

Recycle Options for PVDF Microfiltration and Ultrafiltration Water Purification Membranes

INTRODUCTION

Polyvinylidene fluoride (PVDF) microfiltration (MF) and ultrafiltration (UF) membranes provide a reliable barrier against the threat of water borne pathogens, transform contaminated surface waters into drinking water, and treat wastewater to make this safe for discharge back to the environment. The widespread use of PVDF MF/UF became ubiquitous after the Cryptosporidium and Giardia outbreak that occurred in Milwaukee, Wisconsin in the early 1990's.¹ Cryptosporidium and Giardia are microscopic protozoan parasites that can contaminate water supplies. These pathogens routinely breakthrough conventional media filters and are resistant to conventional chlorine disinfection, but can be removed by rejection when water is passed through porous MF and UF membranes. Adding MF/UF filtration to the water management process gave the Milwaukee residents, water plant operators, local government, and state regulators renewed confidence in the cities' water supply.

PVDF provides additional properties important in a membrane water treatment application, including:

- film-forming properties for manufacture into a porous filtration membrane
- high mechanical strength to withstand trans-membrane pressures (TMPs) and physical impact from foreign matter in a hollow fiber (HF) form,
- high elasticity to withstand mechanical strains from air scour cleaning
- can be made hydrophilic to minimize fouling, cleaning, and water treatment costs
- high chemical resistance for compatibility with commonplace water treatment chemicals
- high purity material to ensure stringent requirements for drinking water certification can be met,
- chemical and mechanical durability with effective filtration lifetimes lasting between 7-20 yrs.

Current end of life options for PVDF membranes include incineration and landfilling, however, due to the stable nature of PVDF, recycling is also a potential alternative. In particular, although PVDF membranes may be assembled into filtration modules with adhesive potting compounds and structural housing materials, 80-90% of the hollow fiber membrane is typically not confounded by these other materials making the PVDF membrane portion accessible and attractive for recovering and recycling. In this study, Solvay - a producer of PVDF - partnered with DuPont to evaluate the ability to recover and recycle PVDF from "end of life" ultrafiltration membranes used in drinking water treatment plants.

In an earlier submission to this consultation process (submission 28, number 6017), the material characterization results of the recovered PVDF material from End of Life membranes were shared. This report will provide additional information and an overall summary of the study. These results support the potential for PVDF used in water treatment membranes as suitable candidates for closed-loop or open-loop recycle processes. The end-of-life opportunity coupled to the evidence provided in the earlier submission further support **the recommendation that PVDF used in water treatment membranes be given a long (>12 years) derogation.** Additionally, **accommodations should be made to allow PVDF from membranes to be recycled.**

¹ Davis, R., 2010. Ten Years of Low-Pressure Membrane Plant Operations in Kenosha. Water and Wastes Digest, 14 October 2010

MATERIALS

Virgin Solef® PVDF material used to make the first life membranes was provided by Solvay.

“Used” PVDF hollow fiber membrane modules were sourced as representative “end of life” PVDF membranes from a large municipal drinking water treatment plant and provided to Solvay for this study. The Municipal Drinking Water plant chosen to source these membranes was close to the site in Milwaukee, Wisconsin where the “massive” Cryptosporidium and Giardia outbreak in 1993 resulted in more than 400,000 cases of waterborne infection, 69 deaths, and cost the region approximately \$92.6 million². It was this event that led to the widespread adoption of PVDF ultrafiltration membranes in water treatment due to their ability to provide a safer and more reliable barrier against water borne pathogens.

At this municipal drinking water treatment plant, surface water was sourced from a local reservoir. Raw water undergoes screening and direct coagulation dosing (1-2 ppm aluminum chlorohydrate, ACH) prior to PVDF UF and chlorine disinfection. The resulting potable drinking water is subsequently distributed to households and businesses serving over 100,000 people in the nearby community. This water treatment plant and its process is common and represents one of hundreds of similar municipal water treatment plants that rely on PVDF ultrafiltration membranes to supply safe drinking water to local communities.

The “used” PVDF hollow fiber membranes chosen for this study had been in operation for 5 years before being removed and provided to Solvay. During operation, foulant cake layers build on the membrane surface and are regularly removed through routine mechanical backwashing and chemical cleaning. This filtration process involved:

- every 30 minutes, a standard mechanical backwash occurred,
- every day a short maintenance wash (MW) was conducted with 200ppm sodium hypochlorite (pH~9.5),
- every 30 days a chemical clean-in-place (CIP) was conducted involving (1) sulphuric acid (pH=2), followed by (2) 1000ppm hypochlorite (pH~10-10.5).

The total chlorine exposure of these membranes was estimated to be approximately 200,000 ppm.hrs. “End of life” HF PVDF membranes were recovered from the membrane modules by separating the HF from the protecting screen and module structure (Figure 1). Likely contaminants remaining on the membranes are expected to include mineral clays (e.g., aluminosilicates), and residual ACH.

² Corso PS, Kramer MH, Blair KA, et al. Costs of Illness in the 1993 Waterborne Cryptosporidium Outbreak, Milwaukee, Wisconsin. Emerging Infectious Diseases. 2003;9(4):426-431. doi:10.3201/eid0904.020417.

Figure 1. “End of life” PVDF hollow fibers



ANALYTICAL METHODS

“End of life” hollow fiber Solef® PVDF membranes were characterized using trace metals analysis, thermal gravimetric analysis (TGA), dynamic scanning calorimetry (DSC), nuclear magnetic resonance (NMR) spectroscopy, and solubility.

The trace metals analysis results were obtained using a PerkinElmer Avio® 550 Maxx ICP-OEX spectrometer with axial and radial view. Samples were weighed in a pre-cleaned platinum crucible and calcined using a microwave muffle. The residue was taken up in hot sulfuric acid, evaporated to dryness, taken up in to hot hydrochloric acid and diluted with ultra-pure water with the addition of Scandium as an internal standard. TGA was performed in air according to ASTM E 1131/ISO 11358. DSC was performed according to ASTM D 4591/ISO 11357. Proton and fluorine NMR spectra were collected using a 500 MHz Varian VNMR spectrometer using a 40 mg samples dissolved in 0.6 mL *d*6 DMSO after heating at 70 °C.

RESULTS

Trace Metals Analysis

Prior to any purification the “end of life” PVDF fibers were found to contain on average 0.81% wt/wt of metal impurities (Table 1). This was not unexpected given the use of coagulants in the drinking water process upstream from the ultrafiltration step and the visually observed foulant on the surface of the fibers.

Table 1. ICP-OES Metals analysis results of “End of Life” Solef® PVDF before purification

Metal µg/g	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	Pb	Sr	Ti	V	Zn
End of Life PVDF	3955	17	1078	<0.5	0.6	2	3	1108	829	734	11	<0.5	221	0.8	0.6	6	68	4	19

Thermal Characterization

Thermal and calorimetric characterization of the “end of life” PVDF fibers showed that these had equivalent thermal stability, crystallization temperature, enthalpy of crystallization, fusion temperature, and enthalpy of fusion; suggesting the physical properties of the “end of life” PVDF fibers were equivalent to the virgin Solef® PVDF. This evidence confirms that the PVDF was stable and had not undergone degradation during 5 years of use in the water treatment application (Table 2).

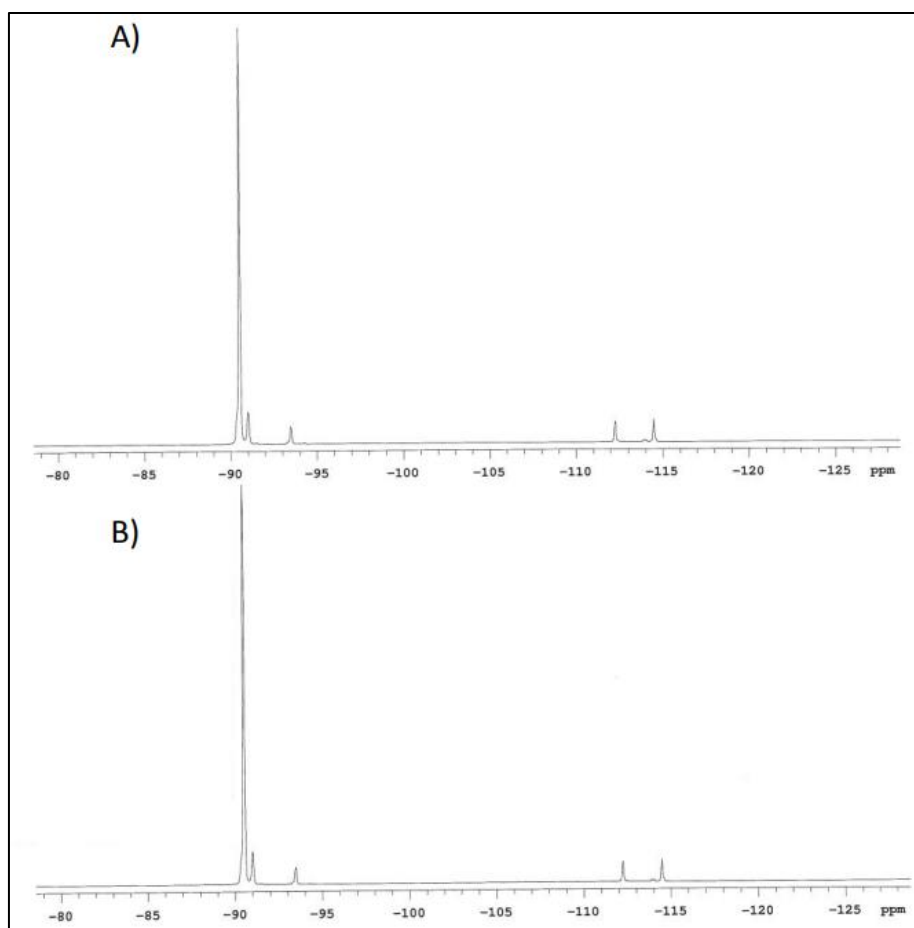
Table 2. Thermal and calorimetric analysis

PVDF Sample	Residue (%wt/wt) T>750°C	[T50]±10°C (%wt/wt)	T crystallization ±5 °C	ΔH Crystallization ±3 J/g	T 2nd fusion ±1°C	ΔH 2nd fusion ±3 J/g
Virgin Solef® PVDF	0	495	134	60	169	57
“End of life” Solef® PVDF fiber	0	489	138	59	170	57

Note: [T50] is the temperature at which the PVDF lost 50% of its initial weight

The stability and absence of degradation was also confirmed by NMR spectroscopy where the 19F-NMR spectra for the virgin PVDF and “end of life” PVDF membranes showed no difference (Figure 2). Most specifically no new signal associated to polymer degradation were observed between -80 to -90 ppm. This result was also confirmed by 1H-NMR with the absence of unexpected signals observed between 5.5-6.5 ppm – apart from the signals of -CF₂H chain end.

Figure 2. ^{19}F -NMR spectrum of A) virgin Solef® PVDF and B) “end of Life” Solef® PVDF



Solubility Testing

Solubility testing was undertaken to evaluate the film forming properties of the recycled “end of life” PVDF. For this, 15 grams of virgin or “end of life” PVDF were dissolved in 85 grams of dimethylsulfoxide (DMSO) or N-methyl-pyrrolidone (NMP) at 65°C in a glass bottle with magnetic stirring. After dissolution, the contents of the bottle were visually inspected and observations recorded.

Solubility testing showed the “end of life” Solef® PVDF was equivalent to the virgin Solef® PVDF in terms of solubilization and viscosity. The only difference observed was that the “end of life” PVDF solution had a slight yellowing turbid appearance, whereas the virgin PVDF was relatively clear and transparent.

Recycled PVDF Application Evaluation: Purification and Application Testing

The proven stability and absence of degradation enabled the “end of life” PVDF to be physically purified using green solvents to produce purified recycled PVDF. Extra purification attempts were completed ensure a metals concentration in the same specification as the virgin material could be obtained. This is a critical parameter to ensure applicability in electronics type applications. The metals could be fully removed however there remained an organic impurity likely from residual additives from membrane production that remained in the PVDF as indicated by the 1% weight loss value. (Table 3). Despite this the resulting material is expected to be applicable in membrane and battery type applications.

Table 3. Analysis of purified “end of life” Solef® PVDF

Sample	Metals %	Weight loss, % T<360°C	$\Delta H(J/g)$
Virgin Solef® PVDF powder	<0.001	0	74
“End of life” Solef® PVDF fiber	0.81	18	56
Purified sample a	0.003	1	70
Purified sample b	0.0008	Not measured	Not measured

The purified PVDF (Figure 3) were tested for reuse as water treatment membranes and as a binder for battery applications. Using recycled PVDF in the manufacture of new water treatment membranes shows a closed-loop recycling opportunity, whereas using the recycled PVDF as a binder for Li-ion battery cathodes provides a high-volume open-loop recycling opportunity. The use of recycled PVDF in each of these applications was evaluated using side-by-side comparisons with 100% virgin Solef® PVDF and 100% recycled Solef® PVDF.

Figure 3. Recycled PVDF Solef® PVDF from “end of life” hollow fibers



Recycled PVDF porous water treatment membranes

Dope solutions were prepared by dissolving recycled or virgin Solef® PVDF at 25°C in N-methyl-pyrrolidone (NMP) (15% wt/wt) along with 3% of standard membrane forming additives. The dope solutions were cast using an Elcometer 4330 casting knife by applying a wet thickness of 250 micron. After casting, the proto-membranes were immersed in a coagulation bath of pure MilliQ water at 25°C to form a porous membrane via diffusion induced phase separation (DIPS). Cast membranes were washed in water for several days before testing (Figure 4).

Figure 4. Membranes cast from Virgin Solef® PVDF (left) and recycled Solef® PVDF (right)



The pure water permeability of three samples from each membrane type were measured at 1 bar pressure over 10 minutes. The porosity was obtained through a gravimetric technique using isopropyl alcohol (IPA). The thickness was measured by digital caliper (Mitutoyo). Membrane testing results are summarized in Table 4 below.

Table 4. Recycled PVDF water treatment membrane characterization

PVDF Sample Conc. 15% wt/wt	Thickness (μm)	Permeability (LMH/bar)	Porosity ($\%\pm 0.5$)
Virgin Solef® PVDF	145 $\pm$ 9	21 $\pm$ 4	82.3%
Virgin Solef® PVDF + 3% Additive – Dope	180 $\pm$ 2	142 $\pm$ 18	88.8%
Recycled Solef® PVDF	150 $\pm$ 24	95 $\pm$ 23	87.7%
Recycled Solef® PVDF + 3% Additive – Dope	170 $\pm$ 35	246 $\pm$ 44	88.4%

The thickness and porosity of each comparative pair of membranes was similar but the permeability of the membranes made with recycled material was slightly higher than the virgin material. Higher permeability is generally a desired attribute in membrane performance, however, the differences observed here were not significant. Overall, the results indicate that viable membranes can be produced using “recycled” Solef® PVDF recovered from “end of life” water treatment membranes.

Recycled PVDF Binder for Li Ion Batteries

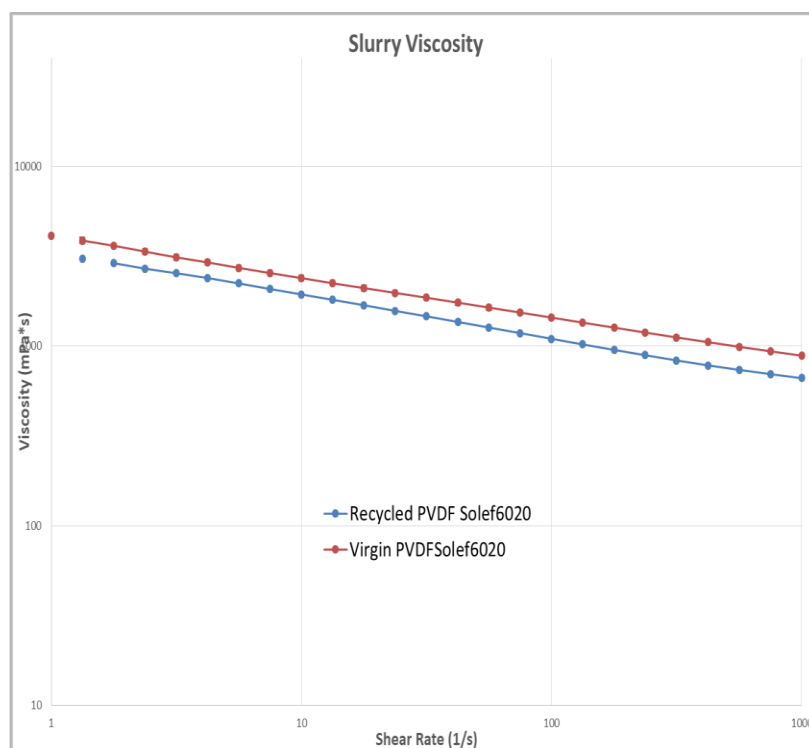
The use of 100% “recycled” Solef® PVDF from “end of life” water treatment membranes was evaluated as a binder in a slurry for Li-ion battery cathode formulation. An NMC811-CNT-PVDF based slurry formulation was used. The viscosity results were conducted in a dry room with -10 °C dew point and are

summarized in Table 4. The respective plots are shown in Figure 5. The formulation properties were compared to a comparative formulation using 100% Virgin PVDF Solef® PVDF.

Table 4. Slurry viscosity characterization

Binder	Normalized Viscosity @ 10 Hz	Normalized Viscosity @ 100 Hz
Virgin Solef® PVDF	1	1
Recycled Solef® PVDF	0.81	0.76

Figure 5. Slurry viscosities



The recycled Solef® PVDF binder shows a slight lower normalized viscosity compared with virgin Solef® PVDF at specific frequency. The reduced viscosity is further confirmed in Figure 4 showing the shear viscosity of both formulations over a range of shear rates. While the recycled PVDF binder formulation showed a slightly lower viscosity, the shear behavior was effectively equivalent to the virgin PVDF binder and within the desired range for use in binder applications indicating the recycled PVDF is suitable for use in Li-ion battery binder formulations.

CONCLUSIONS

PVDF UF membranes provide safe drinking water assurance to communities around the globe. The mechanical strength and chemical resistance of PVDF ensure long useful lifetimes of 7-20 years. This study shows that the PVDF from hollow fiber membranes used in water treatment is stable and does not degrade through use. Importantly, this study further shows the potential to use recycled PVDF reclaimed from water treatment membranes in a circular closed-loop application to make new membranes, or in an open-loop applications to make other products such as Li-ion battery cathodes. Recycling PVDF hollow fibers from water treatment membranes can provide an alternative to landfill or incineration and reduce the environmental impact of water treatment membranes.

By contrast, alternative polymers that have been used for making water treatment membranes are less chemically stable than PVDF, and have been found to degrade through use in the production of safe drinking water. So too, this makes these alternative materials unsuitable for recycling and reuse. This PVDF recycle study provides an important observation that a viable circular economy option for the recycling of end-of-life PVDF membranes is possible. Whereas, alternative polymers will only be left with landfilling or incineration as a viable end of life option.

The EU draft PFAS restriction proposal currently proposes to restrict the use of PVDF in water treatment membranes giving only an 18 month transition period. As written, it also restricts the ability to recycle PVDF from water treatment membranes since PVDF will be above the allowed PFAS concentration limits set for material being recycled. **It is recommended that PVDF use in water treatment membranes be given a long (>12 years) derogation and PVDF from membranes be allowed to be recycled.** Failing to do so will legislate against widely used and proven safe drinking water treatment practices, and viable circular economy options for the water technology industry.