# Chemical Resistance

## of Various Polymers Used in Membrane Manufacturing

*By Sean Stabler, Walt Kosar, Zeena Cherian, and Viral Vora*

### Introduction

In today's demand for purer water, industry is forced to use more aggressive chemicals and techniques to treat water from various sources to make it useable. It is common to use UV, ozone, steam, chlorine, or bromine based chemicals to remove organisms which have contaminated water sources. One common technique to separate the useable water from contaminated water is through polymeric membrane filtration. Before choosing a polymer membrane for filtration, one must first understand that not all polymers can withstand these harsh environments which are becoming more and more common. This article serves as a source to compare common polymer membranes to typical chemicals used in the sterilization and cleaning process.

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Polymeric membrane materials have gained increased attention for water, wastewater, food & beverage, pharmaceutical and other applications. Due to the variety of applications and markets now using membranes, it is important to evaluate the current polymer chemistries commonly chosen. Many of the materials that have worked successfully in the past need to be reviewed as the membrane applications become more demanding.

Kynar® Polyvinylidene Fluoride (PVDF) resins have long been proven a resin in corrosive chemical, high purity, sterilization, and membrane filtration systems since the 1960s. The traditional properties of Kynar® components have made it the choice of engineers

**This article highlights the different chemical performance of polymers used for membrane manufacture.**

**Figure 1: Nylon (PA 6,6) Membrane after Exposure to Chlorine and Sodium Hypochlorite**

due to high mechanical strength, thermo-mechanical stability, excellent chemical resistance, and barrier properties to acids and halogens. The fluorine atoms attached to the back bone of the polymer give tremendous UV, ozone, and chemical resistance. Kynar® membranes in particular have been used in food, water, and biomedical applications since the 1960s. Polysulfone and Polyethersulfones are commonly used for basic water filtration applications where high performance requirements are not required. Nylon 6,6 membranes are known for high abrasion resistance and are commonly used in desalination applications.

Kynar® PVDF, Polysulfones (PSU), Polyethersulfones (PES), and Nylon 6,6

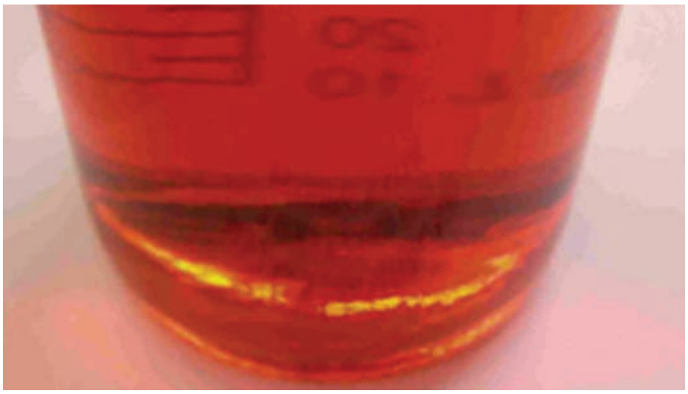

**Figure 2: Nylon (PA 6,6) Membrane after Exposure to Bromine Water**

**Figure 3: Polyethersulfone Membranes after Exposure to Cleaning Chemicals**

**Figure 4: Polysulfone Membranes after Exposure to Cleaning Chemicals**

**Figure 5: Kynar® PVDF Membranes after Exposure to Cleaning Chemicals**

(PA 6,6) are all commonly used in the membrane market as the functional layer in membrane modules. It is also common that these polymers can be components in multi-layer membranes in conjunction with other polymers. With the complexity of multi-layer membranes, chemists need to be aware of how increasingly corrosive their end use membrane environment can be. They need to select the correct material construction for the optimum long-term performance.

The most common cleaning and bleaching agents on the market are sodium hypochlorite, bromine, chlorine, peroxides, ozone, and acidic chemicals. It is not uncommon to shock a system with these chemicals to clean fouled membranes or other common polymer components in water and water related systems. It is important to know the chemical resistance of polymer components when exposed to these harsh chemicals. If the proper material is not chosen, then it could result in untimely, costly expenses.

This article details the physical and chemical resistance properties of several commercially available membrane grade polymers in a range of common chemical environments.

## Experiment

Chemical exposure analysis was conducted on commercially available unsupported membrane samples of Kynar® PVDF, Polysulfone (PSU), Polyethersulfone (PES) and Nylon (PA 6,6). These samples were purchased from a major commercial supplier of flat sheet membranes. The flat sheet membranes were then rolled and inserted into containers filled with exposure solutions for 14 days at 45°C. The films were rolled to simulated applied stress to the films while under chemical exposure. The exposure solutions included sodium hypochlorite in water at 3000 ppm, bromine in water at 3000 ppm, and chlorine in water at 3000 ppm. Membranes were also exposed to pH 1 (hydrochloric acid) and pH 13 (sodium hydroxide). Each solution was checked every other day to monitor bromine or chlorine content.

At the end of the exposure period, the films were removed from solution, rinsed in water, and allowed to oven dry at 110°C for 1 hour. Unexposed and exposed films were all tested for tensile and elongation properties.

## Results

The results of the tensile and elongation testing are below in tables 1 and 2. Cells labeled as 'Degraded,' refers to samples permanently changed beyond the ability perform physical testing due to excessive brittleness.

Each sample was die cut into five 15mm strips using a JDC film sample cutter. The equipment chosen for the testing was a Zwick materials testing system using a 100N load cell. The grip to grip length was maintained at 35mm and a cross head speed of 500 mm/min was used.

The two properties of interest are the tensile stress at break, measured in

MPa, to determine the ultimate strength of each polymer. The other property measured was the elongation at yield, measured in percent. Elongation is an important parameter because in case of MBR systems, hollow fiber membranes are subject to turbulent flow and air sparging. These effects impart significant motion to the fibers, and if the fibers are too brittle (low elongation), they will break.

All membrane polymers survived 14 day immersion to sodium hypochlorite, pH 1, and pH 13 exposures with no significant loss of properties, except for the PA sample. After 14 days, the PA sample reached a complete brittle failure and could not be removed in one piece from the container. The PA membrane also showed some weakening after acid exposure, which is to be expected. The bromine and chlorine solution also proved destructive to the PA, PES, and PSU samples, causing complete brittle failure to the resins and/or complete dissolution. This is consistent with previously published data. The Kynar® PVDF sample, however remained unaffected by sodium hypochlorite, bromine, and chlorine solutions after 14 days exposure at 45°C.

Here are images of the polymer samples tested after just two weeks of exposure. Images 1 and 2 illustrate the effects of the cleaning agents on PA. Note how the PA membrane completely dissolves in the bromine water. Images 3 and 4 show the results of PES and PSU, respectively. In comparison, figure 5 shows the stability of Kynar® PVDF to these cleaning chemicals.

The mechanical data confirms the stability of Kynar PVDF membranes throughout this range of chemical exposure. Due to delicate nature of these membrane samples (typically ~ 100 um thickness) the mechanical data has a variability of ~ 10% on the measurements themselves. Therefore, changes in mechanical properties on the order of 10-15% are not viewed as being significant. Once the magnitude of change exceeds 20%, the feeling is that these changes are significant. Clearly, in the case of brittle failure, the changes are very significant.

## Conclusions

This article highlights the different chemical performance of polymers used for membrane manufacture. The membrane needs to perform its general function of filtration, but it must also possess enough chemical resistance to cleaning chemicals to provide a useful life expectancy. Very few polymers will work universally in all filtration applications, so one must understand the conditions which are possible for the system being designed. The chemistry of the polymers is very important to how they will perform in harsh conditions of time, temperature, pressure, and environment. In all filtration designs, today's systems should be suitable for the initial chemistry that is expected to challenge materials of construction, but also should consider potential new technologies that may not yet exist for cleaning and bacterial control that is currently under development. Bromine, chlorine, chlorine dioxide, ozone, peroxide, acids, alcohols and combinations of the above are all being used and further developed as cleaning agents to assure the suitable quality of purified water.

| Membrane | Control | pH 1 | pH 13 | NaOCl | Chlorine | Bromine |
|---|---|---|---|---|---|---|
| PA 6,6 | 4.52 | 3.55 | 4.3 | Degrated | Degrated | Degrated |
| PES | 5.04 | 5.68 | 5.16 | 4.76 | Degrated | Degrated |
| PS | 7.72 | 7.18 | 8.05 | 7.27 | Degrated | Degrated |
| PVDF | 2.84 | 2.54 | 2.88 | 2.79 | 2.46 | 2.63 |

**Table 1: Tensile Strength at Break (MPa) for Exposed Membrane Samples at 2 Weeks**

| Membrane | Control | pH 1 | pH 13 | NaOCl | Chlorine | Bromine |
|---|---|---|---|---|---|---|
| PA 6,6 | 196 | 137 | 148 | Degrated | Degrated | Degrated |
| PES | 107 | 113 | 93 | 97 | Degrated | Degrated |
| PS | 200 | 194 | 218 | 150 | Degrated | Degrated |
| PVDF | 243 | 212 | 230 | 260 | 220 | 190 |

**Table 2: % Elongation at Break for Exposed Membrane Samples at 2 Weeks**

## About the Authors

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