

초청강연

Structure and Property Relationship of RO Membranes

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Abstract

Reverse osmosis is the opposite process of osmosis occurring through a semipermeable membrane, when a pressure greater than the osmotic pressure is applied to the more concentrated solution which is separated from less concentrated solution via the semipermeable membrane.

There are two types of commercial reverse osmosis (RO) membrane.

One is asymmetric membrane and the other is thin film composite (TFC) membrane.

Historically an asymmetric membrane was first invented by Loeb and Sourirajan in 1962 using cellulose acetate (CA). CA membrane has several drawbacks including low flux, narrow operating pH range (pH 4.5 ~ 7.5), and weak to biological attack. Low flux and easy hydrolysis of the acetate group of CA were the two most damaging factors hindering CA from becoming a high performance RO membrane.

Other polymeric materials such as aromatic polyamide (Nomex, Du Pont) and polybenzimidazolone have been used to improve operating pH range and to resist biological attack. But the problem of low flux still remains as a typical property of asymmetric membranes. Du Pont's Permasep membranes B-9 and 10 made from Nomex have been used widely for water desalination along with CA and CTA (cellulose triacetate) membranes until FT-30 has been invented in 1981.

The concept of a TFC membrane was first proposed by Francis in 1966 and the first TFC membrane was made by laminating a preformed microporous support to a very thin film. In 1972, J. Cadotte first demonstrated that a TFC membrane could be formed by an interfacial reaction of polyethylenimine in water with toluenediisocyanate in Freon on a microporous support and later he invented FT30 in 1981 which was made from the interfacial polymerization reaction of m-phenylenediamine (MPD) with trimesoyl chloride (TMC) on microporous polysulfone support. FT30 showed much higher flux (25gfd) and salt rejection (99%) than the previous TFC and CA membranes (ca. 10 gfd flux and 97 ~ 98 % rejection) at 225 psi.

The high flux and high salt rejection of FT30 has been ascribed to the structure of the cross-linked aromatic polyamide of FT30, which is inherently based on the chemistry and structure of MPD and TMC.

The unique symmetrical structure of FT30 was confirmed by CPK molecular model and also by computer simulated molecular model study by M. Hirose and coworkers. (1)

They also studied other aromatic polyamides from combinations of various polyfunctional acyl chlorides

and MPD to show that the membranes from the polyamides with symmetrical structure exhibit high salt rejection and flux similar to FT30. The membranes from the polyamides with unsymmetrical structure gave poor salt rejection and high flux.

The CPK molecular model of FT30 indicated that FT30 has a pore size of about 12 to 16 Å^o which is quite close to the pore size distribution data (6 to 16 Å^o) of FT30 obtained from nitrogen and carbon dioxide adsorption – desorption experiment (2). The above computer molecular model study showed the pore size of the membranes from the unsymmetrical polyamides is larger than FT30 and other membranes from relatively symmetrical polyamides, and thus the larger pore size (evidently larger than 16 Å^o) can allow a convective water flow through the membranes to result in poor salt rejection and high flux.

Other aromatic polyamide TFC membranes from combinations of various polyfunctional amine and TMC did not also show flux and salt rejection as high as FT30. Most of the polyfunctional amines tested are aliphatic and alicyclic amines and may not produce polyamides as symmetrical as FT30 and thus salt rejection tends to be lower than FT30..

Kwak and coworkers (3) studied the effect of aromatic diamine isomers such as MPD and PPD (p-phenylenediamine), and cross-linking of the polyamides on the salt rejection and flux of the resulting membranes. Even PPD, an isomer of MPD, did not yield membrane as good as FT30, though the aromatic polyamide from PPD – TMC is symmetrical, which may have somewhat larger pores than FT30 to cause a lower salt rejection. They also showed uncross-linked aromatic polyamide membranes from PPD - TPC (terephthaloyl chloride) and MPD - IPC (isophthaloyl chloride) have larger surface area (coarser ridge and valley structure of the TFC membrane surface) than the corresponding cross-linked polyamide membranes and exhibited higher flux at the expense of salt rejection.

Thus cross-linking the aromatic polyamides seems to be necessary to achieve the right pore size for high salt rejection. After securing the high rejection, high flux could be obtained by increasing the surface area (surface roughness) of the membranes. This was accomplished by adding alcohols (4) and other additives (5) to MPD solution to perturb the interface to result in higher ridge and valley structure of the membranes. The method produced membranes showing much higher flux (40 – 50 gfd) and 98-99 % salt rejection at 225 psi using 1500 ppm NaCl. The surface roughness and the flux were linearly increased as the amount of the additives increases.

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