as a solvent, after five days of storage at 80 °C. The turbidity of the PSU solution made of competitor A increases significantly after one week while the solution of Ultrason® S 6010 stays mostly clear. Table 2 shows that the turbidity value of competitor A solution is much higher when compared to that of Ultrason® S 6010 after seven days of storage.

PSU Source	Turbidity [NTU]	
	Day 0	Day 7
Ultrason® S 6010	14	49
Competitor A	10	233

Table 2: Stability of PSU casting solution made of Ultrason® S 6010 and of PSU by Competitor A (tested with 25wt% PSU dissolved in DMF; storage conditions: 7 days at 80 °C)

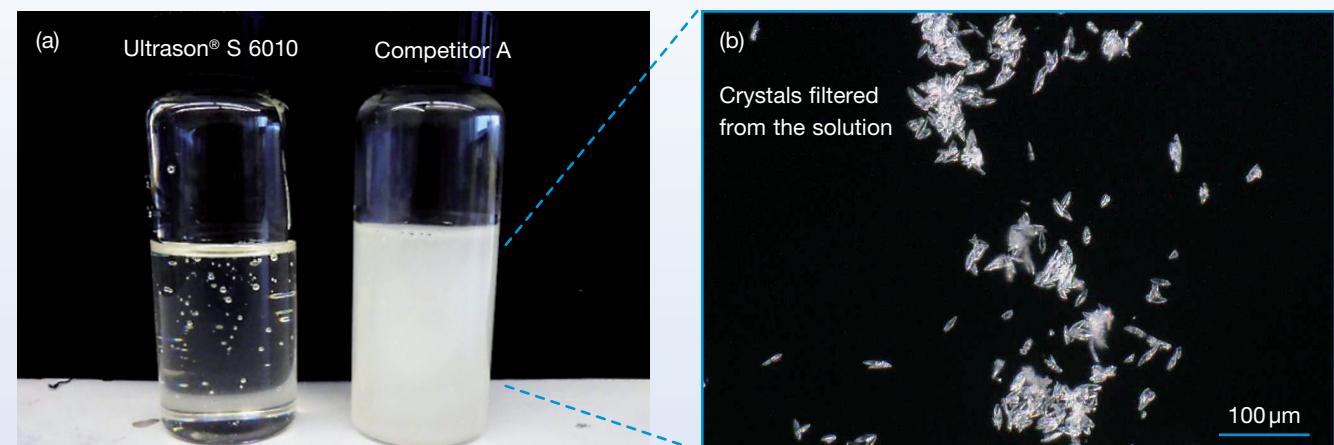


Fig. 6: Stability of PSU casting solution (tested with 25wt% PSU dissolved in DMF; storage conditions: 5 days at 80 °C):
(a) Ultrason® S 6010 and Competitor A
(b) Filtered crystals from Competitor A solution

When the highly turbid and milky solution of competitor A was filtered, numbers of transparent crystals with agglomeration sizes up to 100 µm were found indicating a high level of oligomer content (Figure 6b). Analytics proved that these crystals consist mostly of the Cyclic Dimer of PSU. A high content of undissolved crystals in the PSU solution (competitor A) could reduce the stability of the membrane fabrication leading to potential defects in the PSU layer and a higher cleaning frequency of piping system and filters.

Preparation of the PSU casting solution

Drying procedure

Ultrason® granules can absorb moisture and should be dried before preparation of the casting solution for at least three to four hours in a vacuum drying cabinet or a dry-air dryer at 130 °C to 150 °C.

Formulation

In order to achieve a PSU layer with suitable properties for RO membranes, the typical formulation used in the RO industry is rather straightforward. 16 to 17 wt% of Ultrason® S 6010 is dissolved in DMF as a solvent and the polymer concentration can be further adjusted according to the casting speed. The solution viscosity should be in a defined range.

A too low solution viscosity facilitates deeper intrusion of the PSU solution into the (non-)woven support. This leads to:

- a higher resistance towards water transport across the membrane, contributing to lower flux (lower water production)
- macrovoid structures, contributing to lower mechanical resistance against pressure
- an irregular thickness of the PSU layer due to high lateral flowability of the PSU solution during casting.

On the other hand, a too high solution viscosity could result in

- a reduction of RO water flux due to a denser PSU layer with a higher resistance to the water transport across the membrane
- an insufficient penetration of the PSU solution into the (non-)woven fabric leading to possible delamination of the PSU layer from the support.

Dissolution procedure of PSU pellets in the solvent

In order to prevent agglomeration during mixing, it is recommended to first add the solvent into the mixing tank followed by switching on the stirrer. In the next step, Ultrason® S 6010 can be added gradually into the mixing tank. Sufficient stirring speed is required to prevent agglomeration among pellets during the dissolution process in the solvent. To speed up the dissolution time of the pellets, the mixing temperature can be increased up to 80 °C.

Once the pellets have been fully dissolved, the stirrer can be switched off and the solution can be degassed (potential air bubbles are removed). Remaining air bubbles can result in voids in the support layer. It is possible to apply a reduced pressure to facilitate this process.

After degassing is completed, the temperature of the polymer solution can be reduced to room temperature as the casting is typically conducted at room temperature. Once the casting temperature has been reached, the casting of PSU layer can be started.

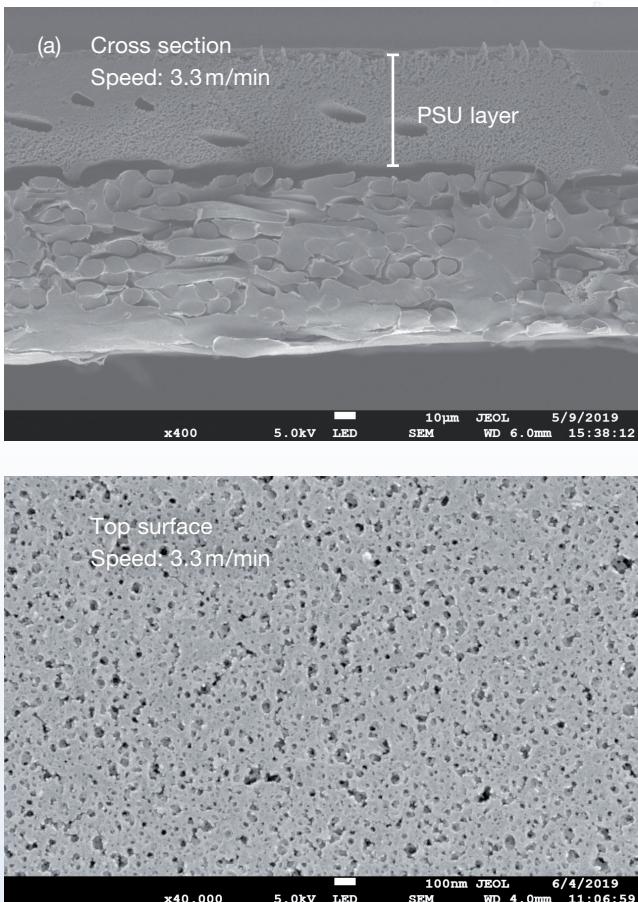
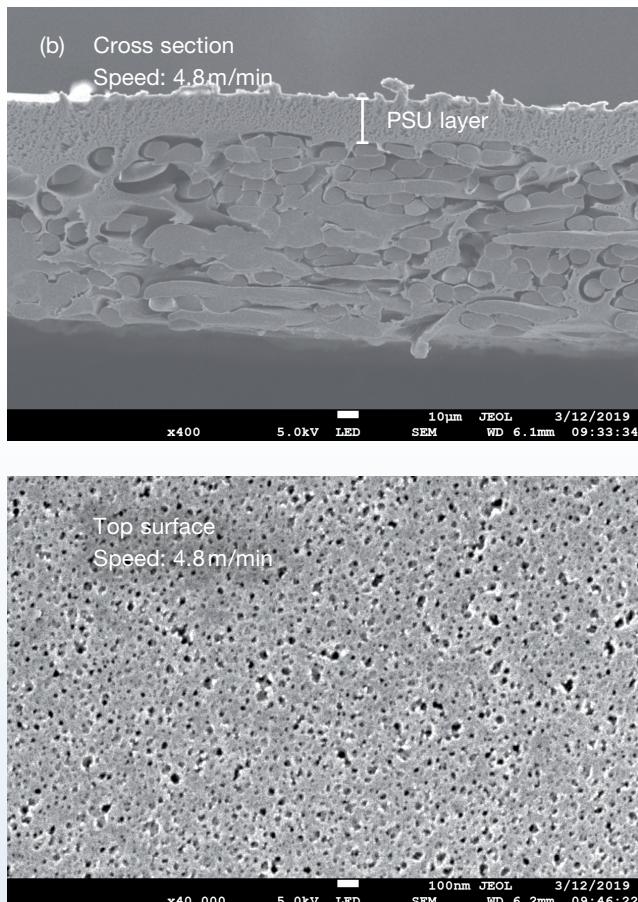


Fig. 7: SEM surface view of different types of cross sections and top surface morphology of a PSU layer with a casting speed of
 (a) 3.3m/min
 (b) 4.8m/min

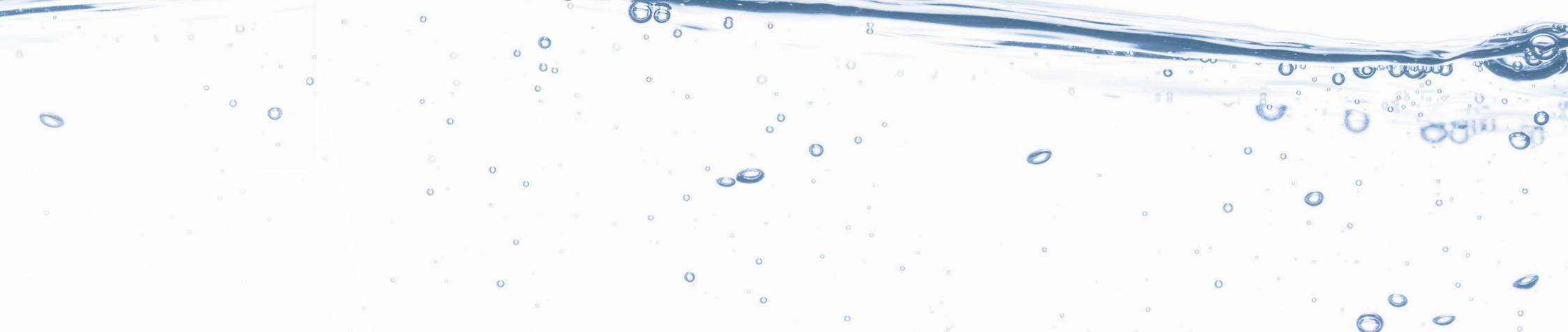


Critical casting parameters of the PSU support layer influencing the RO membrane performance

In order to ensure a consistent quality of the PSU layer, several parameters should be controlled during casting process: the casting thickness and speed, the ambient temperature and relative humidity, the coagulation bath temperature and the solvent content in the coagulation bath.

Casting thickness

Besides a controlled polymer concentration and good precision of the casting blade, the temperature of the polymer solution should be strictly monitored to minimize variations on the thickness of PSU layer. Higher casting temperatures lead to lower polymer viscosities and, as a result, to thinner PSU layers, and vice versa.



Some thickness variations could be also due to non-uniform mechanical stretch and pull of the (non-)woven along the guiding roller. This potential issue could be minimized by regular calibration in the production facility.

It is important to ensure uniformity of the PSU layer thickness in both longitudinal and transverse direction. Regular checks on the uniformity of the PSU thickness is recommended in both directions.

Casting Speed

The optimal casting speed is important to

- provide sufficient adhesion between the support layer and the PSU layer
- allow for polymer relaxation in the cast solution after the casting-blade induced shear-orientation of the polymer
- ensure a uniform PSU layer thickness (a casting speed too fast could lead to uneven coating)

Figure 7 shows that the variation of the PSU casting speed significantly influences the top surface and cross-section morphology of the PSU layer. A higher casting speed results in a more sponge-like structure and a thinner PSU layer with rather similar surface pore size and porosity. In terms of UF properties, the PSU layer cast at higher speed shows thinner thickness with higher water permeability and comparable pore size distribution (Table 3).

Parameters	Casting Speed (m/min)	
	3.3	4.8
Thickness of PSU layer (μm)	40.5	14.3
Pure water permeability (ml/min)	9.7	40.8
MWCO (kDa)	73	75

Table 3: Properties of PSU layers with a casting speed of
(a) 3.3 m/min
(b) 4.8 m/min



Ambient temperature and relative humidity

During the PSU casting process, the ambient temperature and relative humidity must be controlled for a stable quality of the PSU layer.

Although the exposure time to the ambient conditions is quite short (before immersion into the coagulation bath), it can lead to a variation of the PSU properties in terms of surface pore size and porosity.

The effect of the relative humidity is shown in Figure 8. The pore size and porosity of PSU membranes is gradually reduced from large to small as the relative humidity is increasing from ~50 % to ~99 %. With the higher relative humidity, the precipitation rate of the PSU layer increases, which triggers the morphology change from a sponge-like to macrovoids structure. Such variations can easily occur in regions with a high fluctuation of the relative humidity between winter and summer. Therefore, it has to be well controlled in the PSU membrane casting area exposed directly to the air. Therefore, a housing is recommended.

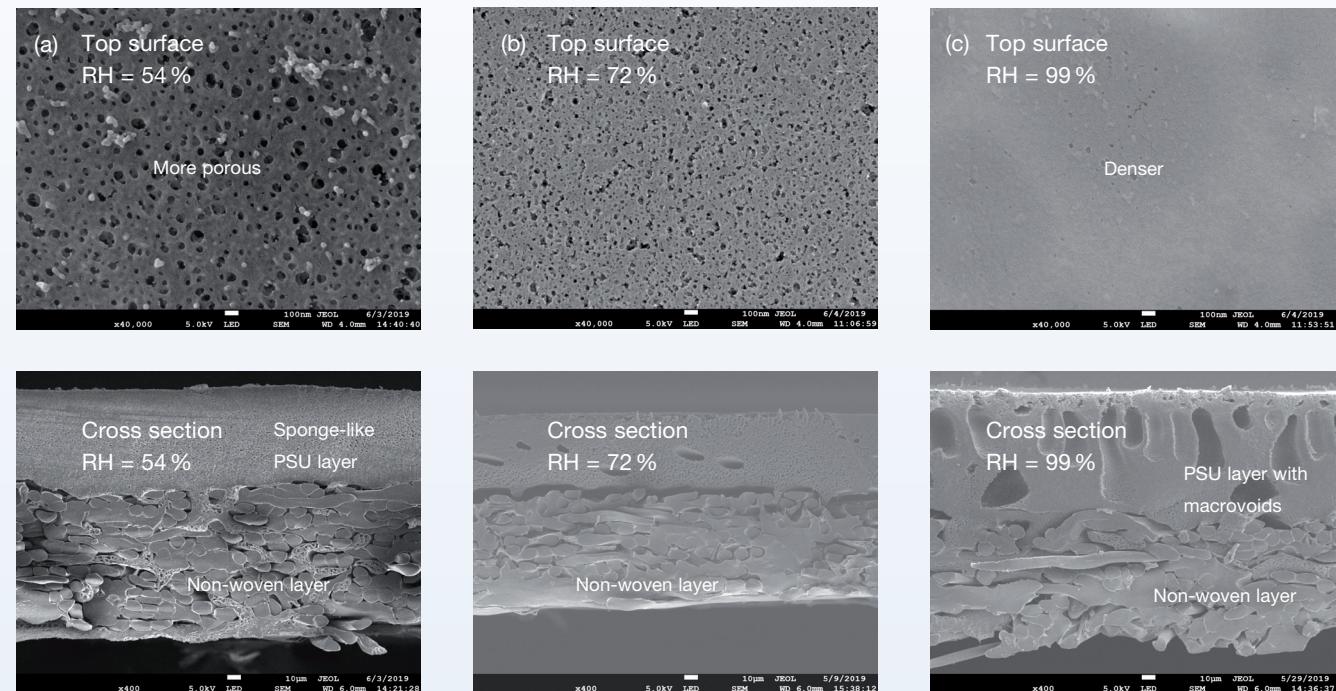


Fig. 8: Effects of relative humidity (RH) on the top surface porosity and cross section morphology of PSU layers at
(a) RH = 54 %
(b) RH = 72 %
(c) RH = 99 %

Coagulation bath temperature

Low coagulation bath temperatures, i.e. in the range of 5 to 15 °C, are typically used to obtain sponge-like PSU layer structures with a controlled pore size on the top surface.

The coagulation bath temperature allows to control the resulting pore size as well as the overall porosity. Thus this parameter should be well controlled during casting.

Limit of the solvent content in the coagulation bath

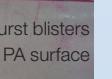
In a continuous production of the PSU layer, the solvent concentration in the coagulation bath would constantly rise due to the solvent removal process from the casting solution.

Since the NIPS process is critical depending on the precipitation strength of the coagulation bath, the limit of the solvent (DMF) concentration in the coagulation bath must be defined and controlled in a narrow window.

Such a steady state can be accomplished by constantly replacing a certain amount of the coagulation bath with fresh deionized water. A too high solvent concentration can lead to a larger pore size. The optimal solvent concentration is depending on many factors like the width of the cast membrane, the casting speed, the temperature and others. It needs to be determined on the production equipment used.

Ultrason® S

Troubleshooting for problems in RO membrane manufacturing

Description of Problem	Root Cause	Location	Impact on RO Performance
Delamination between non-woven and PSU layer	No sufficient penetration of PSU solution into the non-woven during membrane fabrication	Interphase between PSU and non-woven layer	<ul style="list-style-type: none"> ■ Salt leakage/reduction or fluctuation in salt rejection ■ Mechanical failure during RO operation
Defects or uneven coating of PSU layer	<p>Non-woven with too high porosity (too high permeability) and/or non-uniform porosity</p> <p>Non-uniform pulling force across non-woven, i.e. weaker/stronger in different area</p> <p>Air bubbles were not completely purged from the PSU polymer solution</p> <p>Too high coating speed</p> <p>Insufficient flow of polymer solution</p> <p>Non-uniform thickness of casting gap/wear-off casting knife</p>	<p>Non-woven layer</p> <p>PSU layer</p>	<ul style="list-style-type: none"> ■ Salt leakage/reduction or fluctuation in salt rejection ■ Increment or fluctuation of water permeability
High compaction in PSU layer leading to densified support layer	Large macrovoids structure in PSU layer	PSU layer	<ul style="list-style-type: none"> ■ Reduction in water permeability ■ Increment in salt rejection
Collapse of PSU or non-woven layer under high pressure	<ul style="list-style-type: none"> ■ Large macrovoids structure in PSU layer ■ Insufficient thickness of PSU layer 	PSU layer	<ul style="list-style-type: none"> ■ Salt leakage/increment in salt rejection ■ Spike in water flux
Uneven PA layer/Blisters in PA layer  	<p>Too large pore size or uneven pore distributions on top surface of PSU layer</p> <p>Uneven wetting of PSU layer during casting</p>	<p>Non-woven layer</p> <p>PA layer</p>	<ul style="list-style-type: none"> ■ Lower salt rejection ■ Increase in water flux
Variation in surface roughness in PA layer	<ul style="list-style-type: none"> ■ Variation in the pore size in PSU layer ■ Variation of wettability of PSU membrane surface 	<p>PSU layer</p> <p>PA layer</p>	<ul style="list-style-type: none"> ■ Variation in water flux ■ Variation in fouling behaviour

Analysis Method

- SEM morphology
- Salt rejection test
- Water permeability

- SEM morphology
- Thickness measurement
- Salt rejection test

- | | |
|-------------------------|-------------------------|
| ■ SEM morphology | ■ Salt rejection test |
| ■ Thickness measurement | ■ Pulling force testing |

- | | |
|-------------------------|--|
| ■ SEM morphology | ■ Salt rejection test |
| ■ Thickness measurement | ■ Visual check of polymer solution for bubbles via viewing glass |

- SEM morphology
- Thickness measurement
- Salt rejection test

- Water flux and salt rejection test
- SEM morphology

- Water flux and salt rejection test
- SEM morphology

- | | |
|--|--|
| ■ Dye test to check uniformity of PA layer | ■ SEM morphology on pore size of PSU layer |
| ■ SEM morphology in PA layer
(represent only very small area) | ■ Water flux and salt rejection test |

All above + visual check on the excess water on the PSU surface during coating

- AFM characterization
- SEM on PA surface
- Water flux

Recommendations

- Optimize casting speed (to provide sufficient time to anchor PSU into the non woven during casting process)
- Select non-woven with sufficient and uniform porosity, and high surface roughness
- Check the viscosity of PSU solution (too high viscosity could prevent the penetration of PSU into the non-woven)

Select non-woven with smaller air permeability and uniform porosity

Check pulling force in different points along the width of non-woven

Prolong degassing time/increase degassing temperature

Adjust coating speed

Increase polymer solution flowrate

- Calibrate casting gap in the knife
- Check knife condition

Change macrovoids into more sponge-like structure by:

1. optimized formulation for PSU layer, i.e. increase polymer concentration
2. adjust casting parameter, i.e. lower temperature for coagulation bath

- If macrovoid structure is observed --> adjust to sponge-like structure (see above)
- If thickness is too thin, increase casting blade gap

Select non-woven with higher mechanical strength

Check if process parameters during PSU casting are well controlled, i.e. any variation in polymer viscosity, coagulation bath temperature, casting thickness, ambient humidity/temperature, calibration of casting gap, etc.

- Check the drying process particularly for deposition of MPD coating
- Add surfactant in the MPD solution to improve wettability of PSU layer

- Check if there is any change in pore size and porosity of PSU layer
- Check if there is any change in the type or concentration of surfactant used

Selected Product Literature for Ultrason®:

- Ultrason® E, S, P – Product Brochure
- Ultrason® E, S, P – Product Range
- Ultrason® – Resistance to Chemicals
- Ultrason® – Products for the Automotive Industry
- Ultrason® – Injection Molding
- Ultrason® – Special Products
- Ultrason® – Membrane applications
- From the Idea to Production – The Aqua® Plastics Portfolio for the Sanitary and Water Industries
- Stylish, durable and safe: Ultrason® for household and catering
- High-performance and durable reverse osmosis (RO) membranes with BASF's polysulfone (PSU) Ultrason® S – Processing guide

Note

The data contained in this publication are based on our current knowledge and experience. In view of the many factors that may affect processing and application of our product, these data do not relieve processors from carrying out own investigations and tests; neither do these data imply any guarantee of certain properties, nor the suitability of the product for a specific purpose. Any descriptions, drawings, photographs, data, proportions, weights etc. given herein may change without prior information and do not constitute the agreed contractual quality of the product. It is the responsibility of the recipient of our products to ensure that any proprietary rights and existing laws and legislation are observed. (June 2022)



Explore the full potential of Ultrason® and
find the suitable grade for your application!
Ultrason® Product Selector on
www.ultrason.bASF.com

Further information on Ultrason® can
be found on the internet:

www.ultrason.bASF.com

Please visit our websites:

www.plastics.bASF.com

Request of brochures:

plas.com@basf.com

If you have technical questions on the products,
please contact the Ultra-Infopoint:

