MEMBRANES, HOLLOW-FIBER

1. Introduction

The development of hollow-fiber membrane technology (1,2) has been greatly inspired by intensive research and development of reverse-osmosis membranes during the 1960s. Du Pont's pioneer aramid polymer device was commercialized in 1969, followed by a cellulose triacetate polymer developed by the Dow Chemical Co. and Toyobo Co. Ltd. (Japan). The excellent mass-transfer properties conferred by the hollow-fiber configuration soon led to numerous applications (3). Commercial applications have been established in the medical field (see FRACTIONATION, BLOOD, CELL SEPARATION), in water reclamation (purification and desalination) (see WATER, SUPPLY AND DESALINATION), in gas separations and pervaporation; other applications are in various stages of development. A hollow-fiber membrane is a capillary having an inside diameter of $>25 \mu m$ and an outside diameter $<1\,mm$ and whose wall functions as a semipermeable membrane. This semipermeable membrane can be either on the inside or outside wall of the capillary. The fibers can be employed singly or grouped into a bundle that may contain tens of thousands of fibers and up to several million fibers as in reverse osmosis (Fig. 1). In most cases, hollow fibers are used as cylindrical membranes that permit selective exchange of materials across their walls. However, they can also be used as containers to effect the controlled release of a specific material (4), or as reactors to chemically modify a permeate as it diffuses through a chemically activated hollow-fiber wall, eg, loaded with immobilized enzyme (see ENZYME APPLICATIONS, INDUSTRIAL).

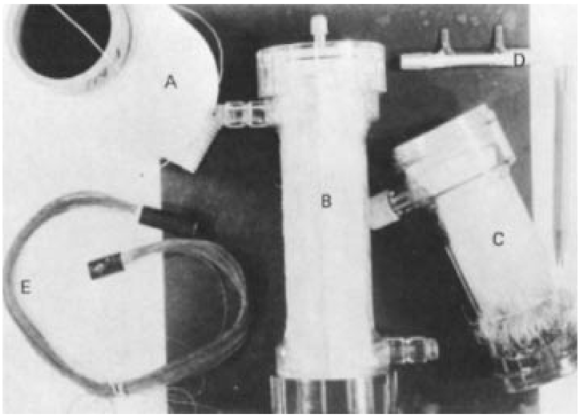

Fig. 1. A, hollow-fiber spool; B, hollow-fiber cartridge employed in hemodialysis; C, cartridge identical to item B demonstrating high packing density; D, hollow-fiber assembly employed for tissue cell growth; E, hollow-fiber bundle potted at its ends to be inserted into a cartridge or employed in a situation that requires mechanical flexibility.

Hollow-fiber membranes, therefore, may be divided into two categories: (*1*) open hollow fibers (Figs. 2**a** and 2**b**) where a gas or liquid permeates across the fiber wall, while flow of the lumen medium gas or liquid is not restricted, and (*2*) loaded fibers (Fig. 2**c**) where the lumen is filled with an immobilized solid,

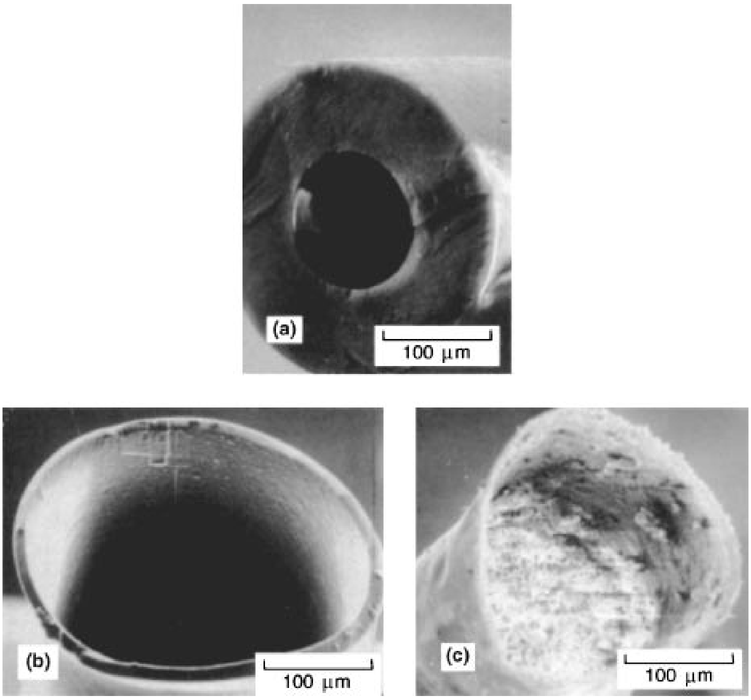

Fig. 2. (**a**) Thick-walled hollow fiber for high pressure desalination; (**b**) thin-walled acrylic hollow fiber; (**c**) sorbent-filled fiber. Courtesy of I. Cabasso.

liquid, or gas. The open hollow fiber has two basic geometries: the first is a loop of fiber or a closed bundle contained in a pressurized vessel. Gas or liquid passes through the small diameter fiber wall and exits via the open fiber ends. In the second type, fibers are open at both ends. The feed fluid can be circulated on the inside or outside of the relatively large diameter fibers. These so-called large capillary (spaghetti) fibers are used in microfiltration, ultrafiltration (qv), pervaporation, and some low pressure ($<1035\,\mathrm{kPa} = 10\,\mathrm{atm}$) gas applications.

In open fibers the fiber wall may be a permselective membrane, and uses include dialysis, microfiltration, ultrafiltration, nanofiltration, reverse osmosis, Donnan exchange (dialysis), osmotic pumping, pervaporation, gaseous separation, and stream filtration. Alternatively, the fiber wall may act as a catalytic reactor and immobilization of catalyst and enzyme in the wall entity may occur. Loaded fibers are used as sorbents, and in ion exchange and controlled release. Special uses of hollow fibers include tissue-culture growth, heat exchangers, and others.

Hollow fibers offer three primary advantages over flat-sheet or tubular membranes. First, hollow fibers exhibit higher productivity per unit volume; second, they are self-supporting; and third, high recovery in individual units can be tolerated. The high productivity is derived from a packing density that results in a large surface area. Surface area-to-volume ratio varies inversely with fiber diameter. Thus, for example, a $0.04\,\mathrm{m}^3$ ($1.5\,\mathrm{ft}^3$) membrane device can easily accommodate $575\,\mathrm{m}^2$ ($6200\,\mathrm{ft}^2$) of effective membrane area in hollow-fiber form ($90\,\mu\mathrm{m}$ in diameter), compared to about $30\,\mathrm{m}^2$ ($330\,\mathrm{ft}^2$) of spiral wound flat-sheet membrane and about $5\,\mathrm{m}^2$ ($50\,\mathrm{ft}^2$) of membrane in a tubular configuration. Because they are self-supporting, the hollow-fiber membranes greatly simplify the hardware for fabrication of a membrane module. Whereas flat-sheet membranes employed in microfiltration, ultrafiltration, nanofiltration or reverse-osmosis modules must be assembled with spacers, porous supports, or both, a bundle of hollow fibers can simply be potted into a standard size tube of plastic or metal, as shown in Figure 1. The primary disadvantage of the hollow-fiber unit as compared to the other membrane configurations is its sensitivity to fouling and plugging by particulate matter due to a relatively low free space between fibers. In commercial applications, this problem is greatly lessened by designing systems with good pretreatment of feeds to the hollow fiber devices.

Hollow fibers can be prepared from almost any spinnable material. The fiber can be spun directly as a membrane or as a substrate which can then be post-treated to achieve desired membrane characteristics. Analogous fibers have been spun in the textile industry and are employed for the production of high bulk, low density fabrics. The technology employed in the fabrication of synthetic fibers applies also to the spinning of hollow-fiber membranes from natural and synthetic polymers. A significant manufacturing difference is that synthetic fiber fabric production is accomplished at line speeds considerably faster than the line speeds employed in making membrane hollow fibers.

2. Properties

2.1. Morphology. The desired fiber-wall morphology frequently dictates the spinning method. The basic morphologies are isotropic, dense, or porous; and

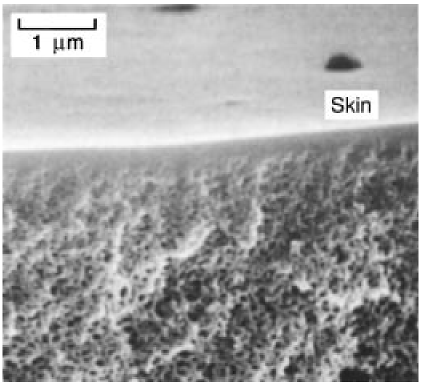

Fig. 3. Anisotropic hollow-fiber morphology exhibiting a dense skin. Courtesy of I. Cabasso.

asymmetric (anisotropic), having a tight surface (interior or exterior) extending from a highly porous wall structure (Fig. 3). The tight surface can be a dense, selective skin, permitting only diffusive transport, or a porous skin, allowing viscous flow of the permeate as in conventional ultrafiltration (Fig. 4), microfiltration, nanofiltration or reverse osmosis. Membrane-separation technology is achieved by use of these basic morphologies. The semipermeability of the porous morphology is based essentially on the spatial cross section of the permeating species, ie, small molecules exhibit a higher permeation rate through the fiber wall. The semipermeability or anisotropic morphology of the dense membrane, which exhibits a dense skin, is obtained through a solution—diffusion mechanism. The permeating species chemically interacts with the dense polymer matrix and selectively dissolves in it, resulting in diffusive mass transport along a

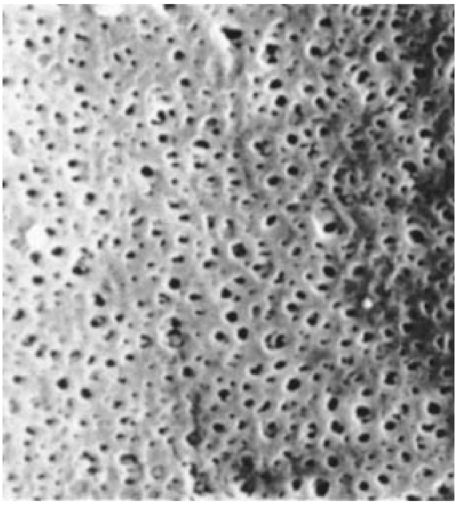

Fig. 4. Surface of a polysulfone ultrafiltration hollow-fiber membrane spun with polyvinylpyrrolidinone (5). Surface pore diameter is 0.2–0.4 μm.

chemical potential gradient. Thus, the dense membrane may exhibit semipermeability toward the large molecules with which it interacts, whereas the smaller, noninteracting species do not permeate. This is well demonstrated in the pervaporation process, where one-stage separation of toluene, as the permeating species, from its mixture with hexane or pentane can be accomplished employing alloys of cellulose acetate–polyphosphonate for the hollow fibers (6).

The asymmetric configuration is of special value. In the early 1960s, the development of the asymmetric membranes (7) exhibiting a dense, ultrathin skin on a porous structure provided momentum to the progress of membrane-separation technology. The rationale behind this development is that the transport rate through a dense membrane is inversely proportional to the membrane thickness, and membrane permselectivity is independent of thickness. Thus, membranes with this structure permit high transport rates, yet can yield excellent separation. High manufacturing standards of reproducibility and quality control are required to maintain the integrity of the separation process. In addition, mechanical integrity problems associated with ultrathin membranes are obviated by use of asymmetric morphologies.

2.2. Mechanical Considerations and Fiber Dimensions. The hollow fiber is self-supporting, and is actually a thick wall cylinder. The ratio of outside to inside diameter in some reverse-osmosis applications is about 2 to 1 thus providing the strength to withstand high operating pressures, commercially up to 10,000 kPa (96 atm), without collapsing. A hollow fiber that is exposed to external pressure would exhibit a collapse pressure P_c that depends on the inner and outer fiber radii (IR, OR) and the Young's modulus E and Poisson ratio ν of the material. The approximate relationship is given by the expression

$$P_c = \frac{2E}{1-\upsilon^2}\left[(OR-IR)/(OR+IR)\right]^3 \tag{1}$$

For most hydraulic pressure-driven processes (eg, reverse osmosis), dense membranes in hollow-fiber configuration can be employed only if the internal diameters of the fibers are kept within the order of magnitude of the fiber-wall thickness. The asymmetric hollow fiber has to have a high elastic modulus to prevent catastrophic collapse of the filament. The yield-stress $\sigma\gamma$ of the fiber material, operating under hydraulic pressure, can be related to the fiber collapse pressure to yield a more realistic estimate of plastic collapse:

$$P_c = \sigma\gamma(OR-IR)/OR \tag{2}$$

For the asymmetric membranes, progressive yield can cause a loss of production rate due to compaction of the matrix in a prolonged operation. The pressure at which hollow-fiber compaction is initiated, $P\gamma$ can be approximated:

$$P_\gamma = \sigma\gamma \ln\,(OR/IR) \tag{3}$$

This value is taken into account when planning hollow-fiber dimensions. A partial account of these considerations can be found in References 8 and 9. In practical applications, ie, reverse osmosis, membrane compaction with time is experimentally derived as a function of the polymeric material at given temperatures and pressures (10).

When the operation of the hollow-fiber membrane is to be reversed, and permeation from the bore to outer zone is required, circumferential stress and pressure drop along the fiber capillary (bore) must be considered in the design of the fiber unit. The circumferential stress, S_c, is expressed as

$$S_c = \frac{P_b IR}{(OR - IR)} \tag{4}$$

where P_b is the bore fluid pressure (11). Knowing the relationship between S_c, the applied pressure, and the membrane radius of curvature thickness, one can determine the minimum yield stress or ultimate tensile strength required to prevent failure or massive distension under maximum anticipated transmembrane pressure.

The relationship between the bore fluid pressure drop, ΔP_b, and its flow rate is defined by Poiseuille's law:

$$\Delta P_b = K \frac{\eta L J}{\pi (2IR)^4} \tag{5}$$

(for laminar flow) where K, η, L, and J are dimensional constant, viscosity, fiber length, and flow rate, respectively (12).

Fiber dimensions have been studied for hemodialysis. When blood is circulated through the fiber lumen (*in vivo*), a significant reduction in apparent blood viscosity may occur if the flow-path diameter is below 100 µm (13). Therefore, current dialyzers use fibers with internal diameters of 180–250 µm to obtain the maximum surface area within a safe range (see Dialysis). The relationship between the fiber cross section and the blood cells is shown in Figure 5. In

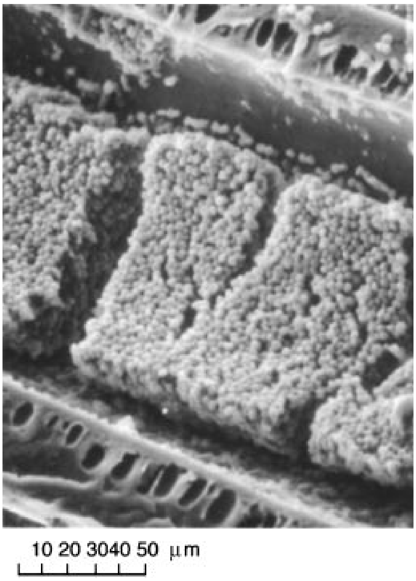

Fig. 5. Cross section of blood-clogged hemofiltration acrylic hollow-fiber membrane. The spheroids are red blood cells. Courtesy of I. Cabasso.

many industrial applications, where the bore fluid is dialyzed under elevated pressure (>200 kPa or 2 atm), fibers may burst at points of imperfection. Failure of this nature is especially likely for asymmetric fibers that display a large number of macrovoids within the walls.

In microfiltration and ultrafiltration, the largest commercial uses for hollow fibers in new applications, transmembrane pressures can be relatively low, thus, resulting in low energy consumption. In these processes, systems operate at vacuum and pressures up to 400 kPa (4 atm) with the feed flow either on the outside of or within the capillary tube.

3. Spinning

In preparation of permselective hollow-fiber membranes, morphology must be controlled to obtain desired mechanical and transport properties. Fiber fabrication is performed without a casting surface. Therefore, in the moving, unsupported thread line, the nascent hollow-fiber membrane must establish mechanical integrity in a very short time.

Various common principles of hollow-fiber spinning processes are illustrated in Figure 6, which describes the dry-jet wet method. In this scheme, the spinning dope, consisting of a viscous, degassed, and filtered polymer solution (20–40% polymer by weight) is pumped into a coaxial tubex jet spinneret. The polymer content is usually close to the precipitation point. The thread line emerging from the spinneret is quickly stabilized by an internal quench (coagulating) medium (nonsolvent liquid or gas) as it emerges from the jet orifice. The nascent hollow thread is further stabilized in a quench bath. At this point, the fiber has sufficient mechanical integrity to pass over guides and rollers under moderate tension. In most commercial production lines, the spinning rate is 10–1000 m/min and is governed by the spinning method, dope compositions, and the morphological and dimensional requirements. Therefore, dope

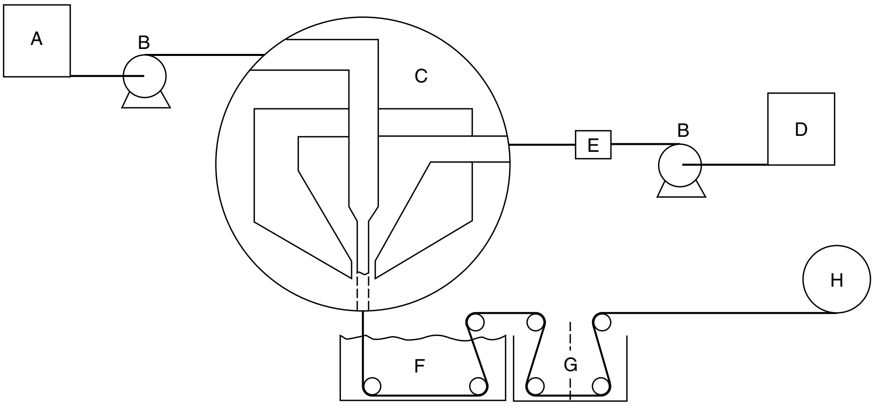

Fig. 6. Schematic of dry-jet wet spinning employing tube-in-orifice spinneret: A, bore injection medium (liquid, gas, or suspended solids); B, pump; C, spinneret; D, polymer spinning solution; E, micrometer (μm) "dope" filter; F, coagulation or cooling bath; G, quench bath; and H, collection spool.

compositions and spinning conditions are sought that result in establishment of the hollow fiber immediately on emergence from the orifice. Residual quenching liquid and solvent are usually removed by some sort of a washing step prior to use.

There are three conventional synthetic fiber spinning methods that can be applied to the production of hollow-fiber membranes: in melt spinning, a polymer melt is extruded into a cooler atmosphere which induces phase transition and controlled solidification of the nascent fiber; in solution (wet) spinning, the spinning dope, consisting of the polymer(s) predissolved in a volatile solvent mixture, is spun into a liquid coagulating bath (14). A combination of these first two methods is applied for hollow-fiber fabrication in the dry-jet wet-spinning technique, in which the spinneret is positioned above a coagulation bath (Fig. 6). In this process, all three mechanisms of formation (temperature gradient, solvent evaporation, and solvent–nonsolvent exchange) can be combined. The morphology of the fibers, particularly for the ultrafiltration applications is a function of the spinning solution viscosity and the ternary polymer/solvent/nonsolvent phase diagram (15).

3.1. Spinnerets. In all methods, a tubular cross section is formed by delivering the spinning dope through an extrusion orifice. Four schemes of spinneret nozzle cross sections are shown in Fig 7: (*1*) the segmented-arc design, which has a C-shaped orifice, is suitable for melt spinning. The extrudate rapidly coalesces to complete the annular configuration. There is no need for gas injection to prevent collapse of the hollow fiber, because the gas is drawn through the

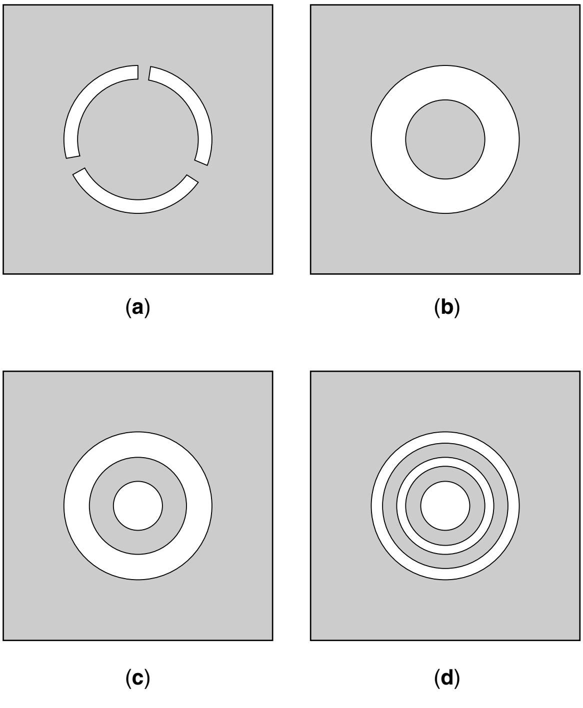

Fig. 7. Spinneret faces: (**a**) segmented-arc design; (**b**) plug-in-orifice design; (**c**) tube-in-orifice; (**d**) multiannular design.

unwelded gaps. (*2*) The plug-in-orifice simply provides the extrudate with the annular shape; however, a gas supply is usually required to prevent collapse. (*3*) The tube-in-orifice jet design is the most versatile combination since it can be applied to all three spinning techniques mentioned above. Gas, liquid, or suspended solids can be delivered through the inner tube to maintain the annular structure, and/or to control coagulation of the fiber bore, as well as to encapsulate gases, liquids, or solids to form the so-called loaded fibers. (*4*) The multiannular design is employed in spinning of multilayer fiber walls, or for entrapping (encapsulating) activated species in a composite hollow-fiber wall. In all cases the gas used is usually inert (nitrogen) so no chemical interactions occur between gas and organic polymer(s).

The spinnerets in a production line assembly consist of multiple groupings of orifices; thus the number of fibers from a single spinning cell can vary. All three spinning techniques mentioned above commonly employ spinning lines that carry as many as 250 fibers (sometimes referred to as a rope) drawn from a single multiorifice spinneret.

The multi-orifice spinnerets require a high degree of precision in design and manufacture. The main problems encountered are the delivery of identical quantities of dope to each orifice and the instantaneous self-adjustment of the spinneret's internal pressure if an orifice plugs during spinning.

In most spinning processes, the fiber emerging from the spinneret is drawn down to a desired dimension before complete solidification. In some production lines, a laser beam is utilized to monitor the dimensions of emerging thread; any alteration is recorded; and, if required, the dope delivery rate, take-up rate, and internal-injection medium delivery rate are adjusted automatically.

3.2. Melt Spinning. Melt spinning is the simplest spinning process. The spinning rate can be fast (over 1000 m/min), and fiber reproducibility is high. The polymer is extruded through the outer capillary of the spinneret. Melt spinning is often limited by the thermal stability of the polymer melt. Thermal degradation, cross-linking, and other modifications of the polymer melt can easily occur at high temperatures. To obviate these difficulties, polymers are sometimes melt spun with volatile or extractable plasticizers (as much as 50 wt%), which are blended with the polymer prior to spinning. For example, grades of cellulose triacetate, whose melting points are 292–314°C, can be spun at 150–230°C if premixed with sulfolane, dimethyl sulfoxide, glycerol, diethylene glycol, caprolactam, 2-pyrrolidinone, or other compounds (see FIBERS, CELLULOSE EASTERS). Melt-spun fibers can be stretched as they leave the spinneret, facilitating the production of very thin fibers, a significant advantage over solution spinning.

Other important operating parameters include plasticizer changes, gas type and pressure, gap length between spinneret and quench bath, line speed, and rope tension. All variables must be carefully controlled to obtain a hollow fiber of desired characteristics.

A common modification of the melt-spinning technique involves using dopes containing polymer-diluent pairs compatible in the melt but incompatible at lower temperatures. Thus, phase separation follows phase transition from melt to solid. Examples of such dope compositions are poly(2,6-dimethyl-*p*-phenylene oxide) (PPO) with caprolactam (qv) and cellulose esters with dimethyl phthalate–glycerol mixtures (8). In such spinning, the gelled fiber walls consist of two phases: a continuous polymer matrix and solid or liquid domains of the diluent. Leaching of the latter with an appropriate solvent (water or aqueous solution) produces a porous matrix. This aspect is discussed in further detail below. Conventional melt-spinning methods tend to yield isotropic (dense or porous) wall structures. Asymmetric structures result, in most cases, from rapid loss of the diluent by evaporation, or by interaction with the quench medium when the nascent fiber is extruded into a gas flow-through chamber, or into an aqueous cooling bath. The fibers have low void volume and hence low permeabilities. The latter is overcome by use of high packing densities (very large surface areas) in a bundle. Polymers not soluble in common solvents have an advantage using this process.

3.3. Solution (Wet) Spinning. The key to the dry spinning of hollow-fiber membranes is the utilization of volatile solvents that boil below 40°C. Wet spinning techniques yielding cellulose acetate hollow-fiber membranes have been reported by Chemical System, Inc. (16). In this process, methyl formate (bp 30°C) and propylene oxide (bp 35°C) are employed as solvents. Such highly volatile solvents are necessary because the extruded fiber must be self-supporting over a considerable drop height (6–7 m) in the spinning cell, and completely dry after minimal festooning to maintain lumen potency during take-up. The spinneret generally consists of two concentric capillaries, the outer capillary having a diameter of approximately 400 μm and the central capillary having an outer diameter of approximately 200 μm and an inner diameter of 100 μm. Polymer solution is forced through the outer capillary while gas (usually nitrogen) or liquid is forced through the inner one. The rate at which the core fluid is injected into the fibers relative to the flow of polymer solution governs the ultimate wall thickness of the fiber (17).

Fibers spun by this method may be isotropic or asymmetric, with dense or porous walls, depending on the dope composition. An isotropic porous membrane results from spinning solutions at the point of incipient gelation. The dope mixture comprises a polymer, a solvent, and a nonsolvent, which are spun into an evaporative column. Because of the rapid evaporation of the solvent component, the spinning dope solidifies almost immediately upon emergence from the spinneret in contact with the gas phase. The amount of time between the solution's exit from the spinneret and its entrance into the coagulation bath has been found to be a critical variable. Asymmetric fibers result from an inherently more compatible solvent/nonsolvent composition, ie, a composition containing lower nonsolvent concentrations. The nature of the exterior skin (dense or porous) of the fiber is also controlled by the dope composition.

3.4. Wet- and Dry-Jet Wet Spinning. Although melt and solution (wet) spinning are convenient methods for obtaining dense isotropic morphologies, wet- and dry-jet wet methods can be used to obtain almost every known membrane morphology. The desired fiber morphology dictates the selection of the solvents, coagulants (interior and exterior), and the location of the spinneret, as well as other specific parameters. In most production lines, an aqueous solution serves as an exterior coagulant. The spinning dope, therefore, is composed of water-soluble solvents that are eventually extracted from the nascent fiber through the exterior zone of the fiber, although coagulant is often injected through the bore of the emerging fiber as well (Fig. 6). Thus, a skin can be formed either on the external fiber surface or on the bore surface. The spinning rate in this method is relatively low (up to 100 m/min, but usually 15–50 m/min).

Many parameters are involved in the dry-jet wet technique, and these interact during the extrusion/coagulation steps. The principal variables are more or less the same for all spinning techniques and include dope composition, dope viscosity, spinning temperature, dope-pumping rate, composition of coagulants (interior and exterior), spinneret distance from the coagulation bath, interior-medium flow rate, coagulation temperature, and fiber draw rate (take-up rate). For example, the relationships among fiber dimensions, fiber morphology, fiber properties, and spinning variables are given in the literature for polysulfone hollow fibers spun from a dope composition of polysulfone/poly(vinylpyrrolidinone) (PVP) in dimethylacetamide (DMA) (5,9,18). The composition of the bore fluid and the rate of its delivery are important parameters for the initiation of fiber formation. The dope emerging from the orifice immediately interacts with the interior medium (which can be either gas or liquid), and the pressure within the nascent bore determines the initial filament diameter. For some dope compositions, the bore fluid contains dry nitrogen or mineral oil, whose only function is to maintain the annular configuration of the fiber as it is drawn down and coagulated from the exterior zone. Instant coagulation at the orifice can take place if the interior fluid is a strong coagulant. In such an event, an internal skin is formed and the fiber draw-down rate is relatively low.

To increase the viscosity of a spinning solution, a coagulant-soluble additive polymer may be included in the dope composition. For example, polysulfone cannot be spun adequately from low viscosity solution mixtures, ca 13–16 wt% of a polysulfone in dimethylformamide (DMF). However, if PVP is added to the polysulfone spinning dope, the solution viscosity is increased, and the viscosity required to maintain the falling lumen configuration is obtained. Then, the PVP, a water-soluble polymer, dissolves in the coagulation bath, leaving behind a porous hydrophobic polysulfone matrix; the wall porosity and structure of the fiber can be controlled by varying the polysulfone/PVP/DMF composition (5,9,18) (Fig. 4).

The interplay between exterior and interior coagulation results in the range of fiber wall morphologies desired for various applications. Two underlying principles are (*1*) the nascent fiber wall facing a strong coagulant forms a skin and (*2*) the nature of the skin, degree of porosity, macrovoid formation, and other morphological traits chiefly depend on the dope composition. For example, cellulose acetate spun from acetone as solvent (25 wt% polymer) forms a dense wall if coagulated in water. If the solvent mixture consists of 60/40 acetone/formamide (formamide is a poor solvent for cellulose acetate), a skin resting on a porous structure is formed upon coagulation with water. If the bore fluid contains 70/30 water/glycerol, and the fiber is spun into a water coagulation bath, a skin forms in the exterior zone. If the coagulants are reversed, the skin forms on the interior bore wall. A cellulose acetate dope composition consisting of 40/60 acetone/formamide is at the point of incipient gelation. Therefore, in the dry-jet wet-spinning method, if the injected bore fluid is 60/40 glycerol/water, the nascent fiber may gel before contact with the water. In this case, the gelled matrix is plasticized by the glycerol, and the fiber can be drawn down from the spinneret orifice to give an isotropic porous morphology as shown in Figure 8.

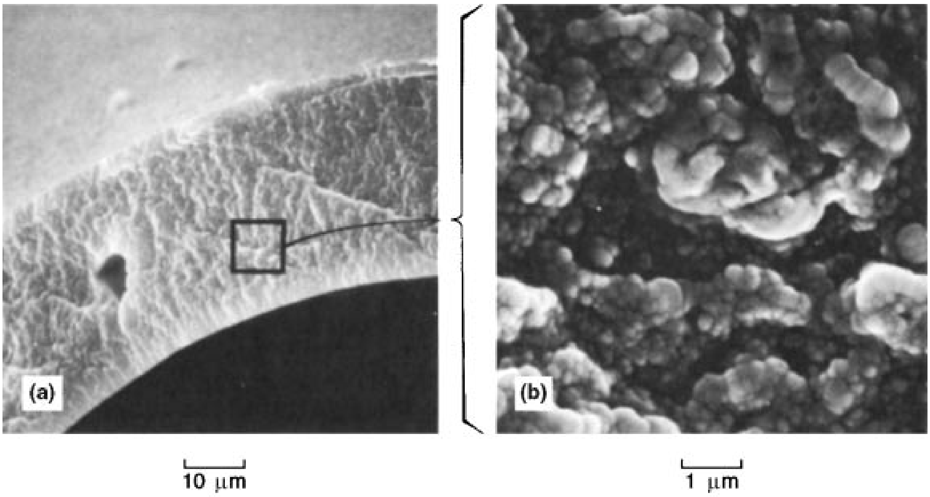

Fig. 8. (**a**) Cross section of cellulose acetate isotropic porous hollow-fiber dry-jet wet spun at incipient gelation point of dope mixture; (**b**) magnification at the central cross section of (**a**). Courtesy of I. Cabasso.

3.5. Macrovoids. Hollow-fiber membranes that are solution-spun by the foregoing methods can exhibit large voids in conical, droplet, or lobe configurations. These voids may extend through the entire fiber cross section (Fig. 9). The voids, in general, result from fast coagulation of a spinning solution that is relatively low in either polymer concentration or viscosity. Fast coagulation does not allow for a gradual exchange of solvent with nonsolvent at the nascent-membrane surface. In most cases, the voids occur when the coagulant intrudes into the extrudate at an early stage of gelation. The gross inward contraction of the surface at subsequent stages causes the surface to seal around the intrusion, forming a tight surface skin. The use of a less severe quenching medium, on the other hand, yields a macrovoid-free hollow fiber (19).

The presence of macrovoids in hollow-fiber membranes is a serious drawback since it increases the fragility of the fiber and limits its ability to withstand hydraulic pressures. Such fibers have lower elongation and tensile strength.

4. Fiber Treatment

4.1. Treatment In-Line. The coagulated fiber on the moving threadline may be subjected to cooling (for melt spinning, or for dry-jet wet spinning conducted at high temperatures), washing to remove trace solvents and dope additives, swelling with diluted solvent and/or plasticizers, stretching between godets, and heat-treating (annealing) to consolidate its morphology and impose transport properties (such as closing the skin pores of an asymmetric hollow-fiber membrane for reverse-osmosis applications). In the continuous processing of hollow fibers, these steps add little to costs but are fundamental to achieving the desired functionality of the product.

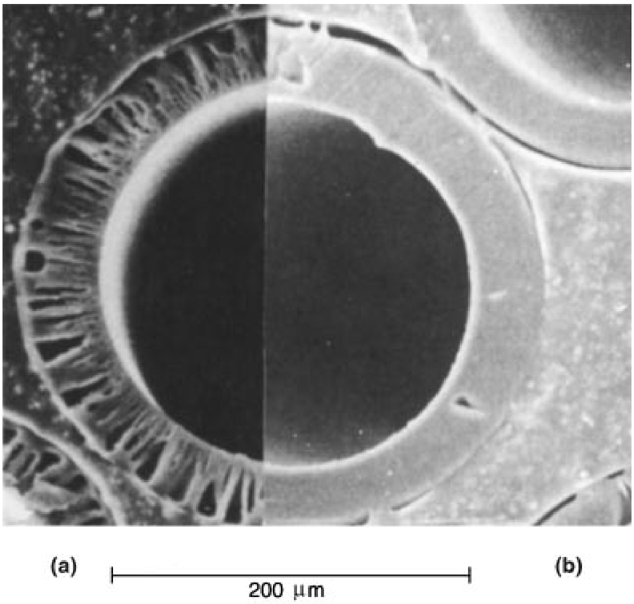

Fig. 9. Cross sections of acrylonitrile hollow fibers spun by the dry-jet wet-spinning method. The two fibers were spun from the same dope composition into a water bath and were internally coagulated by aqueous solutions. Section (**a**) was spun with strong coagulation bore fluids resulting in tight interior skin with macrovoids extending to the exterior zone, and (**b**) was spun with a moderate bore coagulant, slowing the gelation rate of the nascent fiber. The relatively few macrovoids seen in (**b**) are in reverse direction to those in (**a**), and were caused by the water (a strong coagulant) in the quenching bath. Courtesy of I. Cabasso.

4.2. Post-Treatment of Hollow Fibers.

End use of the hollow-fiber membrane dictates the type of post-treatment, if any. There are three main categories: fibers that are spun, fibers that will be chemically or physically modified, and fibers that will serve as a porous matrix for support of another (active) polymer deposited (or entrapped) upon (or within) its walls. There is no theoretical impediment to the inclusion of all conventional treatments in the spinning line: photochemical cross-linking, fluorination, and antiplasticizers have been successful. Fibers that are wet or melt spun with a plasticizer additive often need to be kept plasticized (or wet) to retain their morphology and membrane properties. This is true for many cellulosic, cellulose–ester, and polyamide fibers, as well as for fibers spun from other synthetic materials. However, dried (by gas) fibers, although unsuitable for one application, eg, reverse osmosis, can be good for another, eg, gas separation. The fibers may be plasticized in line; often, however, the hollow-fiber spool is subsequently submerged in a plasticizing medium (batch treatment). The plasticizing agents most commonly used are glycerol, poly(ethylene glycol), Triton X-100 (alkylphenoxylpolyethoxyethanol), and related compounds. Formaldehyde or sodium *meta*-bisulfite is often added to protect the fiber from biological fouling. Using formaldehyde is discouraged due to health concerns with this chemical. In some cases fiber stability is enhanced by adding a soluble divalent cation, eg, magnesium ion, to a storage solution. Calcium can also be employed, but, in aqueous solutions, care must be exerted to prevent the precipitation of sparingly soluble calcium salts.

4.3. Fiber Modification. Chemical modification of the fiber is usually a separate operation. The largest such commercial processing is the deacetylation of cellulose acetate hollow fibers, which converts them into regenerated cellulose hollow fibers employed in hemodialysis. The Cordis-Dow (Miami, Fla.) hemodialyzer shown in Figure 1 is prepared from such fibers. The modification is an alkaline hydrolysis in which bundles of fibers are hydrolyzed, thoroughly washed, neutralized, and plasticized with glycerol in preparation for cutting and encasing into the dialysis cartridge. Another example is provided by Du Pont (20) where a strong oxidizing agent is employed to increase the porosity of a reverse osmosis hollow fiber. The resultant product found application in concentrating fruit juices. This process has been discontiued due to poor economics.

4.4. Composite Hollow-Fiber Membrane. Composite membranes consist of highly porous substrates, having minimum resistance to the permeates, which support ultrathin semipermeable membranes. The appeal of this concept is that it combines the properties of two or more different materials to yield a desired product. It has a special value in membrane technology where compounds that have the required semipermeabilities cannot be extruded into hollow fibers but can be deposited on the interior or exterior surface of a fiber. This technique is also valuable in situations where very thin membranes are desired. Composite hollow fibers, consisting of a polysulfone support matrix coated with cross-linked polyethyleneimine (PEI) or furan resin, are shown in Figure 10. The thickness of the deposited dense layers (resting on a porous, asymmetric polysulfone fiber) is 0.1–1 μm. Such fibers were developed for desalination of saline waters (brackish water and seawater) using the reverse-osmosis process (see WATER, SUPPLY AND DESALINATION). The principal fabrication difficulty is in maintaining continuity of the ultrathin layer, which requires adequate methods of deposition. The production scheme for a composite hollow-fiber

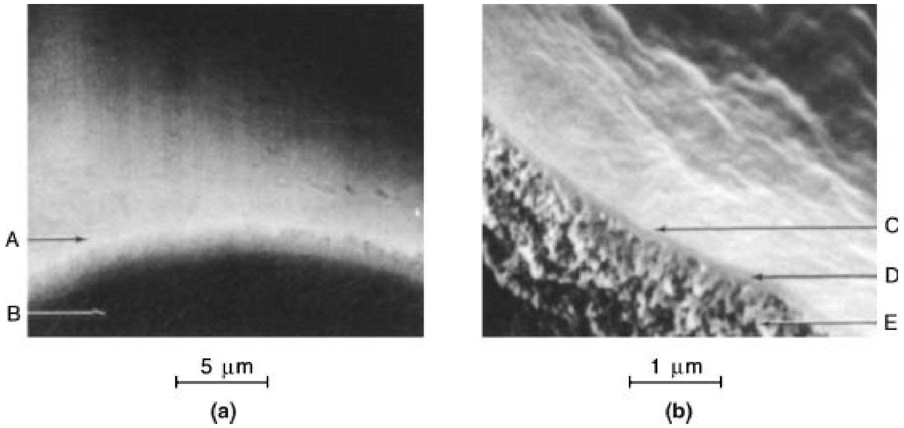

Fig. 10. Composite hollow-fiber membranes: (**a**) polysulfone hollow fiber coated with furan resin. A and B denote furan resin surface and porous support, respectively; (**b**) cross section of composite hollow fiber (PEI/TDI coated on polysulfone matrix). C, D, and E denote tightly cross-linked surface, “gutter” gel layer, and porous support, respectively. Both fibers were developed for reverse osmosis application (18).

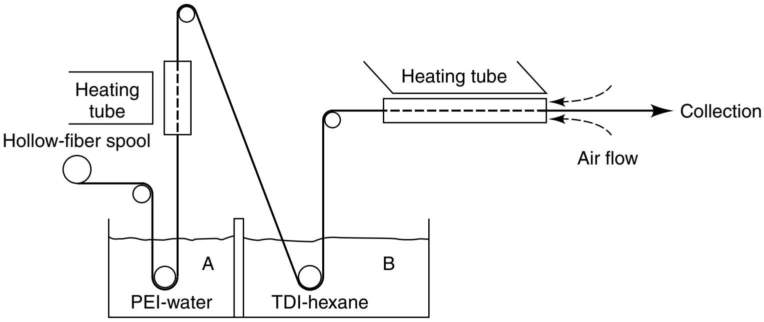

Fig. 11. Composite hollow-fiber production scheme (PEI = polyethyleneimine; TDI = toluene 2,4-diisocyanate). Anisotropic (porous skin) polysulfone hollow fiber is rolled into bath A and is lifted vertically (to avoid droplet formation) into a heating tube. The fiber is then passed through bath B and is annealed in a ventilated heating tube (110°C).

membrane, consisting of polysulfone coated by PEI that is cross-linked *in situ* (on the exterior surface of the fiber), is shown in Figure 11. The furan-resin-coated polysulfone hollow fiber is produced by passing the fiber through a furfuryl alcohol solution followed by treatment with sulfuric acid (21,22), to effect *in situ* cationic polymerization on the exterior surface as shown in Figure 10**a** (see MEMBRANE TECHNOLOGY).

Although these composite fibers were developed for reverse osmosis their acceptance in the desalination industry has been limited due to insufficient selectivity and chemical and oxidative stability. The concept, however, is extremely viable; composite membrane flat films made from interfacial polymerization (23) have gained wide industry approval. Hollow fibers using this technique to give equivalent properties and life, yet to be developed, should be market tested in the coming decades.

4.5. Interpenetrated Wall Matrix. Ion-exchange hollow fibers can be produced by polymerizing an ionic monomer within the porous wall matrix of a hollow fiber. For example, 4-vinylpyridine has been polymerized in a porous wall matrix of polyacrylonitrile (PAN) hollow fiber (24), and monomers containing sulfonic acid moieties have been polymerized in the wall matrix of polysulfone to yield ion-exchange hollow fibers (employed in Donnan-type dialysis). Requirements of such a fabrication are (*1*) the monomers should not dissolve or plasticize the polymer from which the fibers are made; (*2*) the heat generated during the polymerization and contraction prior to the formation of new interpenetrating polymer should be minimized; and (*3*) the polymerization should not occur within the lumen (and hence cause plugging of the fiber). The fabrication of such fibers is accomplished by forcing the monomers into the matrix under pressure while maintaining a flow of gas or liquid in the bore. High charge densities can be obtained by cross-linking the polymer network; for example, by employing sulfonated phenol-formaldehyde as the ionic species, highly cross-linked resin within the fiber wall is obtained (25). Drawbacks of such fibers are brittleness.

4.6. Fiber Handling and Unit Assembly. Most hollow fibers can be collected on spools by winding machines analogous to those used in the textile industry. Individual or multifilaments can be crosswound, or may be wound in a simple parallel arrangement (for highly plasticized, or large ID fibers, where cross-winding intersections may weaken the structure). Subsequent handling of the filament depends on the intended use of the hollow fiber.

Assembling and potting (cementing together) of hollow-fiber bundles, as shown in Figure 1, require great care and precision technology. The potting agent must be compatible with the function assigned to the fiber, as well as with the fiber material. For example, the potting materials employed in a hemodialysis cartridge (Fig. 12) must be blood-compatible and nontoxic, and adhere to the exterior surface of the fibers as well as to the fiber-housing unit. Another factor important in the selection of a potting agent is its surface tension (ability to wet fibers yet not excessively wick). Commonly employed potting agents include epoxy resins (qv), polyurethanes, and silicone rubbers. A potting agent is used in a liquid form that is eventually polymerized and cured in bulk (without solvent). In general, the potting agent must not shrink or evolve excess heat when cured; it must not penetrate the fiber, plug the bore, wick on the fiber walls, or damage any ultrathin coating. It must be hard enough after curing so as not to creep under pressure (crucial for microfiltration, ultrafiltration, gas separation,

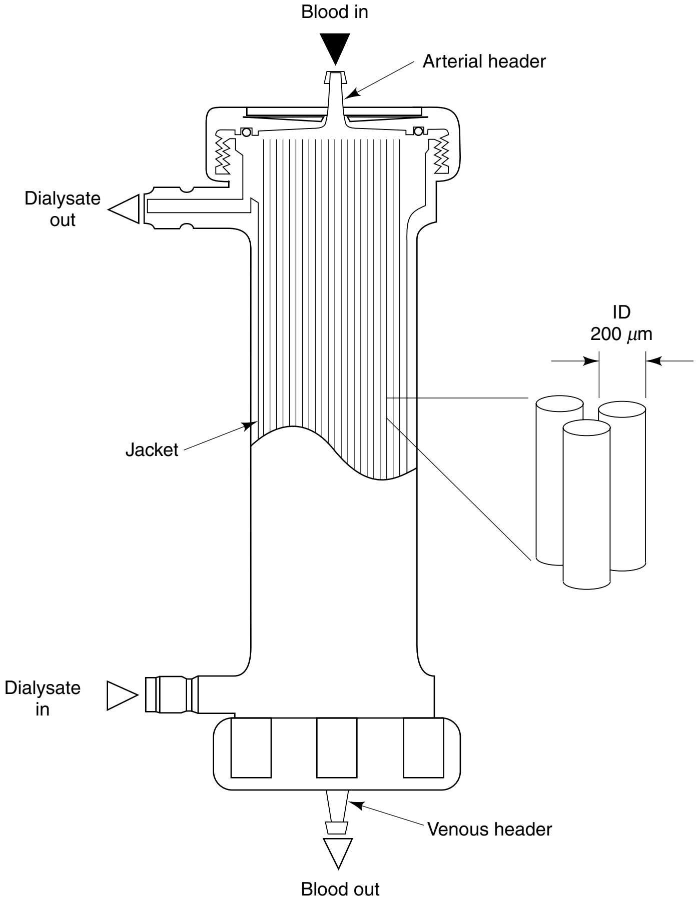

Fig. 12. Schematic of hollow-fiber membrane cartridge employed for blood dialysis. Courtesy of Cordis-Dow.

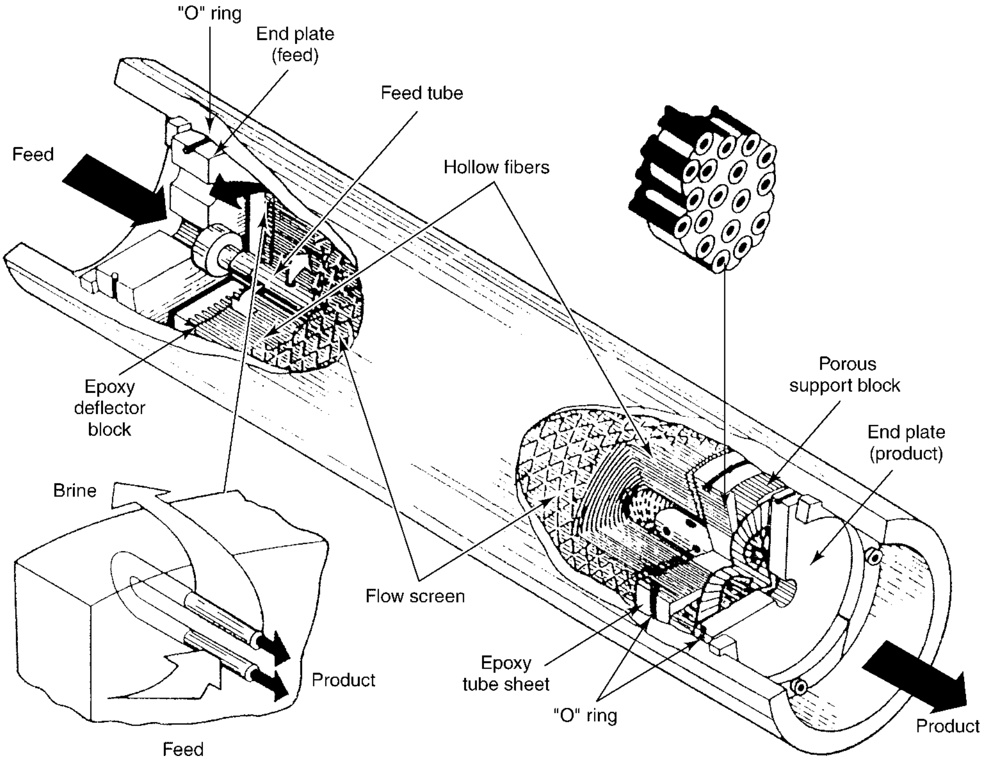

Fig. 13. Du Pont hollow fine fiber Permasep permeator.

nanofiltration and reverse osmosis) and to be capable of further mechanical machining, ie, placed in a lathe and cut to open hollow-fiber bores for reverse osmotic flow.

For the high pressure reverse-osmosis and nanofiltration units, epoxy resins that can withstand elevated hydraulic pressures (>10,000kPa, 1,450psi) are used as potting agents. Composite polysulfone hollow fibers have been potted with an epoxy resin sandwiched between two layers of silicone rubber. The rubber has low adhesion to the fiber, but protects it from epoxy wicking and breakage near the potting fixation spots and permits cutting of the fibers while they are fixed in the rubbery medium. In large commercial reverse-osmosis (RO) units for desalination of seawater and brackish water (eg, Permasep, Hollosep), the fibers are assembled in a U shape (Fig. 13) and are epoxy-potted. Winding of RO hollow-fiber membranes into a permeator is described in References 8, 20, and 26. Various types of blood-compatible polyurethanes are available for hemodialysis potting; others that resist attack by solvents are available for liquid mixture separation by per-vaporation. A difficulty sometimes encountered with ion-exchange hollow fiber is their tendency to undergo dimensional changes when wetted. Since most potting agents require dry potting conditions, the adhesive bond may fail after several wet-dry cycles. To circumvent this problem, chemical treatment is employed to neutralize the ion-exchange sites at the ends of the bundles.

A useful technique commonly employed in manufacturing dialyzers is centrifugal potting, in which the potting agent is introduced to the ends of the pre-assembled rotating cartridge. The potting agent cures while the centrifugal forces assure bubble-free, maximum potting density. The hemodialysis units shown in Figures 1 and 12 contain thousands of fibers that were potted in this manner.

For reverse osmosis and nanofiltration, the feed enters outside the fiber; permeate is inside the fibers and flow can be cocurrent and countercurrent. In the second, for large diameter fibers, where the feed has a high loading of particulates, the feed is through the fiber bore; permeate is outside the fiber; flow can be cocurrent and countercurrent. A third method is essentially dead-end flow wherein the feed is on the outside of the bundle and the permeate is removed from the fiber cores. Microfiltration, ultrafiltration and gas permeation use all three flow patterns (27).

5. Materials

The components employed in spinning-dope formulations must be consistent in every batch preparation, because numerous parameters are involved in the spinning process. Thus, stringent criteria are imposed on the selection of components to be used in each spinning operation. The components are rigorously tested for purity, molecular weight, molecular weight distribution, chemical composition, viscoelastic properties, and other specific parameters that might influence hollow-fiber production and final membrane properties. This often requires close cooperation between the producers of the polymer and the hollow fiber manufacturers.

5.1. Cellulose. Cellulosic hollow fibers are produced chiefly by either of two methods: (*1*) wet spinning of a dope mixture containing cellulose dissolved in cuprammonium solution, eg, Cuprophan fibers, or (*2*) deacetylating cellulose acetate fiber to produce a regenerated cellulose fiber. The cuprammonium process involves mixing and dissolving cellulose at a low temperature. The dope solution can then be stored for prolonged periods if kept in an oxygen-free container. In the spinning process, the water-swollen, coagulated filament gel is thoroughly washed, and the copper is separated from the regenerated cellulose fiber by acid extraction (see FIBERS, REGENERATED CELLULOSE). The process has been perfected to the point of virtually full recovery of ammonia and copper residue. This recovery rate has reduced the cost of manufacturing the fiber, and this factor plus reusability enables the hollow-fiber artificial kidney to dominate the hemodialysis market, though the initial cost is considered somewhat high.

The cellulosic fibers produced by both processes are used primarily for hemodialysis. The blood to be cleaned is circulated through the fiber bore (200–300 μm ID) in a cartridge such as that shown in Figure 12. Metabolic waste, consisting of low molecular weight components, eg, urea and uric acid, rapidly diffuses through the cellulosic fiber wall (thickness of 16–25 μm) which contains 40–60 wt% water. The pore radii generally are smaller than 6 nm. Surface areas range from 0.3 to 3.0 m^2, depending on the model. Manufacturers adjust the surface area by varying the length of the fibers (150–300 mm) and the number of fibers (3,000 to 20,000) employed (28).

The Cuprophan hollow fiber is manufactured with a bore fluid (isopropyl myristate) that has to be removed before the fiber is packed into a dialyzer. In general, the fiber bundles are drained, washed with alcohol, plasticized with glycerol, and sterilized with ethylene oxide. The hollow fibers are interwoven with thread and grouped into bundles. Other sterilization techniques for dialyzers include stream autoclaving, gamma ray, and formaldehyde. The Cuprophan hollow-fiber (and flat-sheet) membranes are often thinner than the cellulose acetate hollow-fiber membranes. They are produced by Enka Glanzstoff AG (Wuppertal, Germany) and Cordis-Dow. Three such bundles are contained in the annular space between two stainless steel tubes and encapsulated with polyurethane at each end (the tubesheets). The inner tube acts as a conduit feeding the shell side of the module, the flow exiting at one end of the outer tube. Two such submodules of 28 cm effective fiber length are joined in series giving 22.5 m^2 membrane area (27).

Gas separation using ethylcellulose hollow fiber has also become important. General Electric A/G Technology is leading this effort. Fluoroaceylated ethylcellulose is reported to have good gas permeation and blood compatibility (29). In China, good results have been obtained using a cellulose solution containing *N*-methylmorpholine-*N*-oxide as solvent and water as a nonsolvent internal and external coagulant additive. Gas permeation for CO_2, N_2, CH_4 and H_2 have been demonstrated. The membrane water content is an important variable for permeation rates (30).

Cellulose Ester. Among the cellulose esters, cellulose acetate [9004-35-7] and cellulose triacetate [9012-09-3] have drawn the most attention. Both polymers have been developed commercially for desalination of brackish water and seawater. When dried the polymers are suitable for gas separation. Commonly, these hollow fibers have an asymmetric structure with a dense skin at the outer surface. Reverse osmosis permeators were manufactured by Dow Chemical (Dowex) until the mid-1980s and consisted of cellulose triacetate (CTA) fibers comprising two types of membrane: asymmetric CTA fat hollow fiber (250 μm OD, 90 μm ID) that is melt-spun into a cooling-leaching bath, and an isotropic melt-spun dense fiber (90 μm OD, 35 μm ID). The first is designed for desalination of brackish water, and the second for seawater. Today, the only CTA hollow fiber manufacturer is Toyobo Co. Ltd (Japan) whose fibers have dimension of 70 μm ID by 165 μm OD. The advantage of CTA over cellulose acetate, which has a degree of acetylation in the range of 2.3 to 2.7 per glucose unit, is that the latter is more vulnerable to biodegradation and hydrolysis (narrow pH operating range of 5–7). Toyobo has about a 4% market share of the desalination reverse osmosis market with its products mostly employed for seawater desalting. One problem encountered with CTA is its long term stability in an aqueous environment that contains a low concentration of chlorine (needed to prevent microbial attack). Chlorine will both oxidize and hydrolyze the CTA membrane. To overcome this problem and still maintain biological control, Toyobo employs chlorine as a shock dose into the system on an infrequent inteval such as 0.5 mg/L for one hour once per day.

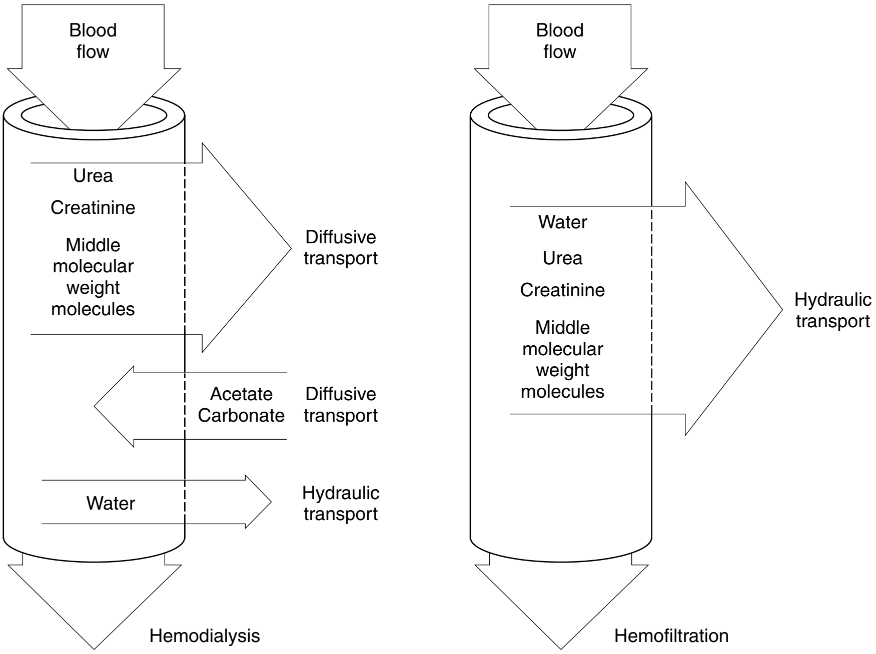

Fig. 14. Mass transfer across hemodialysis and hemofiltration hollow-fiber membranes.

An early historical case description on the production and performance of cellulose acetate (CA) fibers for reverse osmosis is given in References 8 and 31. Since then, CA hollow fibers have had limited commercial use (see also REVERSE OSMOSIS). A cellulose acetate unit, such as that shown in Figure 12, is also manufactured for hemofiltration by Cordis-Dow. The difference between hemodialysis and hemofiltration lies essentially in the transport mechanism; the first is based on diffusive transport, and the second on hydraulic transport, as shown in Figure 14. Cellulose acetate butyrate [9004-36-8] is another membrane polymer with low industrial acceptance.

One report (16) describes the procedure for spinning dry asymmetric cellulose acetate fiber with a bore skin. Such fibers are spun in a modified dry-spinning process in which a volatile liquid (methyl formate) is used as the cellulose acetate solvent. The bore coagulating liquid is isopropyl alcohol, which is subsequently removed. The advantages of these dry fibers over most cellulose acetate membranes are that they can be stored dry, they are wet-dry reversible, they can be sterilized and packed dry, and they are ready for use without removal of preservatives.

5.2. Polysulfone. Polysulfone is a commercial polymer that is a product of bisphenol A and 1,1′-sulfonylbis (4-chlorobenzene) (see POLYMERS CONTAINING SULFUR, POLY(PHENYLENE SULFIDE)). This high strength thermoplastic can be spun into hollow fiber by melt- or dry-jet wet-spinning techniques. The polymer is hydrophobic, but is soluble in water-miscible solvents such as DMF. This fiber has been investigated as a matrix component for the preparation of composite hollow-fiber membranes (5,9,18). Composite hollow-fiber membranes consisting of polysulfone fibers coated by semipermeable ultrathin furan-resin membranes (22) are being manufactured by FRL Corp. (Dedham, Mass.). Various companies (Amicon-Millipore; Romicon-Koch Industries; and Berghof GmBH, Germany) manufacture an essentially asymmetric polysulfone hollow fiber with a core skin for industrial and medical ultrafiltration. Since polysulfone is a hydrophobic material, wetting agents (eg, glycerol, dodecyl sodium sulfate) are often incorporated into the porous walls of the dry fiber after manufacturing. Polysulfone hollow fibers by Fresenius and Amicon employed in hemofiltration display exceptionally high interaction with blood and plasma proteins. Membrane thickness is in the 40 to 70 μm range. For gas separation, membranes can be made into defect-free thin skin structures by coating the membrane in a post-treatment with a dilute solution of silicone rubber. Since the silicone rubber is thin, its permeability is high, thus sealing defects in the base membrane without materially affecting the permeability of the membrane. The Monsanto Prism separator embodies this concept. Encased ultrafiltration size fibers have found use in laboratories as a bioreactor. The molecular weight cut-off of 10,000 daltons is advantageous (32). Separation of cells from fermenter broths, purification, and concentration of antibiotic products and enzymes are other limited use areas .

5.3. Polyethylene. Microporous high-density polyethylene (HDPE) and low-density polyethylene (LDPE) hollow fibers membranes have been prepared from polyethlylene–diisodecyl phthalate solution via thermally induced phase separation. The density of the polyethylene has a large affect on morpohology. HDPE has about 5 times higher water permeability than the LDPE due to the larger pore and higher porosity at the outer membrane surface. This higher permeability was due to both the initial larger structure formed by spinodal decomposition and the suppression of the diluent evaporation from the outer membrane surface. This was a result of the high solution viscosity (34).

5.4. Poly(methyl methacrylate). Poly(methyl methacrylate) (PMMA) is a hydrophobic polymer that is soluble in some water-miscible solvents, such as dimethyl sulfoxide and DMF (see METHACRYLIC POLYMERS). Membranes that are produced by casting atactic PMMA into a water gelation bath have poor mechanical and transport properties. However, solution compositions consisting of isotactic and syndiotactic PMMA mixtures form thermoreversible sol-gel stereotopic complexes that can be cast or spun into hollow fibers with controlled wall porosity and improved mechanical strength (35,36). Such dope solutions are spun hot into a subambient ($<30°C$) atmosphere; there, the nascent fiber forms a gel and is subsequently passed through water to effect an exchange of water for solvent. Since matrix formation is established during gelation, the microstructure of the fiber wall does not collapse when submerged in water, and water-swollen fiber (ca 65 wt% water content for dope composition spun with 20 wt% polymer) is obtained. Toray Industries, Inc. (Japan) has developed a PMMA hollow-fiber membrane. Use of this polymer has found some application as a hollow-fiber artificial kidney. Membrane thickness is in the 30–40 μm range (28).

5.5. Polyamide. Nylon hollow fibers are produced by Du Pont, Berghof GmbH, and many others. The development of hollow fiber initially from nylon-6 or nylon-6,6 was a natural extension of technology established in the textile industry (see POLYAMIDES, FIBERS). These materials were aimed toward the desalination of brackish water employing high pressure reverse osmosis. Fiber dimensions were 50–60 μm OD and 25–30 μm ID. Hydraulic permeability through these aliphatic nylon derivatives was very low. The second generation of asymmetric polyamide hollow-fiber membranes developed for high pressure reverse osmosis consist of derivatives of aromatic polyamides (aramids) with improved water permeability and water (brackish and seawaters) separation. Before 1998, they were the largest consumers of hollow fibers. The fibers are spun from a solution of inorganic salts and DMA while a nitrogen stream is maintained through the nascent fiber bore. The extrusion is carried into a high temperature nitrogen atmosphere, resulting in solvent evaporation, and skin establishment in the outer zone is annealed. These fibers must be stored wet to retain the asymmetric morphology essential for high hydraulic permeability.

Du Pont introduced two types of hollow-fiber permeators for desalination and water reclamation: the B-10 Permasep permeator for desalination of seawater at up to 8300 kPa (up to 83 atm), and the B-9 Permasep module for low pressure brackish water operations (1400 to 2800 kPa, 14 to 28 atm) (37). The fiber dimensions for the B-9 permeator are 91 μm OD and 44 μm ID, and for B-10 module 95 μm OD and 42 μm. In comparison to the smaller diameter fibers mentioned above, Berghof GmbH has developed an ultrafiltration fiber (aromatic polyamide) by the dry-jet wet-spinning method. A variety of asymmetric fibers with bore skin having large inside diameters (600–1500 μm) and a molecular weight cut-off of 2,000–50,000 are being manufactured for industrial and medical ultrafiltration processes. Fibers with dimensions of about 200 μm (ID) have been developed for hemofiltration, and are manufactured in cartridges 0.1 to 0.3 m long containing 1 to 2 m^2 of membrane area. Gambio in Sweden is a leading supplier. DuPont, because of high manufacturing costs, has retired from commercial operations. However, throughout the world, a number of brackish and seawater desalting plants are still in operation employing their modules. These facilities are slowly being converted to spiral composite polamide membrane elements.

The literature notes many other polyamide hollow fibers, none of which have achieved significant commercial success. Included in this category are such polymers (some of which are cross-linked) as piperazinamides, hydrazine, substituted acrylamide, and modified and grafted nylons.

5.6. Other Nitrogen-Containing Polymers. Polymeric membranes which are nitrogen based appear to be preferred for their overall combination of properties; high selectivity, good flux rate, longevity, and relative stability to oxygen and other chemicals. Other than the polyamides an example would be polybenzimidazole. Polybenzimidazole polymers have been spun chiefly from poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] (PBI) (38,39) (see POLYIMIDES). Asymmetric fibers with outside skins have been spun from a solution consisting of 20–25 wt% PBI in DMA by the dry-jet wet-spinning technique. An inert hydrocarbon liquid is used as the bore fluid, and the fiber is annealed in-line at elevated temperatures (140–180°C) in ethylene glycol. The PBI fibers, which have excellent chemical resistivity and mechanical properties have not realized their full potential because PBI is still an expensive polymer (see HIGH

PERFORMANCE FIBERS). There is limited use in microfiltration, ultrafiltration, reverse osmosis and gas separations.

Another example is polyacrylonitrile (PAN). Hollow fibers consisting of polyacrylonitrile and its copolymers have been developed by Gulf South Research Institute (Figs. 2**b** and 9) and are manufactured among others by Hospal and Asahi Medical Corp. Commercially available acrylonitrile copolymers are soluble in water-miscible solvents such as DMA and DMSO, and therefore can be spun by the dry-jet wet-spinning technique with a water coagulant. These fibers are used for pervaporation, microfiltration, ultrafiltration and hemofiltration, and as porous substrates (interpenetrated networks) for the production of ion-exchange hollow fibers (24) (see ACRYLONITRILE POLYMERS, SURVEY AND STYRENE-ACRYLONITRILE (SAN)). In dialyzers these membranes have received a lot of attention since the 1970s. Problems associated with their costs and high permeability to water have limited use. Additional nitrogen-containing polymers for which hollow fibers have been made include polyimides, polyoxadiazole, nitrogen-substituted aromatics (29), polyurea, and polyethylenimine. PAN hollow fibers when treated with ammonium dibasic phosphate and then further oxidized in air, carbonized in nitrogen and activated with CO_2 gave strong adsorption properties. By changing the paramter ratios, the number of micropores and mesopores can be alteres as can their physical properties (40).

5.7. Natural Polymers. A relatively new hollow fiber membrane line is made from chitosan (41). Chitin is a polymer of *N*-acetlo-d-glucosamine. It is biocompatible with athrombogenic and hemostatic. Difficulties in forming chitosan hollow fibers are in the choice of chitosan. Molecular weight is very important as is obtaining a proper concentration of the low viscosity solution. The patented method for the wet spinning production of the hollow fibers is using two coagulants–ammonia or a mixture of ammonia with nitrogen and sodium hydroxide in a highly viscous solutions in acetic acid. These membranes have application in medicine in dialysis and blood separation and biotechnology as membrane reactors.

5.8. Glass and Inorganic Hollow-Fiber Membranes. The development of porous, glass hollow fibers for membrane applications is reported in Reference (42) (see also GLASS). The glass material provides higher dimensional and chemical stability than most polymeric materials, but the fibers have the disadvantages of brittleness and low permeabilities. The glass is essentially composed of the system, Na_2O-B_2O_3-SiO_2. In the processing, an induced microphase separation results in rich alkali borate domains. When leached with mineral acids, the fibers are left with a porous silica matrix ($>$96% silica). Fibers having diameters of 0.3 mm ID are manufactured by Schott for ultrafiltration. In general, the economics of the production are poor and use is limited.

Inorganic membranes (33,43) are generally more stable than their polymeric counterparts. Mechanical property data have not been definitive for good comparisons. Industrially, tube bundle and honeycomb constructions predominate with surface areas 20 to 200 m^2. Cross-flow is generally the preferred mode of operation. Packing densities are greater than 1000 m^2/m^3. Porous ceramics, sintered metal, and metal oxides on porous carbon support (for microfiltration and ultrafiltration) are the most common materials.

Use of glass and inorganic membranes has been held back by the difficulty in developing tube sheet seals which prevent mixing of feed with permeate. Among the current solutions are epoxies, Teflon, Viton, polyester, and silicone rubber. In general, these types of membranes, due to their chemical inertness, are finding application in very difficult waters, ie, highly contaminated waste industrial streams, toxic systems, whey, juice manufacture.

5.9. Others. Hollow-fiber membranes have been spun from various other polymers, including polyesters, silicone rubber, silicone rubber/polycarbonate copolymers, ceramics, porous metallics, and polyphosphazenes for gas separations. Microfilters and ultrafilters and reverse osmosis hollow-fiber membranes have been made from polyfuran poly(vinylidene fluoride), polyethylene, and poly(vinyl alcohol). A patent by Du Pont in 1971 (44) identified a number of noncrystalline (glassy) polymer materials with high intrinsic permeabilities, providing by melt spinning the potential for gas separations using hollow fibers and for composite hollow-fiber membranes; as such, *in situ* plasma polymerization on the surface of porous hollow fibers has been reported (45). There are numerous compounds that can be plasma-deposited on a porous fiber to yield a multitude of classes of composite membranes. Such fibers will become more readily available as plasma polymerization technology progresses (see PLASMA TECHNOLOGY). Ethylene—vinyl alcohol fibers are under study as hemofiltration membranes (46).

6. Microfiltration and Ultrafiltration (Low Pressure Membranes)

The most successful hollow fiber membranes for new applications are those used in microfiltration and ultrafiltration (47,48). Annual growth rates are in the 10% to 15% range in the municipal and waste water markets, as a pretreatment for reverse osmosis and nanofiltration, medical applications and industrial sales for juice and soft drink manufacturers. Hollow fibers constitute about 90% of the market versus flat sheet and plate and frame. Feed flow direction is mostly outside the membrane into the fiber bore (outside-in) or inside-out. Some units operate in a dead-end manner. Typical flow direction is direct, crossflow and feed and bleed. Polymer materials are polyproplyene, poly(vinylidene fluoride), polysulfone, polyether sulfone and cellulose derivative. Other low volume polymers are nylon and PTFE. System applied pressures range from vacuum to 600 kPa (4 atm). To control this transmembrane pressure, essentially all large scale systems are delivered with a cleaning system as part of the membrane package. These cleanings can be performed in place (CIP), with and without air scouring. Most systems have timed air or water blow back in order to flush most foulants from the membrane surface. Timing can be for example 10 seconds every minute or two. With this designed sequence, complete chemical cleanings are, then, required at infrequent intevals.

The elements can be delivered with their own pressure housing or can be mounted in such a manner that a relatively large number of elements can be placed, either vertically or horizontally, into a tank and a vacuum applied to the fiber bores to remove the permeate. This vacuum system, referred to as submersible vacuum or immersed microfiltration or ultrafiltration, is gaining

Fig. 15. Immersed hollow fiber cassette. Courtesy of ZENON Environmental, Inc.

prominence because of low energy consumption and large productivity per unit of vessel volume (49), see Figure 15. Pressure microfiltration or ultrafiltration have larger energy consumptions than the submerged systems, but their fluxes can be higher than submersible systems. Low flux rates, however, tend to extend the period between chemical cleanings.

Microfiltration pore size generally ranges from 0.05 μ to 10 μ, typically 0.1 μ to 0.8 μ. Ultrafiltration range is .005 μ to 0.15 μ, typically 0.01 μ to 0.05 μ (300 to 300,000 Daltons). Thus, microfiltration is satisfactory for rejections of most colloids, bacteria, fungus cysts and some viruses while ultrafiltration can reject these plus essentially all viruses, colloids and pathogens. The exact pore size range that defines each process is not in uniform agreement.

Microfiltration and ultrafiltration do not reject low molecular weight organics and ionic species. Thus, they are complementary to reverse osmosis and nanofiltration. The key to industrial success appears to be mainly commercial factors of cost per unit permeate flow, reliability, life, and on-stream time. To date, there is no standardization of products or performance. Customers generally operate pilot facilities to define the performance value of each system that is being considered employing as feed actual site waters over a time span that covers the important seasonal variations.

The growth areas for microfiltration and ultrafiltration is as a protective barrier for the drinking water supply from microbes, turbidity and color, now quantified and mandated by the Surface Water Treatment Rule, US Environmental Protection Agency. Water treatment plants are quite large, eg, 70 million gallons a day in Minneapolis, Minn. and 42 million gallons a day in Kamloops, British Columbia (50). A secondary large use is as a pretreatment for brackish reverse osmosis and nanofiltration. Seawater pretreatment by these low pressure membranes is currently being demonstrated. Because of the superior quality of the permeate, microfiltration and ultrafiltraion are supplanting conventional filtration as the purification technology of choice.

In highly turbid waters, to improve productivity and lower cleaning costs, sometimes a simple sand filter is placed before these low pressure units (51). Disinfection is also provided. Costs are now comparable to gross media filtration with expectations, due to improving technology and manufacturing, and competition, of lowering further capital and operating costs.

Membrane bioreactors (52) that use microfiltration or ultrafiltration are now coming on-stream commercially (53,54). These units are being employed as tertiary and sometimes secondary treatment systems for municipal wastes. A large number of pilot tests have shown that bioreators give superior quality water at competitive costs. They occupy a significantly smaller plant footprint.

7. Sorbent Fibers

7.1. Filled Fibers. Interest in the encapsulation of specific active materials (eg, activated charcoal, enzymes, drugs) led to the development of encapsulation spinning, usually employing a wet- or dry wet-spinning process. In the encapsulation process, the filling ingredient is suspended or dissolved in the bore liquid medium (usually a coagulant) which is injected through the internal orifice during the spinning process (Fig. 6). Subsequent quenching and washing in a water bath are employed. Reports on the spinning of polysulfone, cellulose acetate, and polyacrylonitrile fibers filled with activated charcoal, enzymes, drugs, ion exchangers, and phosphate sorbents are described in References 55 and 56. The spinning conditions and materials for such fibers must not reduce the activity of the encapsulated ingredient. Ion-exchange beads encapsulated in a lumen of cellulose acetate hollow fiber (developed at Gulf South Research Institute) are shown in Figure 2**c** (see MICROENCAPSULATION).

The rationale for the development of such fibers is demonstrated by their application in the medical field, notably hemoperfusion, where cartridges loaded with activated charcoal-filled hollow fiber contact blood. Low molecular weight body wastes diffuse through the fiber walls and are absorbed in the fiber core. In such processes, the blood does not contact the active sorbent directly, but faces the nontoxic, blood compatible membrane (see CONTROLLED RELEASE TECHNOLOGY, PHARMACEUTICAL). Other uses include waste industrial applications as general as chromates and phosphates and as specific as radioactive/nuclear materials.

7.2. Hollow Fiber with Sorbent Walls. A cellulose sorbent and dialyzing membrane hollow fiber was reported in 1977 by Enka Glanzstoff AG (57). This hollow fiber, with an inside diameter of about 300 μm, has a double-layer wall. The inner wall consists of Cuprophan cellulose and is very thin, approximately 8 μm. The outer wall, which is ca 40-μm thick, consists mainly of sorbent substance bonded by cellulose. The advantage of such a fiber is that it combines the principles of hemodialysis with those of hemoperfusion. Two such fibers have been made: one with activated carbon in the fiber wall, and one with aluminum oxide, which is a phosphate binder (also see DIALYSIS).

8. Future Prospects

Membrane science began emerging as an independent technology only in the late 1960s, and its concepts still are being defined. Intra- and interprocess competitive pressures are the driving force. Many developments evolved from fundamental studies that were government-sponsored. However, in the 1990s as it has become a feasible technology in the industrial complex, corporate investment and resources have resulted in substantial growth opportunities for membranes. Acedemia is providing theoretical foundations as scientists try to expand the versalitity of hollow fibers into a number of applications, particularly in bioengineering and biotechnology. Currently, hollow-fiber membrane units are used in water separations in large volume applications; they are well established in hemodialysis and the potential in gas separation is very large. Hollow fiber membranes and chromatographic resin beads are commonly employed in a variety of bioseparation processes (58). This application is a small volume, high price opportunity, but its uniqueness and value of the end-product allows for high profit margins.

Microfiltration and ultrafiltration have emerged at the beginning of the 21st century as the leading uses for new hollow fiber systems. The driving force has come from the desire to protect municiple water systems from bacteria, viruses and pathogens. The United States Environmental Protection Agency has quanitatively defined the limits for these microbes and turbidity in drinking water streams.

Hollow-fiber technology is difficult to advance versus flat-sheet membrane technology, chiefly because the laboratory casting of the latter is simple and does not require special equipment. Nevertheless, the hollow-fiber configurations are commercially competitive.

Hollow-fiber membranes are subjected to extensive studies for gaseous separation (eg, CO_2, H_2, O_2, N_2, H_2S, CO, CH_4), where the capillary configuration has an advantage over the spiral-wound flat film (59) and plate-and-frame devices. Such fibers achieved first niche commercial prominence in such medical purposes as membrane oxygenators. Commercializations and development activities are now occurring rapidly at a number of corporations including A/G Technology, Dow Chemical Co., Du Pont, Monsanto, Perma Pure, Toyobo, Ube Industries, and Union Carbide. For high pressure applications it appears glassy rigid polymers as polysulfone, polycarbonate polyaramid, and polyamide are preferred. Sintered inorganics, ie, iron, nickel, aluminas, and carbides are involving much attention. Glassy polymers have an amphorous polymeric material that is below its softening or glass-transition temperature under the conditions of use. This concept is opposed to a rubber polymer which is employed above its glass-transition temperature. The rigidity of the glassy polymers offer better selectivity than the rubbery polymers (27).

Another significant area of development and commercialization is pervaporation. These membranes are dense, rather than porous structures. Generally asymmetric composite constructions are employed with the ultrathin membranes on an open support. Key economic variables for commercial viability require high productivity, excellent selectivity, life expectancy, and low internal pressure drops. Hollow fibers inherently can satisfy these needs vs flat films but problems with temperature variations with length have to be considered. Some common membrane materials are poly(vinyl alcohol), silicones, cellulose acetates, polysulfones, polyacrylic acid, polyetheramides, polyolefins, ion-exchange resins, and combinations of these. Acceptance is being gained for use in separation and recovery of liquid mixtures, ie, dehydration of ethanol, isopropyl alcohol, and ethylene glycol.

Supported liquid membranes in the configuration of porous hollow-fiber matrices (33,60) consist of an organic solution of an extracting agent (carrier), absorbed on a thin microporous support. The supported liquid membrane separates the aqueous solutions initially containing the permeating ions (feed solution) from the aqueous solution initially free of these ions. In this process, metal ions are pumped across the membrane, from a low to a highly concentrated solution, via coupling of metal ion to another ion. In such a process, the recovery of metals (eg, copper, gold, silver, platinum, or uranium) from dilute leach solution is possible. Within the same concept is the recently developed hollow fiber containing liquid membrane (27) for gas and liquid separations. In this process, thousands of microporous hydrophobic hollow fibers are packed into a permeator shell filled with the aqueous solution that acts as the membrane. The fibers are present in two distinct sets, feed set and the sweep set, with the ends of each set being separated. The feed gas mixture flows through the lumen of the feed hollow fibers and is swept into the second hollow fibers via an aqueous nonwetting membrane liquid solution. The liquid membrane concept is experimental at this time.

Significant research and development effort is being placed on a chlorine-resistant membrane that will maintain permeability and selectivity over considerable time periods (years). This polymer activity is not limited to hollow fibers, but the thick assymetric skin of hollow-fiber construction might offer an advantage in resolving the end use need as opposed to the ultrathin flat-sheet composite membranes. Similarly, in recent years, membranes that are "fouling resistent" have appeared commercially. There have been several iterations of these membranes so a product that is fully free from biological and colloidal fouling has yet to be produced.

Sorbent fibers were developed in the late 1970s, particularly by California Institute of Technology and Gulf South Research Institute. The concept of encapsulation within a hollow fiber, gas, liquid, suspended solid, catalyst, or others, has potential. For example, Massachusetts Institute of Technology is researching this field in conjunction with developing an artificial pancreas (61). Similarly, University of Minnesota, Cellex Biosciences, Regenerex and Baylor College of Medicine are looking at artificial livers using hollow fibers (62). Progress, however, in the 1980s and 1990s has been slow in medicine, agriculture, waste recovery, and other fields mostly due to low value-in-use and high development and acceptance costs.

A full listing of all U.S. patents issued between February 1970 through February 1981 is given in Reference (29). Similar related material on membranes, microfiltration, ultrafiltration, and reverse osmosis can be found in References 63–66.

BIBLIOGRAPHY

"Hollow-Fiber Membranes" in *ECT* 3rd ed., Vol. 12, pp. 492–517, by I. Cabasso, Gulf South Research Institute; in *ECT* 4th ed., Vol. 13, pp. 312–337, by I. Moch, Jr., E. I. du Pont de Nemours & Co., Inc.; "Hollow-Fiber Membranes" in *ECT* (online), posting date: December 4, 2000, by I. Moch, Jr., E. I. du Pont de Nemours & Co., Inc.

CITED PUBLICATIONS

1. H. K. Londsdale, *J. Membrane Science* **10**, 81 (1982).
2. R. O. Noble and S. A. Stein, *Membrane Separations Technology – Principles and Applications*, Elsevier, Amsterdam, 1995.
3. H. I. Mahon and B. J. Lipps, in N. M. Bikales, ed., *Encyclopedia of Polymer Science and Technology*, Vol. **15**, Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1971, p. 258.
4. R. W. Baker and H. K. Lonsdale, in A. C. Tanquary and R. E. Lacey, eds., *Controlled Release of Biologically Active Agents*, Plenum Press, Inc., New York, 1974.
5. I. Cabasso and co-workers, *J. Appl. Polym Sci.* **21**, 1883 (1977).
6. I. Cabasso and I. Leon, *Boston AIChE 80th National Meeting*, microfiche no. 32, 1975.
7. S. Loeb and S. Sourirajan, *Adv. Chem. Ser.* **38**, 117 (1962).
8. T. A. Orafino, in S. Sourirajan, ed., *Reverse Osmosis and Synthetic Membranes*, National Research Council, Ottawa, Ontario, Canada, 1977, p. 313.
9. I. Cabasso, E. Klein, and J. K. Smith, *J. Appl. Polym. Sci.* **20**, 2377 (1976).
10. *Permasep Products Engineering Manual*, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1992.
11. F. L. Singer, *Strength of Materials*, 2nd ed., Harper & Row, New York, 1962, p. 17.
12. K. H. Keller, *Fluid Mechanics and Mass Transfer in Artificial Organs*, American Society of Artificial Internal Organs, Apr., 1973.
13. R. H. Haynes, *Am. J. Physiol.* **198**, 1193 (1960).
14. L. Rebenfeld, in N. M. Bikales, ed., *Encyclopedia of Polymer Science and Technology*, Vol. **6**, Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1967, p. 505.
15. F. Tasselli, J. C. Jansen, and E. Drioli, *J. Appl. Polym. Sci.* **91**, 841–853 (2004).
16. U.S. Pat. 4,035,459 (July 12, 1977), R. Kesting (to Chemical Systems, Inc.).
17. D. R. Lloyd, ed., "Materials Science of Synthetic Membranes," *ACS Symposium Series 269*, ACS, Washington, D.C., 1985.
18. I. Cabasso, E. Klein, and J. K. Smith, *J. Appl. Polym. Sci.* **21**, 165 (1977).
19. I. Cabasso, in A. Cooper, ed., *Ultrafiltration*, Plenum Press, New York, 1980.
20. U.S. Pat. 4,938,872 (July 3, 1990), J. W. Strantz and W. J. Brehm (to E. I. du Pont de Nemours & Co., Inc.).
21. I. Cabasso and A. P. Tamvakis, *J. Appl. Polym. Sci.* **23**, 1509 (1979).
22. A. F. Allegrezza, Jr. and co-workers, *Desalination* **20**, 87 (1977).
23. U.S. Pat. 4,277,344 (July 7, 1981), J. E. Cadotte (to Filmtec Corp.).
24. A. Rembaum and E. Selegny, eds., *Polyelectrolytes and Their Applications*, Vol. **2**, Reidl Publishing Co., Boston, 1975.
25. E. Klein and co-workers, *Polym. Lett.* **13**, 45 (1975).
26. U.S. Pat. 3,690,465 (Oct. 15, 1970), P. R. McGinnis and G. J. O'Brien (to E. I. du Pont de Nemours & Co., Inc.).
27. W. S. W. Ho and K. K. Sirkar, eds., *Membrane Handbook*, Von Nostrand Reinhold, New York, 1992.
28. M. A. Newberry, *Textbook of Hemodialysis for Patient Care Personnel*, CC Thomas, Springfield, Ill., 1989.
29. J. Scott, ed., *Hollow Fibers Manufacture and Applications, Chemical Technology Review No. 194*, Noyes Data Corp., Park Ridge, N.J., 1981.
30. X. Jie, Y. Cao, B. Lin, and Q. Yuan, *J. Appl. Polym. Sci.* **91**, 1873–1880 (2004).
31. T. A. Orofino, *Progress Report No. 549*, Office of Saline Water Research and Development, U.S. Dept. of the Interior, Washington, D.C., May 1970.

32. J. C. Gomez and co-workers, *Progress in Membrane Biotechnology*, Birkhauser Verlag, Boston, 1991.
33. L. Cecille and J. C. Toussaint, *Future Industrial Prospects of Membrane Processes*, Elsevier Applied Science, London, 1989.
34. J. Sun, G. Wu, and Q. Wang, *J. Appl. Polym. Sci.* **93**, 602–607 (2004).
35. Y. Sakai and co-workers, *Preprint, 178th Meeting ACS*, Division of Colloid and Surface Chemistry, Washington, D.C., Sept. 1979.
36. Y. Sakai and H. Tanzawa, *J. Appl. Poly. Sci.* **22**, 1805 (1978).
37. V. P. Caracciolo, N. W. Rosenblatt, and V. J. Tomsic, in Ref. , p. 343.
38. F. S. Model and L. A. Lee, in H. K. Lonsdale and H. E. Podall, eds., *Reverse Osmosis Membrane Research*, Plenum Press, New York, 1972, p. 285.
39. F. S. Model, H. J. Davis, and J. E. Poist, in Ref. , p. 23.
40. H. Matsuyama, K. Hayashi, T. Maki, M. Teramoto, and N. Kubota, *J. Appl. Polym. Sci.* **93**, 471–474 (2004).
41. Z. Modrzejewska, *Biopolymers* **73**, 61–68 (2004).
42. R. Schnabel and W. Vaulont, *Desalination* **24**, 249 (1978).
43. R. R. Bhave, *Inorganic Membranes Synthesis, Characteristics and Applications*, Van Nostrand Reinhold, New York, 1991.
44. U.S. Pat. 3,567,632 (Mar. 1971), J. W. Richter and H. H. Hoehn (to E. I. du Pont de Nemours & Co., Inc.).
45. H. Yasuda, in Ref. 8, p. 263.
46. M. R. Pillarella, *Solute Transport in Hollow Fiber Membranes and its Application to Hemifiltration and the Bioartificial Pancreas*, PhD Dissertation, University of Delaware, Newark Del., 1989.
47. M. Cheryan, *Ultrafiltration Handbook*, Technomic Publishing Co. Lancaster (1986).
48. A. S. Michaels, *Chemtech* **11**, 36 (1981).
49. P. Cote, *Immersed Membrane Options for Water Reuse*, Internation Desalination Association World Congress, Bahamas, 2003.
50. Water Desalination Report, volume **41**, No. 9 and 10, 2005.
51. K. Andes, C. R. Bartels, J. Long, and M. Wilf, *Design Condiserations for Wastewater Treatment by Reverse Osmosis*, International Desalination Association World Congress, Bahamas, 2003.
52. A. S. Michaels, C. R. Robertson, and S. N. Cohen, *Hollow Fiber Bioreactor – A Novel Approach to Continuous Immobilzed Whole Cell Biochemical Synthesis*, 180th National Meeting of the American Chemical Society, Las Vegas, NV., 1980, pp. 24, 28.
53. G. Crawford, J. Lozier, R. Bergman, P. Mueller, and G. T. Daigger, *Procurement of Membrane Equipment: Differences Between Water Treatment and Membrane Bioreactor (MBR) Applications*, American Water Works Association Membrane Technology Conference, 2003.
54. S. Adham, J. DeCarolis, and L. Wasserman, *Optimization of Various MBR Systems for Water Reuse*, International Desalination Association World Congress, Bahamas, 2003.
55. E. Klein and co-workers, *Trans. Am. Soc. Artif. Intern. Organs* **24**, 127 (1978).
56. U.S. Pat. 3,875,008 (Apr. 1,1975), M. Yoshino, Y. Hashino, and M. Morishita (to Asahi Kasei Kogoyo Kabushiki Kaisha).
57. *Cuprophan Technical Information Bulletin No. 12.1 Enka AG*, Product Group, Wuppertal, Germany, 1977.
58. X-P. Dai, S. Majumdar, R. G. Luo, and K. K. Sirkar, *Biotechnol. Bioengineering* **83**(2), 20/7 (2003).
59. D. L. MacLean and T. E. Graham, *Chem. Eng.* **54** (Feb. 25, 1980).
60. W. C. Babcock and co-workers, *Symposium on Separation Science and Technology for Energy Applications*, sponsored by DOE and Oak Ridge National Laboratory, Gatlinburg, Tenn., Oct. 1979, p. 46.

61. *Chem. Eng. Prog.*, 13 (Nov. 1993).
62. In Vivo, the Business & Medicine Report, 17 (Nov. 1993).
63. J. Scott, ed., *Membrane and Ultrafiltration Technology 1980*, *Recent Advances, Chemical Technology Review No. 147*, Noyes Data Corp., Park Ridge, N.J., 1980.
64. J. Scott, ed., *Desalination of Seawater by Reverse Osmosis, Pollution Technology Review No. 75*, Noyes Data Corp., Park Ridge, N.J., 1981.
65. S. Torrey, ed., *Membrane and Ultrafiltration Technology, Developments Since 1981*, Noyes Data Corp., Park Ridge, N.J., 1984.
66. R. W. Baker and co-workers, *Membrane Separation Systems, Recent Developments and Future Directions*, Noyes Data Corp., Park Ridge, N.J., 1991.

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