Solution Processing Guide for Polymer Membranes

Introduction

Over the last twenty years, the use of porous polymer membranes has achieved a significant position as a cost-effective means of non-destructively separating components from fluid mixtures. Membrane technology possesses a number of attractive features, in that it can be carried out continuously under mild operating conditions and requires little space. It is also environmentally friendly in that energy consumption is generally very low and no additives are required. It is both a cleaning and clean technology.

Solvay offers more high-performance polymers for membranes than any other company in the world. Solef® and Hylar® polyvinylidenefluoride (PVDF), Udel® polysulfone (PSU), Gafone™ polyethersulfone (PESU), and Radel® polyphenylsulfone (PPSU) are used extensively to manufacture isotropic and anisotropic porous hollow fiber and flat sheet membranes for the entire range of the filtration spectrum from microfiltration (MF) to reverse osmosis (RO). Dense-film gas purification membranes are also readily prepared with these materials.

Excellent chemical resistance over a large pH range, combined with hydrolytic stability, high strength, and broad agency certifications, makes these polymers the materials of choice for membranes in demanding end-use environments. Application areas include water purification, wastewater treatment, pharmaceutical production, blood purification, and a variety of industrial process separations, such as food and beverage processing, electropaint recovery, gas separation, and more.

Many of the processes considered to make separation membranes require dissolving the polymer in a solvent. Solef® and Hylar® PVDF and Udel®, Gafone™, and Radel® sulfone polymers are soluble in conventional solvents allowing them to be solvent cast by the diffusion-induced phase separation or "DIPS" process. This process is also sometimes called a non-solvent-induced phase separation or "NIPS".

The DIPS process is highly sensitive to spinning process variables and dope solution variability. It is therefore essential to closely control both the membrane casting and dope preparation processes. This can only be accomplished using polymers of high quality with minimal lot-to-lot variability.

This document will provide you with some guidelines for the preparation of dope solutions in order to help improve the stability and efficiency of your membrane preparation process.

PVDF Fluoropolymers

Polyvinylidenefluoride (PVDF) is a semi-crystalline polymer obtained by the polymerization of vinylidene fluoride.

Solvay Solexis offers a wide range of PVDF homopolymers and copolymers made by suspension polymerization under the Solef® tradename. Emulsion polymerized PVDF homopolymers are sold using the Hylar® tradename.

Solvay PVDF polymers are readily soluble and offer a wide range of desirable properties. In particular, Solef® PVDF polymers have found widespread use in a variety of membrane filtration applications due to these outstanding features:

- Excellent toughness, impact strength, and abrasion resistance
- Unsurpassed chlorine resistance
- Stability at pH levels from 1 to 11
- Low level of insoluble material and high ionic purity
- Excellent UV resistance and weatherability
- Low level of extractable material
- Broad agency approvals (e.g., NSF 61, FDA, U.S.P. VI, UL, etc.)
- Readily cast into porous MF and UF flat sheet and hollow fiber membranes.

In addition to PVDF homopolymers, which are recognized worldwide for their excellent performances in membrane applications, Solvay Solexis has developed a wide range of vinylidenefluoride-hexafluoropropylene (VF2-HFP) copolymers and vinylidenefluoride-chlorotrifluoroethylene (VF2-CTFE) copolymers to respond to specific needs of the market. The general structure of the Solef® PVDF homopolymers and copolymers, along with some popular commercial grades, are shown in Table 1.

Molecular Weight

Solef® homopolymers are available in several grades that encompass a broad molecular weight range. Each grade has a narrow molecular weight distribution, which provides controlled viscosities and makes it easier to fine-tune dope solutions and maximize process stability. Two series of Solef® homopolymer products are available: the 1000 series and the 6000 series. They differ slightly in crystallinity, molecular weight distribution, and particle density.

Table 2 lists the various Solef® PVDF homopolymer and copolymer membrane grades and presents typical molecular weight data. Molecular weight data shown were obtained by gel permeation chromatography in dimethylacetamide (DMAC), calibrated using a polystyrene standard. The results are useful for comparing grades.

PVDF Solubility

Solef® PVDF polymers are soluble in aprotic polar solvents such as dimethylformamide (DMF), dimethylacetamide (DMAC), and N-methyl-2-pyrrolidone (NMP). Table 3 shows some common solvents for these materials in which solubility is greater than 10% by weight at 23°C.

Table 2

Typical Molecular Weights of Selected Solef® PVDF Grades

Solef® Grade	Mn*	Mw*	Mpeak*	Mw/Mn
Homopolymers				
1010	153	352	237	2.3
1012	180	396	288	2.2
1013	194	434	292	2.2
1015	238	573	418	2.4
6008	135	255	209	1.9
6010	151	322	241	2.1
6012	179	380	296	2.1
6013	201	444	328	2.2
6020	313	687	574	2.2
Copolymers				
11008	127	268	190	2.1
21216	271	596	452	2.2

* g/mol x 10^3

Table 3

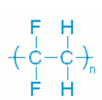
Solvents for Solef® PVDF

Solvent	Solef® PVDF Homopolymers	Solef® PVDF Copolymers
N,N-dimethylformamide (DMF)	X	X
N,N-dimethylacetamide (DMAC)	X	X
N-methyl-2-pyrrolidone (NMP)	X	X
Triethyl phosphate (TEP)	X	X
Dimethyl sulfoxide	X	X
Tetrahydrofuran (THF)		X

Table 1

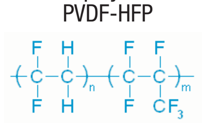
Solvay PVDF Homopolymer and Copolymer Resins

Vinylidenefluoride
Homopolymer
PVDF



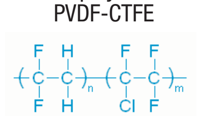
Solef® 1010
Solef® 1013
Solef® 1015
Solef® 6012
Solef® 6020
Hylar® 461

Vinylidenefluoride
Hexafluoropropylene
Copolymer
PVDF-HFP



Solef® 11008
Solef® 11010
Solef® 21508
Solef® 21216

Vinylidenefluoride
Chlorotrifluoroethylene
Copolymer
PVDF-CTFE



Solef® 31008
Solef® 31508
Solef® 32008

Solubility Limits

Solvent polarity has a strong effect on the solubility of PVDF homopolymers and copolymers. Copolymers are soluble in a broader range of solvents than homopolymers, due to their lower crystallinity level. Figure 1 shows maximum solubility of Solef® 1010 (PVDF homopolymer) and Solef® 21508 (PVDF copolymer).

Solution Properties Solef® PVDF

The viscosity of any given polymer solution depends on various parameters including temperature, polymer concentration and solvent as illustrated in Figures 2-5.

Figure 1

Maximum Quantity of Solef® PVDF Soluble in 100g of Solvent at 23°C

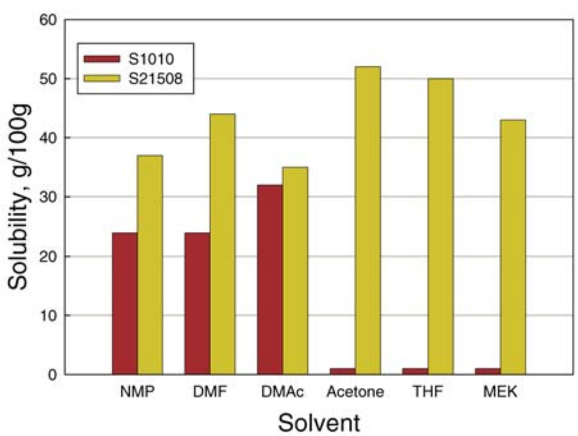


Figure 2

Viscosity Changes with Concentration and Temperature

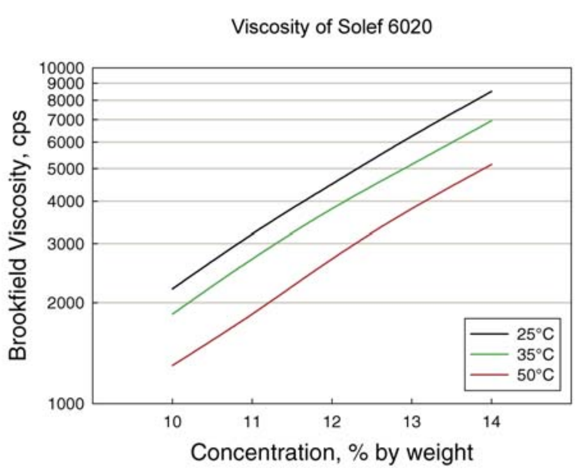


Figure 3

Viscosity of Solef® PVDF Solutions

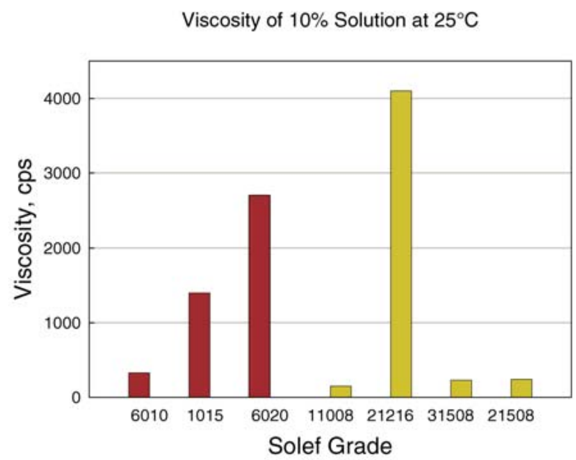


Figure 4

Effect of Molecular Weight and Concentration on the Viscosity of Solef® Resin Solutions

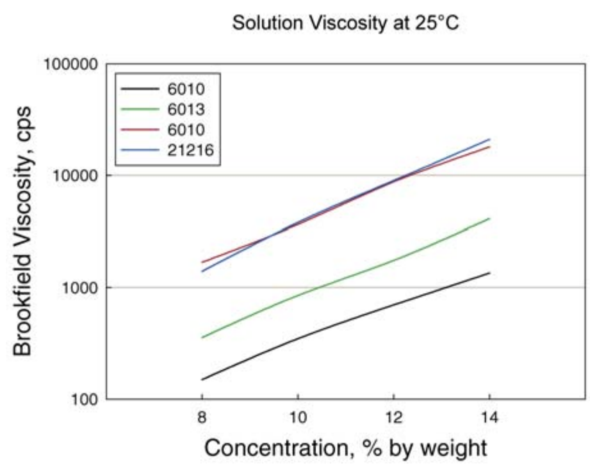
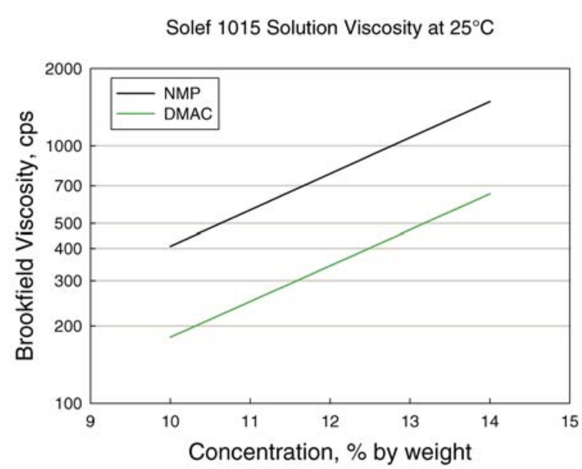


Figure 5

Effect of Solvent on PVDF Solution Viscosity



In particular, solutions of PVDF show generally a Newtonian behavior in a wide range of shear rates, as shown in Figures 6 and 7. Only very high viscosity solutions tend to deviate from the standard behavior at high shear rates.

Figure 6

Solef® 1013 Viscosity vs. Shear Rate

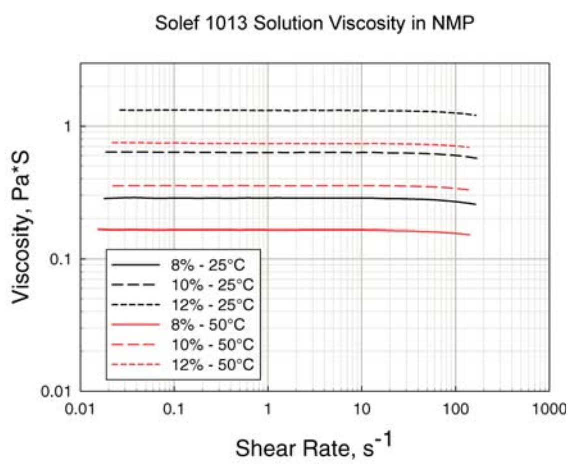
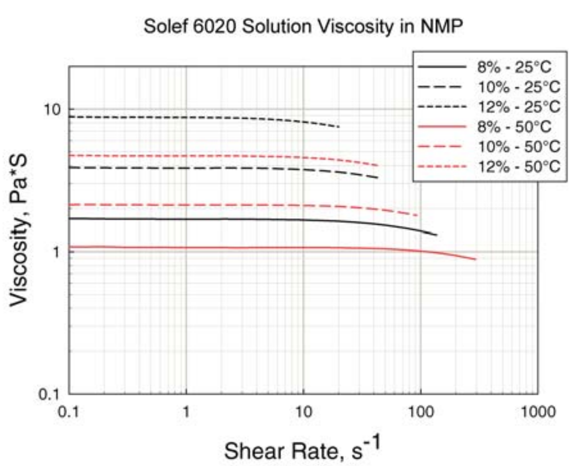


Figure 7

Solef® 6020 Solution Viscosity vs. Shear Rate

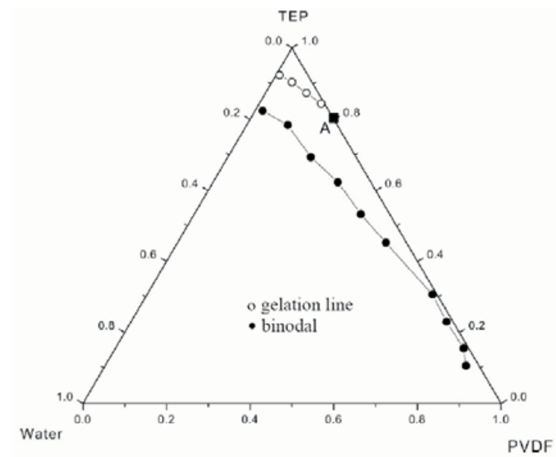


Solef® PVDF Phase Diagrams

Water is most commonly used as the nonsolvent to cause precipitation of PVDF polymers during membrane formation. Figures 8 and 9 show a three-component phase diagram for a system of PVDF and water in TEP and NMP solvents, respectively. The non-solvent concentration in the dope is another critical parameter that governs the rate of polymer precipitation and the final membrane morphology.

Figure 8

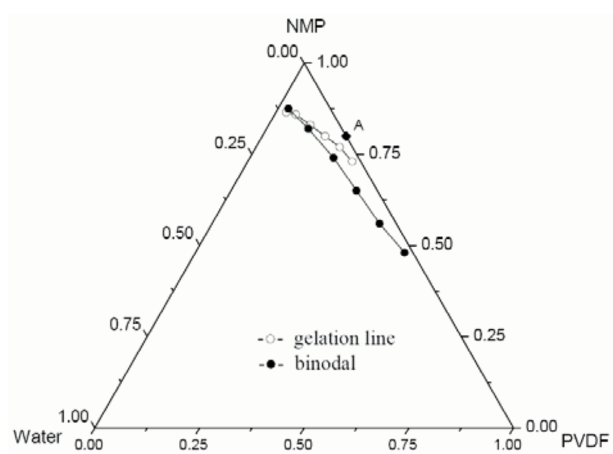
Phase diagram - PVDF in TEP



D.J. Lin et al., Desalination 145 (2002) 25-29

Figure 9

Phase diagram - PVDF in NMP

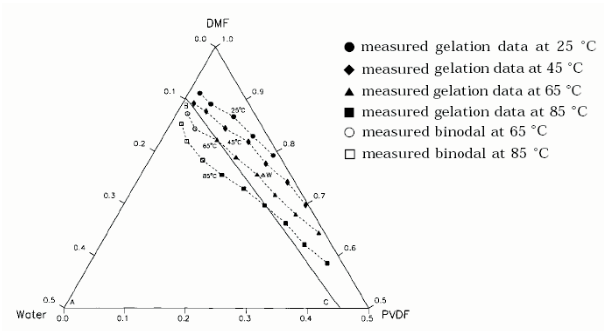


D.J. Lin et al., Tamkang Journal of Science and Engineering, Vol. 5, No. 2, pp 95-98 (2002)

Figure 10 shows the effect of temperature on a system in DMF.

Figure 10

Influence of Temperature on Phase Equilibria



L. P. Cheng, Macromolecules, 32 (1999) 6668-6674

Sulfone Polymers

Sulfone polymers are amorphous thermoplastics comprised of aromatic units (phenylenes) bridged with sulfone, isopropylidene or ether moieties. The chemical structures of Udel® polysulfone (PSU), Gafone™ polyethersulfone (PESU), and Radel® R polyphenylsulfone (PPSU) are shown in Figure 11. Polyethersulfone (PESU) possesses the highest concentration of sulfone moieties in the polymer repeat unit. This structure gives PESU the highest water absorption of the commercial sulfone polymers and is therefore the most hydrophilic sulfone polymer.

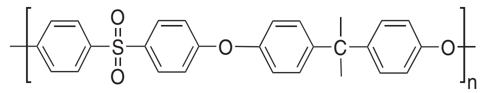
Sulfone polymers offer a unique combination of features that allow their widespread use in a variety of membrane filtration applications, including:

- Very high mechanical strength and creep resistance
- Stable at pH levels from 2 to 13
- Outstanding hydrolytic and caustic resistance and good resistance to moderate concentrations of chlorine
- Low levels of extractible and insoluble materials
- Outstanding biocompatibility
- Broad agency approvals including NSF 61, FDA, U.S.P. Class VI, UL, etc.
- Withstand steam, gamma, and ethylene oxide sterilization methods
- Readily formed into MF and UF hollow fiber and flat sheet membranes with highly controllable pore size and distribution.

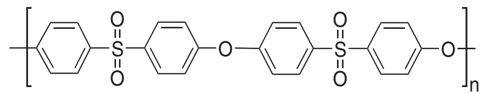
Figure 11

Chemical Structures of Sulfone Polymers

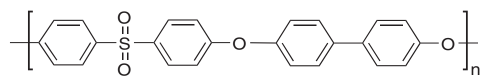
Polysulfone Tg = 190°C



Polyethersulfone Tg = 220°C



Polyphenylsulfone Tg = 220°C



Molecular Weight and Solution Viscosity

As with the PVDF polymers, Solvay's sulfone polymers are offered in a broad range of molecular weight grades. Each grade has a narrow molecular weight distribution, which provides controlled viscosities and makes it easier to fine-tune dope solutions and maximize process stability. Table 4 gives typical solution viscosities for selected sulfone polymers useful for membrane production.

Table 4

Solution Viscosity of Selected Sulfone Polymers*

Polymer Grade	Solution Viscosity Range, cP
Udel® P-1700 LCD	1400-2200
Udel® P-3500 LCD	1750-2550
Udel® P-3500 LCD MB3	2200-3000
Udel® P-3500 LCD MB7	2000 - 2800
Udel® P-3500 LCD MB8	2400 - 3200
Gafone™ 3000P	1225-1650
Gafone™ 3100P	700-900
Gafone™ 3200P	420-550

* 25% solids in DMAC at 40°C

Table 5 lists some selected Solvay sulfone polymer membrane grades and presents molecular weight data. Molecular weight data shown were obtained by gel permeation chromatography according to ASTM method D 5296-05.

Table 5

Typical Molecular weights of Selected Sulfone Resins

Sulfone Resin	Mn*	Mw*
Udel® P-1700 LCD	21	67-72
Udel® P-3500 LCD	22	75-81
Udel® P-3500 LCD MB3	22	78-84
Udel® P-3500 LCD MB7	22	77-83
Udel® P-3500 LCD MB8	23	80-86
Gafone™ 3000P PESU	19	62-64
Gafone™ 3100P PESU	17	52-55
Gafone™ 3200P PESU	16	45-47
Radel® R-5000 PPSU	22	52-55
Radel® R-5500 PPSU	24	55-59

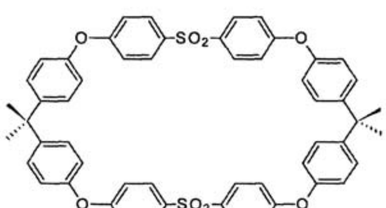
*g/mol x 10^3

Cyclic Oligomers

During the production of polysulfone, side reactions typically occur that produce small quantities of cyclic oligomers. These low degree of polymerization, cyclic molecules have lower solubility than the molecules with the linear structure. The chemical structure of the prevalent specie, the dimer, is shown in Figure 12.

Figure 12

Cyclic Dimer Structure



Solvay exercises careful control of the manufacturing process to minimize formation of cyclic oligomers. For some polysulfone membrane applications, particularly fine hollow fiber membrane production, it has been found beneficial to use a low cyclic dimer (LCD) Udel® grade from Solvay Advanced Polymers in order to prolong dope solution stability and prevent filter clogging or spinneret fouling. The use of Udel® LCD grades can also help minimize fiber breakage and membrane surface defects.

Typically, the cyclic dimer content in Udel® P-3500 LCD is around 1.1%. The processes used to make polyethersulfone and polyphenylsulfone are both characterized by an inherently low quantity of cyclic oligomers.

Solubility

Sulfone polymers are soluble in aprotic polar solvents such as dimethylformamide, dimethylacetamide and N-methyl-2-pyrrolidone. Udel® polysulfone is soluble in a number of other solvents as well. Radel® R PPSU is the most difficult to put into solution, and the process is aided by using ground polymer and slightly elevated temperatures. Table 6 lists some common solvents for these materials in which solubility is greater than 10% by weight at 23°C .

Table 6

Sulfone Polymer Solvents for Membrane Production

Solvent	Udel PSU	Gafone PESU	Radel R PPSU
N,N-dimethylformamide (DMF)	X	X	X
N,N-dimethylacetamide (DMAC)	X	X	X
N-methyl-2-pyrrolidone (NMP)	X	X	X
Tetrahydrofuran (THF)	X		

Sulfone polymer solution viscosity varies between polymers and is strongly influenced by polymer concentration and, to a lesser extent, solvent type, as shown in Figures 13 and 14.

Figure 13

Viscosity of Sulfone Polymers as a Function of Polymer Concentration

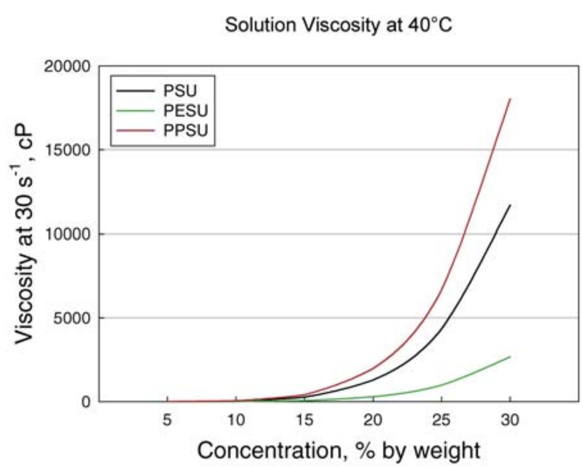


Figure 14

Viscosity of Udel® P-3500 LCD Polysulfone in Different Solvents as a Function of Polymer Concentration.

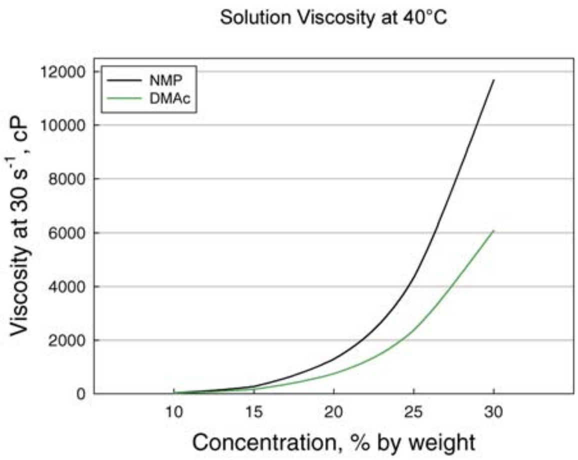
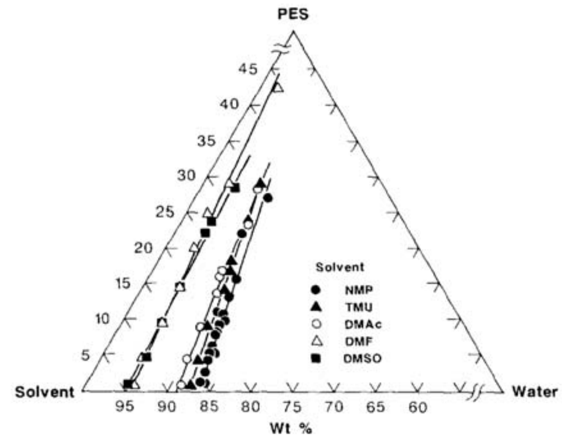


Figure 15

Polymer Precipitation Curves of PESU/Water with Various Solvents at 25°C



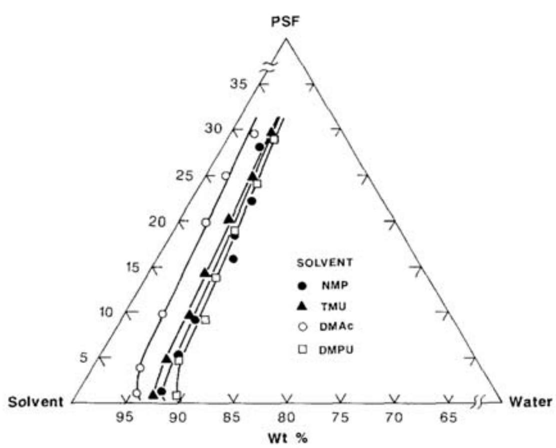
W.W.Y. Lau, M.D. Guiver, and T. Matsuura, Journal of Membrane Science, 59 (1991) 219-7

Sulfone Polymer Phase Equilibria

Figures 14 and 15 show phase equilibria for polysulfone and polyethersulfone in various solvent-water systems.

Figure 14

Polymer Precipitation Curves of PSU/Water with Various Solvents at 25°C



W.W.Y. Lau, M.D. Guiver, and T. Matsuura, Journal of Membrane Science, 59 (1991) 219-7

Solution Preparation

General Guidelines

The choice of solvent is a fundamental and extremely important consideration in dope solution preparation. For a more consistent spinning process, it is important to select a solvent with high purity and minimal water content. When using a solvent recycling system, monitor solvent purity regularly and ensure that the recycling system is working properly.

To optimize dope solution viscosity, it is recommended to select the most appropriate molecular weight polymer, as well as tightly controlling the process parameters. High molecular weight polymers lead to high viscosity solutions and take longer to dissolve, but a higher molecular weight may be required to ensure adequate strength of the nascent membrane during processing or of the finished membrane in use.

Solef® PVDF, Udel® PSU, Gafone™ PESU, and Radel® PPSU polymers are compatible with a variety of pore-forming additives such as polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG). These additives may also improve the hydrophilicity of the finished membrane.

Some precautions may be required when using high molecular weight PVP as a pore-forming additive. PVP can be sensitive to radical degradation. Therefore, to maximize dope viscosity stability, it is always better to select a grade of PVP that contains low peroxide content and is packed in inert packaging. Low gel and other insoluble content is also desirable to minimize filter clogging and membrane defects. Non-solvent additives in membrane dopes include alcohols, water and organic acids.

When preparing membrane polymer solutions, slowly add the polymer to the solvent while agitating. Adding too quickly can lead to the formation of aggregates that will take longer to dissolve. The geometry of the stirrer, the agitation rate, and the temperature all affect the time needed to dissolve the polymer.

The polymers (basic polymers, pore former, additives, etc.) should be dissolved under nitrogen to keep the dope solution viscosity as stable as possible. This is very critical when high molecular weight PVP is used in the formulation. It is recommended that the dope solutions be stored under nitrogen and that they be used within 48 hours of preparation to minimize changes in solution viscosity.

Summary of recommendations for preparing solutions:

- Dissolve the polymer before adding additives,
- Add polymer slowly to the solvent while stirring the solution,
- Be aware that the geometry of stirrer and agitation rate will influence time to dissolve.
- Heat the solution to reduce time to dissolve; the upper temperature limit will depend on the solvent,
- Use dry solvents and dry environment and consider nitrogen blanketing,
- Use pure solvents and avoid contamination with salts or bases,
- Use solutions within 24-48 hours of preparation.

Specific Material Handling Guidelines

Solef® PVDF

Use Solef® PVDF in powder form as it takes less time to dissolve. Raising the solution temperature to 70-80°C (depending on the solvent) will reduce the time to dissolve the PVDF. If the solvent contains a trace of caustic, the solution may become discolored. This phenomenon does not affect properties of PVDF nor the properties of the final membrane.

Sulfone Polymers

Udel® polysulfone in standard pellet form is readily dissolved in DMAC and NMP; however PESU and PPSU polymers will dissolve much more quickly if used in granulated form.

With some solvents, temperatures up to 100°C may be used to dissolve Radel® R PPSU, . Dope solutions are typically extremely viscous, therefore using baffles does not enhance solution preparation. A standard triple-bladed impeller agitator at speeds up to 500 rpm can be used to dissolve materials.

If PVP is included as part of the dope solution formulation, we recommend using a special Udel® LCD grade provided by Solvay Advanced Polymers with improved compatibility with PVP.

Regulatory Approvals

Solvay is committed to maintaining and updating our status with global agencies and specifications. Some of the regulatory approvals held by Solvay's membrane polymers include:

Sulfone Polymers

- FDA Title 21 CFR Parts 177.1560 and 177.2440
- ISO 10993
- National Sanitation Foundation (NSF) STD 51 and STD 61
- European Commission Directive 90/128/EEC and its amendments

PVDF Polymers

- FDA 21CFR 177.2510 and EU 2002/27/EC
- NSF STD 51, NSF STD 61, WRAS (UK), KTW (D) W270 (D)
- U.S. Pharmacopeia (U.S.P.) Class VI

Regulatory status varies by specific grade. Please contact your Solvay representative for current information regarding the regulatory status of specific grades of interest.

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