Much of the current excitement is in the development of advanced polymers for use in separation of organic liquids as well as gas separations. The effort is primarily focused on the manner of introducing porosities of appropriate size and morphology, to design membranes suited for specific end applications.

# Advanced Polymer Nanofiltration Membranes for Molecular Separations


Figure 1

## Fascinating World of Invisible Polymers

In the April - May 2017 issue of POLYMERS Communiqué magazine, I described the applications of polymer membrane as an invisible barrier in functional materials which has found widespread applications in several industrial applications for molecular separations in aqueous and non-aqueous systems. A membrane is a thin layer of a polymeric material that selectively passes one or more components of a feed solution, while retaining others. Polymeric membranes were first used in crossflow filtration operations in the mid-sixties and they have grown fast in the ensuing years. Today, crossflow membrane filtration is a major unit operation that is widely practiced in numerous industries. In turn, this has spawned a vibrant high-performance polymer manufacturing and fabrication industry.

### Mechanisms for Crossflow Membrane Filtration Processes

Crossflow membrane filtration processes operate by multiple mechanisms and use membranes of differing pore sizes from angstroms to several microns in diameter (Refer Table 1)[1].

#### Microfiltration (MF)

This is the coarsest of the process and uses traditional filtration principles.

Figure 1: A typical organic solvent nanofiltration plant. (Courtesy: Borsig Membrane Technology, Germany)

**Dr. S. Sivaram**
Former Director, CSIR-NCL
Honorary Professor and
INSA Senior Scientist
Indian Institute of Science
Education and Research
(IISER), Pune

## Ultrafiltration (UF)

It also operates using traditional size exclusion, but with smaller mesopores, rather than macropores. While both, MF and UF are used to remove undissolved solids, UF membranes are also capable of separating large and small molecules in a solution.

## Nanofiltration (NF)

These membranes contain micropores that are small enough to separate very small molecules, both charged and uncharged. Typically, NF processes are used to repel anions in waste water treatment and can remove up to 80% of hardness and greater than 90% of colour when used in water treatment processes. NF accounts for 65% of the market for water treatment, 25% of dairy and food industry and 10% of the chemical industry. Some of the more promising applications for NF are development of membranes suitable for caustic recovery, separation of gold and silver from the leachate of complex ores containing these metals and decolourisation of sugars and removal of sulphate ions from the brine that is fed to the ion-exchange membrane electrolysers that are used to produce chlorine and alkali. Many membrane module configurations, such as hollow fibre, spiral wound and, plate and frame are used in such applications[2].

## Reverse Osmosis (RO)

The RO membranes were the first to see large-scale industrial use, primarily for desalination of sea water. Here, the separation mechanism is solution / diffusion, meaning molecules dissolve in the polymer membrane, then pass through by diffusion. In desalination, the ions are hydrated and diffuse much more slowly than free water molecules. For this reason, free water passes through while the ions are rejected. RO membranes are non-porous, and the only openings are the interstitial spaces between the polymer chains.

**Table 1: Crossflow Membrane Filtration Processes**

| Membrane Process | Separation Mechanism | Separation Capability | Membrane Pore Size |
|---|---|---|---|
| Microfiltration (MF) | Size exclusion | 0.1 - 10 microns | > 50 nm |
| Ultrafiltration (UF) | Size exclusion | Molecular weight ~1,000 to 5,00,000 g/mol | 2 - 50 nm |
| Nanofiltration (NF) | Size exclusion and electrostatic exclusion | Molecular weight 100 - 1,000 g/mol | < 2 nm |
| Reverse and Forward Osmosis | Solution / Diffusion | Molecular weight < 1,000 g/mol | Molecular dimensions |
| Gas Separation | Solution / Diffusion | Molecular size, 0.0001 micron | Molecular dimensions |

## Gas Separation Membranes

These are the most intricate in terms of molecular architecture of the polymers used as membranes. Since the gas molecules are very small and separation occurs through a combination of size and solubility of the permeate, the pores must be carefully designed.

# Development of Advanced Polymers for NF Membranes

More recently, there has been considerable interest in using NF in organic solvents[3]. Recent development of solvent resistant nanofiltration membranes has

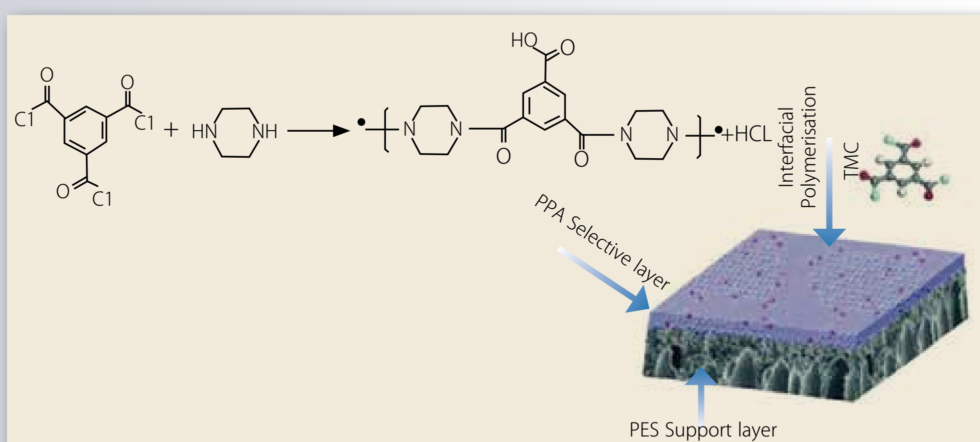


Figure 2: Poly(piperazine-amide) active layer on poly(ether sulfone) support layer.

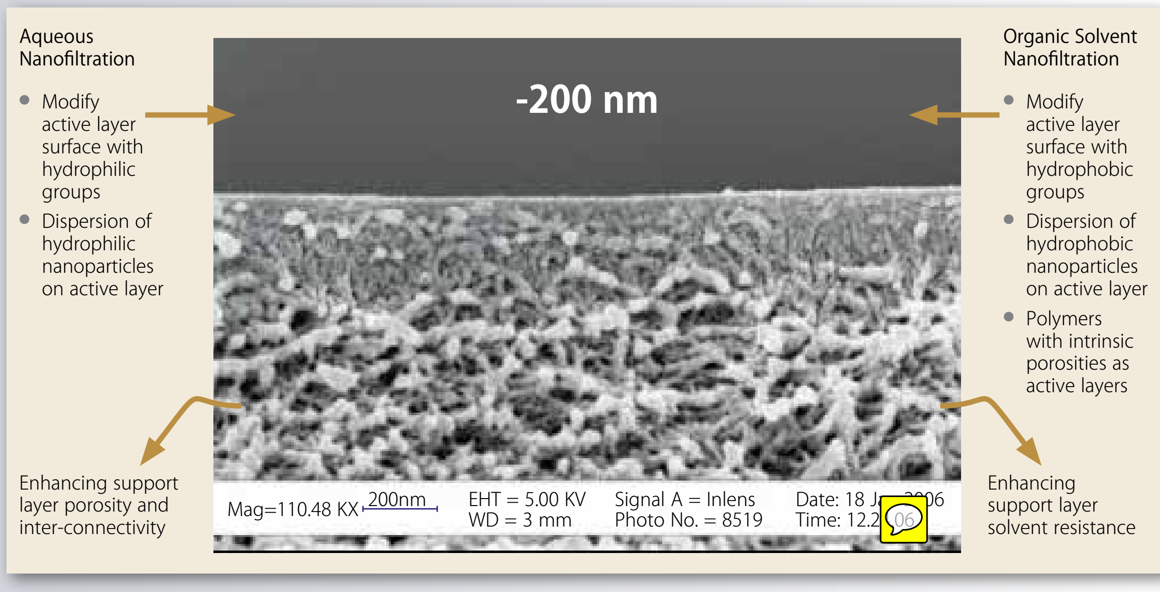


Figure 3: Design strategies for polymers for use as active and support layers in TFC's for aqueous and organic solvent nanofiltration.

NF accounts for 65% of the market for water treatment, 25% of dairy and food industry and 10% of the chemical industry.

triggered development of several applications. This process is now widely termed as 'Organic Solvent Nanofiltration (OSN)'. An intriguing possibility that OSN could even be an alternative to distillation in organic-chemical industry is stimulating considerable R&D in this area (Refer Figure 1). It is generally believed that 40 - 70% of the capital and operating costs in chemical and pharmaceutical industries are dedicated to separations; and a substantial fraction of this cost is related to processing of organic liquids.

NF membrane materials are very diverse in terms of composition and structure. In the early days, most membranes were made from cellulose acetates and this polymer is still used. However, its chemical resistance, pH tolerance and maximum allowable use temperature are limited. So, considerable efforts have been invested in the development of more robust polymers for NF. These include polysulfides, polyether sulfones, polyvinylidene fluoride, polyacrylonitrile, polyamides, PTFE and PP. Most of the membranes used in NF are asymmetric, characterised by a thin selective layer (active layer) on top of a more open support layer (thin film composites, TFC). The deposition of the active layer can be performed by dip-coating or interfacial polymerisation techniques. The active layer is typically about 100 - 200 nm thick. For example, the workhorse polymer that is used in many NF applications in aqueous environment is poly(piperazine-amide), produced by interfacial polymerisation of piperazine with 1,3,5-benzenetricarboxylic acid chloride (Refer Figure 2).

However, much of the current excitement is in the development of advanced polymers for use in separation of organic liquids as well as gas separations (Refer Figure 3). The effort is primarily focused on the manner of introducing porosities of appropriate size and morphology, to design membranes suited for specific end applications. Ultra-thin sub-10 nm polyamide films have been shown to have excellent permeance and high rejection. Intrinsically microporous polymer nanofilms, derived from contorted monomers, have been described which provide much higher interconnectivity of pores and greater permeance. New integrally skinned asymmetric membranes capable of filtration of solutions of DMF and other solvents at over 140°C have been developed using poly (ether-ether ketone) as the polymer.

## Going Forward

In subsequent articles in this series, we will explore in greater depth, the design principles behind the preparation of such polymers, their chemical and physical properties as well as the relationship between the polymer structure and its functions.

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