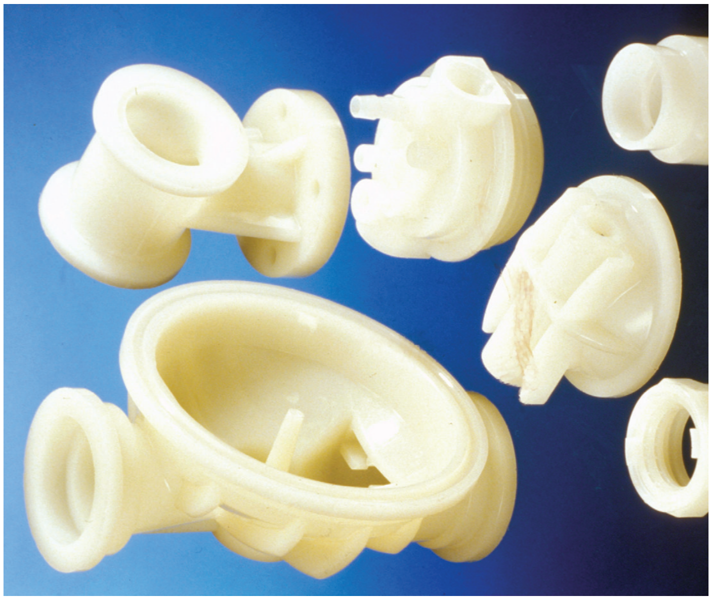
PVDF delivers answers in challenging membranes market

» Use grows in hollow fiber membranes for process-industry water treatment

By Sean M. Stabler

Since its introduction in 1964 by Pennwalt Corp., PVDF (for Polyvinylidene Fluoride) has been well known as a material of construction for chemical-handling applications. Early recognition of its chemical stability to chlorine, bleach, strong & weak acids, oxidants and bromine and its ability to withstand high temperatures up to 150 C led to its use for piping, pumps, filtration cloth, dump tower packing and wire jacketing.

PVDF flat-sheet membranes were first introduced in 1965 for pharmaceutical, biotech and food separation applications. To this day, membrane applications for PVDF continue to annually grow at double-digit rates, in support of modern applications in the same industries.



Kynar® PVDF and Kynar Flex® PVDF resins are used in diverse industries for their special properties, such as high purity, chemical resistance, abrasion resistance and flame retardancy.

In addition to flexibility in regard to exposure environments, Kynar® PVDF is today also known for its excellent thermo-mechanical properties, ranging from -40 C to 150 C, abrasion resistance and toughness, as well as acting naturally as a flame and smoke retardant. Key material properties are listed in Table 1.

Additionally, based on manufacturing techniques that enable inherent purity, PVDF is U.S. FDA-compliant, soluble in select solvents, and compatible with other polymers that could allow good water flux.

Traditionally, PVDF membranes were manufactured using a non-solvent induced phase-separation (NIPS) process for flat-sheet supported or unsupported membranes.

More recently, PVDF use in hollow fiber (HF) made by NIPS and thermally induced phase separation (TIPS) has outpaced the growth of traditional flat-sheet membrane applications. Behind this new use of PVDF lies a global focus on improving water quality before disposal or reuse through purification; design engineer awareness of fluoropolymers' value in many traditional applications; and PVDF product improvements that allow economical membrane manufacture by filtration-component suppliers.

Grade selection

The goal in manufacturing PVDF membranes is either a sheet or tube of solid, porous material suitable for micro- or ultra-filtration membranes. Both the NIPS and TIPS processes achieve this goal. The NIPS process is especially used for flat-sheet and hollow-fiber structures. The TIPS process is primarily only for hollow-fiber membranes.

NIPS uses a water bath to induce coagulation, whereas TIPS uses a water bath to quench molten Kynar PVDF. Both processes require water-soluble pore-forming additives in specific concentrations that dissolve in the water bath, resulting in a narrow distribution of pore structure throughout the membrane thickness.

Arkema Inc., successor to Pennwalt Corp., has developed several commercial PVDF grades to meet membrane manufacturers'

growing requirements. Table 2 lists the most commonly used Kynar PVDF resins for both flat-sheet and hollow-fiber membranes.

For the NIPS process, Kynar PVDF resins are soluble is several solvents. The solvated PVDF is commonly added with non-solvents to produce NIPS flat-sheet and hollow-fiber membranes where typically a higher viscosity resin is required (i.e.

760/1, 761A, MG15, HSV900, 301F), but its use is not strictly limited to high-viscosity resin grades.

Figures 1 and 2 illustrate the effects of percent solids content on the solution viscosities of several grades of Kynar resins. Kynar resins, solvent and non-solvent, are dependent on the solution viscosity of the process and pore structure desired.

Property	Test Method	Nominal Result
Specific Gravity	ASTM D792	1.78 g/cc
Melting Point	ASTM D3418	167 °C
Tensile Yield Strength	ASTM D638	50 Mpa
Tensile Break Strength	ASTM D638	45 Mpa
Flexural Modulus	ASTM D790	2000 Mpa

Table 1: General properties of Kynar PVDF Homopolymer

Kynar® Grade	Melt Viscosity[1] (kpoise)	Solution Viscosity[2] (cpoise)	Material Form
740/1	18	100	Pellet/Powder
760/1	27	400	Pellet/Powder
761A	32	1000	Powder
MG15	37	1700	Powder
HSV900	50	8000	Powder
301F	30	800	Powder
2800/01	25	600	Pellet/Powder

[1] Nominal Kps @ $100s^{-1}$, ASTM D3835, 232°C
[2] Nominal cps for using spindle viscometer at 20 RPM, #2 spindle, 20°C

Table 2: Common Kynar PVDF membrane grades

Many flat-sheet membranes are produced using this NIPS process, the product of which can be spiral wound into membrane modules or used as flat sheets.

Where additional rigidity is desired, a flat-sheet membrane can be cast onto a fibrous film. As shown in Table 2, Arkema offers a broad range of possibilities for Kynar PVDF NIPS process membranes.

In contrast to NIPS, the TIPS process uses thermal energy to melt the resin. The non-solvent blend is then extruded through a die until solidification occurs, forming a hollow-fiber membrane. Most commonly, a lower viscosity resin is preferred when designing a hollow-fiber membrane by means of TIPS, i.e., Kynar 740/1 or 2800/01. However, the process is not limited only to low viscosity resin grades.

More and more applications

Kynar PVDF is a semi-crystalline polymer that allows continuous use at most resin grades at temperatures at up to 150 C.

It is resistant to ultraviolet light, ozone, steam and irradiation sterilization. It is totally resistant to strong acids, strong oxidants, halogens, aromatic & aliphatic solvents and hydrocarbons. It is resistant with conditions to ketones, amines, strong bases and fuming acids.

Mechanically, Kynar PVDF has excellent abrasion resistance, flexibility and toughness. The toughness, chemical resistance, high purity and thermo-mechanical properties of Kynar PVDF has led to its use in water purification, general industrial, food & beverage and pharmaceutical membrane applications.

In particular, the water industry continues adding harsh chemicals to its treatment cycles such as chlorine, chlorine dioxide, hypochlorite, bromine, alcohols, peroxides and combinations, with pH ranging from 1 to 13 to assure purified water quality. Kynar PVDF has a proven history of resistance to all these environments, and is suitable for membrane environments ranging from pH <1 to 13.5.

Kynar PVDF is a material of choice for applications requiring microfiltration and ultrafiltration. The NIPS and TIPS processes commonly produce a porous structure in ranges that lead to the removal of viruses, proteins, sediment, bacteria, spores and paint pigments. As used in industrial water applications,

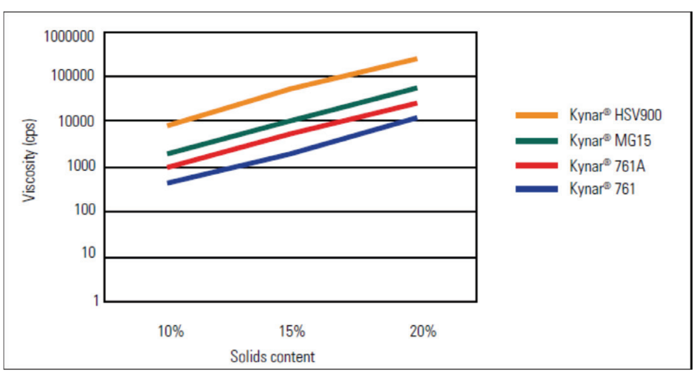


Figure 1: Kynar® PVDF Homopolymer Solution Viscosity in NMP, 25 C @ 10s-1

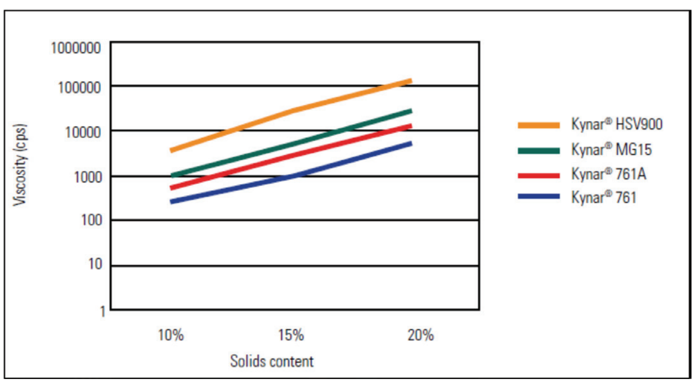


Figure 2: Kynar PVDF Homopolymer Solution Viscosity in DMAC, 25 C @ 10s-1

PVDF membranes allow pretreatment for reverse-osmosis systems applied to seawater or brackish groundwater or membrane bioreactors put to wastewater reuse.

PVDF-based membranes are recognized for their importance in industrial water recovery, recycling, and production of potable water for consumption in municipal and point-of-use water systems. In addition, these membranes are preferred in the pulp-and-paper industry, for concentration and de-watering of minerals, pigments and other contaminants.

Food & beverage industry applications include for concentrated juices, wine & beer, dairy protein isolation, pulp and solids removal and general reduction of effluent loading in processed food production. The pharmaceutical industry applies Kynar membranes in cell harvesting, industrial enzyme manufacturing and enzyme, antibiotics and amino acid purification.

Regulatory approvals

The chemistry of Kynar PVDF opens the door to a range of applications based on its regulatory listings and approvals. Kynar resins are specified NSF-61, NSF-51 and NSF-14 for use in potable water, food equipment and plumbing systems components, respectively. Kynar PVDF meets FDA requirements under CFR sections 177.2510 and 177.2600 for repeated use contact with food.

In the dairy industry, it has been listed as 3-A Sanitary Standards Inc. for multiple-use plastic materials used as product-contact surfaces for dairy equipment.

For the pharmaceutical industry, Kynar PVDF also conforms to USP Class VI testing requirements.

With the growing emphasis on fluids filtration, especially water, manufacturers are producing more PVDF-based membranes, based on its ability to withstand a broad range of performance requirements that other polymers cannot. As chemical treatment combinations and increases in concentrations continue to occur, Kynar PVDF membranes should be considered as a means to meet the needs of these demanding environments.

The outstanding chemical, physical and thermal properties of various grades of Kynar PVDF homopolymers and Kynar Flex PVDF copolymers means they are used extensively in membrane design for water treatment and food & beverage applications and in membrane distillation markets. PVDF is an alternative material solution for applications where long life is needed and where chemicals and heat over time cause performance decline in other commonly used membrane polymers.

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A global chemical company and France's leading chemicals producer, Arkema is building the future of the chemical industry every day. Deploying a responsible, innovation-based approach, we produce state-of-the-art specialty chemicals that provide customers with practical solutions to such challenges as climate change, access to drinking water, the future of energy, fossil fuel preservation and the need for lighter materials. With operations in more than 40 countries, some 14,000 employees and 10 research centers, Arkema should generate annual revenue of approximately $8.3 billion.

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