

STRUCTURAL ASPECTS OF ASYMMETRIC (*SKINNED*) SYNTHETIC POLYMERIC MEMBRANES

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Abstract— Asymmetric, *i.e.* *skinned*, membranes are structured at chemical and physical levels. The influence of various structural features on both processing and end use characteristics are illustrated by reference to the cellulose esters.

The solubility of the cellulose varies with degree of substitution (D.S.) and derivative type. High molecular weight (MW) and narrow MW distribution maximize permselectivity. Cellulose acetate (CA) mixed esters exhibit greater solubility than do the homoesters and represent ideal membrane polymers. Esters containing unsaturated groups permit post formation curing with resultant improvements in hydrolytic stability and compaction resistance. Shielding of the ester group by branching on the alpha carbon increases hydrolytic stability and viscosity. Quaternized cellulose tri-ester (QCTE) membranes contain ~ 0.1 meq/g of quaternary ammonium groups. Analogous polymers containing sulfate groups appear to be less effective. Future chemical modifications can be expected to increase thermal stability, hydrolysis resistance and permselectivity, and to reduce cost.

The physical structure of a *skinned* membrane comes into existence prior to gelation at the moment of phase inversion. The dispersed phase, consisting of polymer coated micelles with a swelling agent core, subsequently coalesces and compacts into the ultimate gel. The latter exhibits several layers of structure. In the dense skin layer, the micelles have fully compacted, apparently becoming folded chain crystallites ~ 200 Å in diameter. Transport occurs within the ~ 30 Å low density interstices which occur at the micelle junctions. These interstitial domains may be validly considered as porous or nonporous. Skin thickness, void volume, and intermicellar spacing are variable and directly affect end use properties. The thick substructural layer contains open cells whose size determines wet-dry stability. Fine ultragels require wet storage; coarser microgels do not. Although the evolutionary trend is clearly toward *skinned* microgels, it is not yet clear which of two competitive membrane fabrication processes will predominate.

INTRODUCTION

The invention by Loeb and Sourirajan (L-S) of the first asymmetric CA reverse osmosis (RO) membrane aroused a considerable amount of interest in synthetic polymeric membranes (1-5). However, in spite of the fact that much knowledge and insight into membrane structure and its relationship to function have been accumulated within the past decade, dissemination and/or acceptance of this body of information does not yet appear to be universal. Therefore, the present paper reviews what is known about the chemical and physical structures of asymmetric cellulosic membranes and attempts to discern future trends in their development.

Much of the terminology which has been applied to asymmetric membranes was conceived by non-morphologists and has, as a result, a nonstructural basis. For example, the broad term *asymmetric* is restricted by convention to very specific bi- or tri-layered structures consisting of a thin dense skin and more porous substructural layer(s). It is usually further restricted to those membranes made from polymer solutions which more or less spontaneously separate into these layers. Ultrathin film (UTF) composites, although *skinned*, are considered totally apart. Other phrases which have been utilized synonymously with *asymmetric* are *modified*, *Loeb and Sourirajan*, and *Loeb and Sourirajan modified*. Fortunately *asymmetric* and *active layer* are gradually being replaced by the more precise and descriptive *skinned* and *skin*, respectively. Other terms that are coming into their own are *ultragel* and *microgel* the former refers to the clear to opalescent gels with cells 0.1-0.5 μ m in diameter, and the latter to opaque white gels with greater than micrometer sized voids.

CHEMICAL STRUCTURE

This discussion will be confined to cellulosic polymers. The most important chemical features of the latter are excellent solubility of a great variety of derivatives, the existence of an endless variety of mixed derivatives, MW and MW distribution, hydrophilic-lipophilic balance, and ion exchange capacity (I.E.C.).

Although a few cellulose ethers represent potentially useful membrane forming polymers, certain deficiencies such as inhomogeneity of substitution, lower acid resistance, lesser oxidative stability, and higher cost, have focused attention upon the cellulose esters. Of these CA constitutes a useful point of departure for a discussion of skinned membranes. The secondary CAs of commerce consist of cellulose triacetate (CTA) which has been depolymerized to a degree of polymerization of between 100 and 200 and deacetylated to a D.S. of approximately 2.45. Manjikian, Chan and McCutchan have established a subtle trend towards superior performance with increasing MW (6). This may be because high MW favors skin integrity by allowing a statistically greater number of tie links between the folded chain microcrystals of which the skin layer appears to be composed. MW distribution should be narrow because polymers of widely different MW tend to come out of solution at different rates, thereby disrupting integrity (7).

Since the acetyl is more hydrophobic than the hydroxyl group, hydrophobicity increases with increasing acetyl content. This in turn reduces swelling thereby increasing permselectivity and decreasing permeability. Furthermore, since structural regularity and hence crystalline order also increase with increasing acetyl content, solubility declines in a parallel fashion until, at a D.S. of approximately 2.7, it drops precipitously. However, because of the greater permselectivity of higher D.S. CAs, many attempts have been made to develop polymers in the trisubstitution range (i.e. D.S. $\geq \sim 2.75$). The first successful such approach was Cannon's 2.72 D.S. blend of CA and CTA from a mixed acetone-dioxane solvent system (9). This solvent system has also recently been utilized for the preparation of true CTA membranes with a D.S. of 2.83 (10). Because of the poor solubility of CTA, the highly soluble CA-mixed esters have also been intensively investigated as candidates for membrane polymers. Mixed esters contain a second acyl component (larger than the acetate group) which disrupts order and hence increases accessibility and solubility. Manjikian found, for example, that commercially available CA butyrate (CAB) was capable of being cast into highly permselective membranes (11). However, the higher than optimum concentration of butyryl groups in commercial CABs brought about internal plasticization and excessive compaction under pressure with the result that they have not found a permanent niche. The present author has investigated commercially available CABs and CA propionate (CAP) for Dry-RO[®] membranes and found that both were unacceptable (12). It may, therefore, be concluded that CA mixed esters must be specifically designed for membrane applications. Since this is easily done, several groups have incorporated small amounts of other acyl components into CAs which were themselves already acceptable membrane polymers. This approach is a good one because such modification, in contrast to the case with noncellulosic polymers, usually results in a useful material (13). Unfortunately, although an excellent beginning was made in the preparation of CAPs, CABs and a few other mixed esters containing 2.45 D.S. acetyl and 0.1-0.4 D.S. of the second acyl component, work with wet process membranes of this type apparently ceased with the discovery of the 2.72 D.S. CA/CTA blend membrane. The borderline solubility of CTA in dry process solvent systems, on the other hand, mandated continued investigation of CA-mixed esters for Dry-RO[®] membranes (14). Dry process casting solutions contain swelling agents on the nonsolvent side of the Polymer-Solvent Interaction Spectrum so that membrane polymers must be highly compatible to avoid solution instability (2). In addition, dry process polymers are generally of higher MW than are those polymers used in the wet process. This requirement arises from the necessity for maintaining solution viscosity in the face of relatively low polymer concentration, a consequence of the relatively low solvent power of dry process solutions. It is advantageous in that higher MW favors integrity and permselectivity. To date all of the mixed esters prepared by the acylation of high MW CAs have been found to be more soluble than CAs or CTAs of equivalent D.S. Solution viscosity was found to decrease with increasing chain length of a normal second acyl component. This is at least partially attributable to a dilution of the weight percentage of cellulose backbone relative to the overall weight of the polymer and to changes in solubility parameter. If carried too far this type of change can hinder the formation of a skinned membrane and lead instead to a dense film. Solution viscosity increases if the acyl group contains secondary (isobutyryl) or tertiary (pivaloyl) groups alpha to the ester linkage. This unexpected effect may be the result of steric hindrance of the ester group to solvation. Such an explanation is consistent with the known increase in hydrolytic stability of ester groups so protected (15). Fortunately, since viscosity effects are additive, modifications with opposing effects can be used to offset one another.

The introduction of even 0.1 D.S. of propionyl groups into CA results in decreased viscosity and increased turbidity. However, in spite of this and because CAP polymers are among the easiest to wash and process, they may be considered the best of the neutral, saturated CA-mixed esters. The extremely high permselectivity of membranes from the CAPs and other

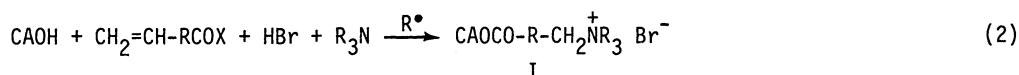
neutral cellulose triesters (CTEs) might have resulted in their application to single pass seawater desalination had it not been for their low permeability because of which they have not been commercialized.

An interesting class of CA-mixed esters is the CAFs, *i.e.* CTEs containing 0.1-0.4 D.S. of unsaturated acyl groups. The CAFs can be fashioned into membranes and subsequently cross-linked to minimize compaction and increase resistance to solvents and hydrolysis. A considerable effort was expended earlier to develop wet process membranes of CA-methacrylate (CAM) with outstanding spot results, but with poor reproducibility due to premature cross-linking (16). Although CAM is no longer under development, problems in its handling could undoubtedly have been overcome by less stringent synthetic procedures and by proper utilization of free radical inhibitors. Any inhibitor which remains in the finished membrane can be removed by washing prior to curing with electron beam, ultraviolet, or redox methods. At present CA crotonate (CAOCO-CH=CH-CH₃), CA sorbate (CAOCOCH=CH-CH=CH-CH₃), and CA undecylate (CA-OCO(CH₂)₈CH=CH₂), are being studied for use as membrane polymers. These materials are of interest not only for their crosslinking potential but also because unsaturated groups represent sites for the introduction of ionogenic groups. The latter are of paramount importance because, although both saturated and unsaturated neutral CTEs have been developed which exhibit solubility, permselectivity, and stability, their lower permeability relative to CA has limited their practical application.

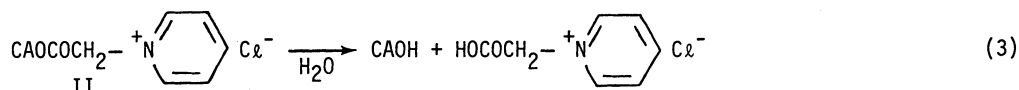
As membranes from neutral cellulosic polymers began to approach their performance limits, two competitive routes to high performance (*i.e.* high permeability coupled with high permselectivity) membranes arose. The ultrathin film composite (UTF) approach was first developed by Cadotte and Francis (17) and subsequently by Riley *et al* (18). Since permeability but not permselectivity is inversely proportional to the thickness of the skin layer, permeability may be increased by decreasing skin thickness. This can be accomplished by the separate preparation of an unskinned microporous membrane and subsequent coating thereof in a series of steps with a thin film of the same or different polymer. The latter can be either a preformed polymer such as CTA or can be formed *in situ*. The principal difficulties of this approach are the large number of fabrication steps and, more fundamentally, the difficulty of preparing a UTF which is both integral and strong enough physically to undergo subsequent processing steps without being damaged. Ironically to accomplish these objectives it was found necessary to increase the skin thickness to approximately the same magnitude as that found in the other types of skinned membranes.

The second approach to developing high performance membranes is modification of the swelling and Donnan behavior of CA by the incorporation of formal charges (19). It is significant that the UTF composite membranes which have been under development for more than a decade have also been found recently to be charge bearing and, in fact, exhibit I.E.C.s of about 0.1 meq/g, a level which is comparable to that found in optimized, ionogenic CTE membranes (20).

Both positively charged, quaternized, CTEs (QCTEs) and negatively charged, anionic, CTEs (ACTEs), have been prepared. Among the synthetic routes to the former are found:



The following variables are significant: MW and D.S. of the CA starting material; nature of R, R₃N, and X, and I.E.C. The importance of the nature of R can be seen by reference to the pyridinium salt of CA-chloroacetate (II), the prototype of the QCTE polymers, where R=CH₂



The electrophilic quaternary ammonium groups on II inductively weakens the ester bond and renders it susceptible to hydrolysis with the result that membranes of this material experience time dependent losses in both flux and rejection. Suitable modifications have been made with the result that commercially available QCTE Dry-RO® membranes are less prone to hydrolysis than is CA *per se*. Significantly, because the quaternary ammonium groups belong to the most generally useful class of biocidal compounds they confer nonbiodegradability upon QCTE membranes. Both the genus of R₃N (aliphatic versus aromatic) and the species have profound effects upon ease of preparation, solubility, stability, swelling behavior and performance characteristics. The nature of X (Cl or Br) affects the rate and extent of

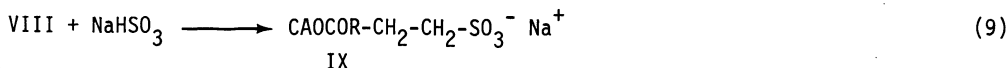
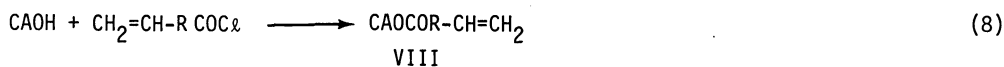
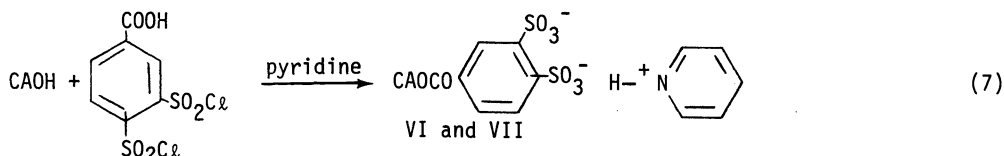
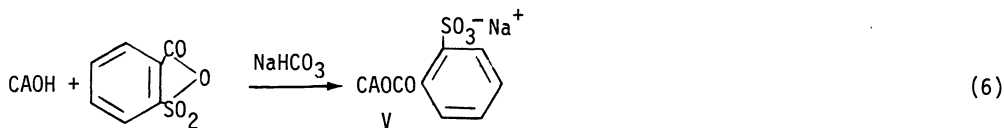
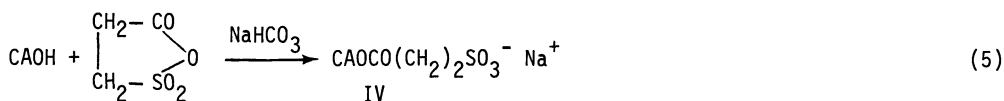
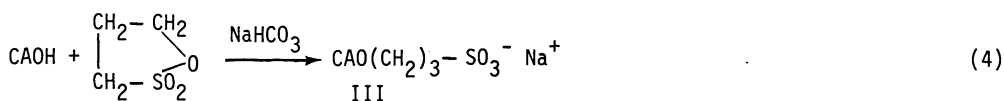
quaternization, stability of the haloacyl halide, and polymer solubility. It does not directly affect the performance characteristics of the finished membranes. The D.S. of haloacyl moiety—so long as solubility is maintained—is of little concern. On the other hand, the I.E.C. is critically important, Table 1.

TABLE 1. The relationship between I.E.C. and the RO performance characteristics of QCTE Dry-RO[®] membranes

Ion exchange capacity (meq/g)	Product flux* (gfd)	Salt rejection (%)
0.053	9.7	96.7
0.072	4.1	98.6
0.148	4.2	99.3
0.214	13.4	99.0
0.221	22.5	98.0
0.332	19.5	92.3
0.450	20.2	82.3
0.593	18.5	75.0

*1.0% NaCl feed at 1000 psi and 25°C

Among the synthetic routes to the ACTEs are:



Compound III was prepared by van der Velden *et al*, but as pointed out by the authors themselves, 1,3 propane sultone is a strong carcinogen so that III will not be practical on a large scale (21). The present author utilized the original synthetic work by Kharasch *et al* (22) for esters similar to IV, Beckman (23) for V, by Lemmerling (24) for VI and VII, and by Dreyfus (25) for VIII and IX, and has made corresponding modifications of CA for application to skinned membranes. Compound IV is hydrolytically unstable, compound V (but not compounds VI and VII) is easy to synthesize and reaction (6) is very nearly quantitative, but the anhydride is expensive. However, compounds of type IX appear to represent a very practical, economic route to the ACTEs.

To date the QCTEs appear to exhibit performance characteristics which are superior to those of the ACTEs. If this trend is ultimately borne out, it may be a result of a stronger water-ordering capacity of the former. At this stage in the development of skinned cellulose membranes, several trends in their chemical structure have become apparent: High performance membranes are invariably ionogenic; although tentative, positive fixed charges appear superior to negative ones; and I.E.C.s of approximately 0.1-0.2 meq/g are optimal.

The chemical evolution of cellulosic RO membrane polymers is depicted schematically in Fig. 1.

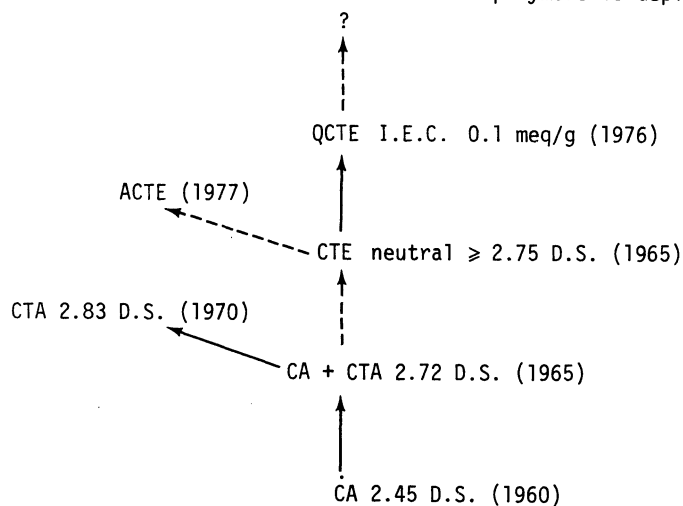


Fig. 1. Chemical evolution of cellulosic RO membrane polymers. The solid line represents commercialized; the broken line represents not commercialized.

One noteworthy trend has been the abandonment of the greater than decade long struggle for higher permeability in favor of a fixed permeability of approximately $0.7 \text{ m}^3/\text{m}^2/\text{day}$. Since permeability has now been fixed, future chemical improvements in RO membranes will occur primarily in the areas of permselectivity, thermal, hydrolytic, and oxidative stability and cost.

PHYSICAL STRUCTURE

Although virtually every aspect of the physical structure of skinned membranes has been unequivocally described by Kesting (26), McIntyre *et al* (27), Panar *et al* (28), Schultz and Asunmaa (29), and a few others, recent publications indicate that some workers remain unaware of the results of these studies. Therefore, after reviewing the mechanism of formation of unskinned and skinned membranes, their various structural details and the factors which influence them will be considered. This will be followed by a discussion of the various membrane manufacturing processes and a forecast of trends in the evolution of the physical structure of skinned membranes.

The first insight into the mechanism of formation of what are now called porous phase inversion membranes (2) was gained in 1960 by Maier and Scheuermann (M-S) and properly concerned the formation of *unskinned*, rather than skinned, membranes (30). (Skinned membranes were not commercially available at that time.) M-S hypothesized that the multicomponent casting solution utilized to prepare membranes became emulsoid in nature after the loss of the volatile true solvent components from the casting solution. After solvent loss progresses to a certain point, the less volatile nonsolvent components separate from the solution as droplets of a second dispersed phase. At the same time and also providing an additional driving force for effecting the separation, the polar polymer molecules—because of their surface activity—coat the surface of these droplets forming the *micelles* which constitute the precursors to the cells which are ultimately found in the finished membrane. Tears in the cell walls throughout the coalescing micellar gel, including the top and bottom surfaces, give rise to a symmetrical, unskinned and open-celled structure. However, as perceptive as their picture was, M-S offered no evidence in support of their hypothesis.

The first significant step in the direct elucidation of the structure of the skin layer in skinned membranes was taken by Schultz and Asunmaa (S-A) (29). S-A, in their EM investigation of the skin side of a skinned CA membrane, observed, as had others before them, a featureless surface. Earlier investigators had erroneously concluded from this that no structure was present, in other words, that the skin consisted of a dense amorphous layer. The latter conclusion conflicted with the differential scanning calorimetric evidence of Morrow and Sauer (31) and the X-Ray diffraction data of McIntyre (27) that suggested an ordered, presumably crystalline, structure in thin dense membranes. Fortunately S-A persevered and after subjecting the skin to ion etching, a technique which preferentially removes softer regions, found a highly structured layer consisting of spheroids 188 Å in diameter in a closely packed array. S-A postulated that the 20-40 Å interstices between these spheroids were free of matter and constituted the pores which had previously been postulated by Sourirajan (32). S-A did not concern themselves with the mechanism of formation of either

the skin layer or of the membrane as a whole. Shortly thereafter, Kesting, who had several years earlier adapted the M-S hypothesis to explain the formation of skinned membranes, developed his dry (complete evaporation) process for the preparation of Dry-RO[®] membranes (14). He then studied the "ghosts of the nascent membranes" by lyophilizing skinning membranes during their formative phases. The results demonstrated the essential validity of the M-S hypothesis and showed further that no qualitative difference existed between the mechanism of formation of skinned and unskinned membranes on the one hand, or of skin and substructure in skinned membranes on the other (26). Shortly thereafter, Panar *et al* (28) found a micellar structure in wet CA and polyamide membranes which was similar to that found in Dry-RO[®] membranes of CA. This proved further that the mechanism of formation of wet and dry membranes was essentially the same. Fig. 2 shows how micelles in what eventually becomes the skin, coalesce, densify, and interpenetrate to a greater extent than do those which are found in subdermal layers.

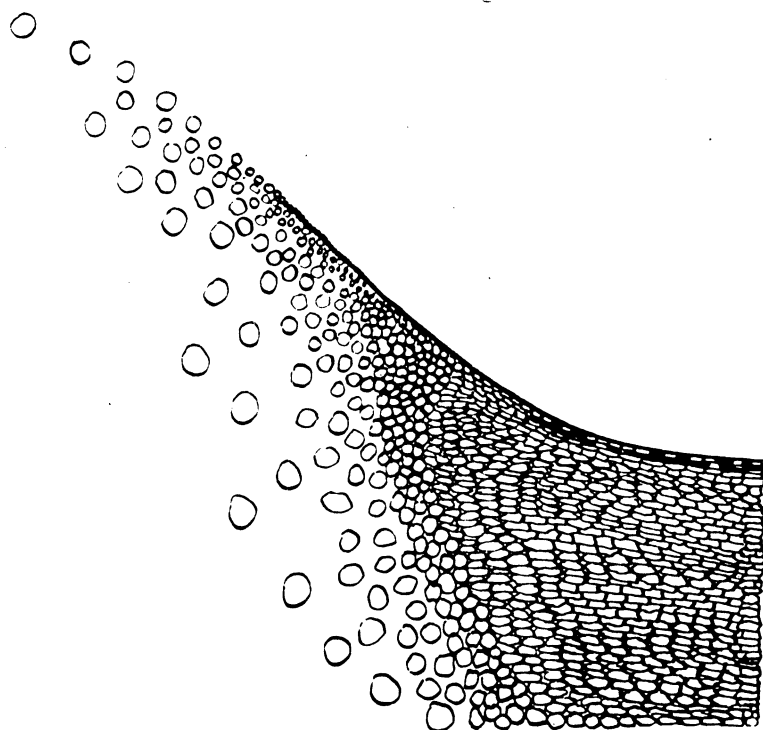


Fig. 2. The mechanism of formation of skinned membranes.

Provided only that the pore producing (swelling agent) components are on the nonsolvent side of the Polymer Solvent Interaction Spectrum, the micelles in the substructure are restrained from densification by isotropic forces due to the presence of other micelles on all sides. Membranes are skinned or unskinned as functions of polymer, solvent, and swelling agent concentrations and the proximity to the point of incipient gelation of the primary sol. If the time between the onset of evaporation and gelation is short, little or no skinning can result. If polymer concentration is high and/or swelling agent concentration low, then skinning will occur. If excess time is allowed for consolidation prior to gelation, the skin will increase in thickness. To prevent such an occurrence with its adverse effect upon permeability, solvent vapor must be removed from vicinity of the air/skin interface as rapidly as possible or (as in the case of the wet process) the evaporation period should be minimized.

The skin structure in Dry-RO[®] membranes was found by Kesting to be similar to that found by S-A in wet CA membranes (26). *It appears probable that the S-A interpretation of salt rejection based on the presence of ordered water within the interstices between the micelles is also essentially correct. It is not, however, necessary to postulate that these interstices are free of matter. They are probably, as Kedem has suggested, regions of lower polymer density (33). This assumption would partially reconcile the views of those who insist that the skin is free of pores since there would be no empty spaces greater than a few Å. On the other hand, those who support Sourirajan's contention that pores exist can validly cite the existence of the 20-40 Å low density regions (32). Ordered water can presumably be ordered in what may be termed ordered amorphous regions between crystallites as well as in free*

capillaries. Integral and nonintegral skins exist (34). The former is one which completely covers the porous substructure. As the skin is made thinner it will be comprised of fewer layers of the folded chain microcrystals which were originally coalescing micelles. At some thickness, presumably several layers of microcrystallites, coverage of the substructure will be incomplete and the skin will be nonintegral. Factors which influence integrity in both skin and substructure are solution viscosity, polymer MW, MW distribution, and the composition of the solvent system. High viscosity, high MW, and a narrow MW distribution favor structural integrity. If fluidity is too high and a skin forms, solvent vapors will not be able to diffuse rapidly enough through the skin and will accumulate in subdermal pockets before eventually diffusing out, thereby destroying integrity. The macrovoids which are sometimes encountered in a membrane's substructure are usually of this origin although, in the case of wet membranes, they may also infrequently be the result of aqueous intrusions. It is possible to distinguish between these two causative factors: Solvent vapor causes an unskinned interface between void and normal membrane structure and aqueous intrusions, a skinned interface.

Skin thickness is one of the most important factors determining permeability—the others being the polymer's hydrophilic–lipophilic balance and I.E.C. Skin thickness can be varied by the concentration of swelling agent in the solvent system. Thickness decreases with increasing concentration because overall gelation is hastened relative to skin buildup.

Skin density is greater than that of the substructure. Occasionally it is possible to clearly distinguish a layer of intermediate density, the transition layer, which consists of closed cells. This layer whose obvious cause is retarded gelation adds to the effective skin thickness because there is no easy passage from one closed cell void to another. In pressure driven membrane separation processes, but not in those driven by differences in chemical potential, the open celled substructure offers little resistance to liquid transport and serves primarily as a physical support for the thin skin layer. The bottom surface layer may be simply an extension of the porous substructure or, in some cases, may itself be skinned. Such a bottom surface skin can serve a useful role as a physical bond between membrane and support (26).

There are important physical differences between the various types of skinned membranes made by the various manufacturing processes and these can affect such important properties as wet-dry reversibility or lack thereof. In fact, a clear trend has been developing in the evolution of membrane physical structure. This trend can be envisioned in much the same manner as is used to depict biological evolution, beginning at the bottom with the most primitive and proceeding upwards to the more advanced types Fig. 3.

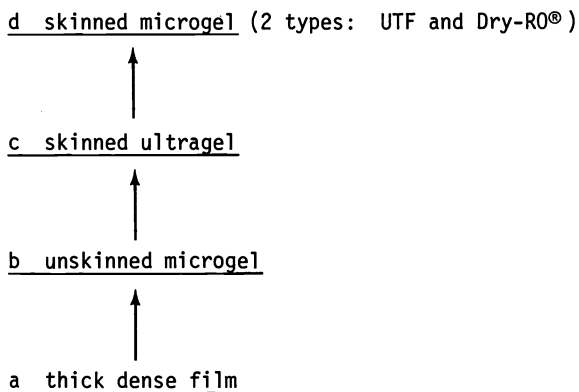


Fig. 3. Evolution of membrane physical structure.

The most elementary type of membrane is a thick dense film Fig. 3a. Where the film is sufficiently permeable and not too thick, such membranes can be useful. Examples are cellulose films for hemodialysis and silicone films for blood oxygenation. However, for the majority of membrane separations, thick dense films are too impermeable. One method of increasing permeability is to decrease polymer density. The ultimate in low polymer density is an unskinned microporous membrane Fig. 3b. Such structures function as both sieve and depth filters and serve for the filtration of bacteria, yeast cells, etc. Obviously if the size of the particles to be filtered decreases, permselectivity will decrease. Commercially available membranes of this type are microgels and hence are wet-dry reversible. The next type of structure is the skinned ultragel of the type invented by Loeb and Sourirajan Fig. 3c. Such membranes are permeable and permselective because of the presence of an integral skin, but must be kept wet to avoid densification. Because it is as permselective as the skinned ultragel and in addition wet-dry reversible, the skinned microgel qualifies as the most advanced form of membrane Fig. 3d. *In fact, barring the extremely unlikely development of an*

ultrathin film which is sufficiently stiff and strong as not to require support, skinned microgels should eventually dominate all pressure driven membrane separation processes.

The origin of the differences between skinned ultragels and microgels can perhaps best be understood by a circumspection of the manufacturing processes which give rise to them. Skinned ultragels generally are the result of wet- or, in the case of fibers, gel spinning-processes. Since the two are similar in principle, a discussion of the Loeb-Sourirajan (L-S) Wet Process will suffice for both. The L-S Process utilizes concentrated polymer solutions and swelling agents, e.g., aq. $Mg(CO_3)_2$, formamide, etc., which are on the solvent side of the Polymer Solvent Interaction Spectrum. Because of the high polymer concentration, swelling agent polymer interaction is essential to maintain compatibility. However as a result, the polymer and solvent system are so compatible that no phase separation will occur spontaneously even after the volatile solvent has evaporated. This necessitates an *external source* of incompatibility such as immersion in a nonsolvent gelation medium to evoke phase separation. Furthermore, high polymer concentration coupled with solution compatibility results in fine micelles which culminate in fine (0.1-0.5 μm diameter) cells in the finished membranes. The small size of the cells in turn results in such substantial capillary forces on drying that the membrane would densify if not kept wet. Wet membranes are usually annealed to drive the micelles more closely together to improve permselectivity.

The simplest route to a skinned microgel is the one step Kesting Dry (KD) Process for the preparation of Dry-RO[®] membranes. KD Process solutions utilize swelling agents on the non-solvent side of the Polymer Solvent Interaction Spectrum and, therefore, contain an *internal* source of incompatibility which spontaneously evokes phase separation upon evaporation of the solvent. Lesser compatibility and lower polymer concentration effect the formation of the larger micelles which are the precursors of a microgel structure. Microgels are wet-dry reversible because the relatively large size of their cells results in capillary forces during drying which are too weak to effect cell collapse. Furthermore, annealing is not required because micelles in the skin have already coalesced and compacted to the fullest possible extent as a result of complete evaporation. There are two other, albeit more complicated, routes to the formation of skinned microgels. The Justice variation of the L-S Wet Process (34) utilizes modified L-S type solutions and a gelation bath at higher than ambient temperatures. The second is the previously mentioned UTF composite approach. Since Justice type membranes contain substructural macrovoids, their future is uncertain. As for the KD and UTF processes, only time will tell whether both will succeed, or whether one will eventually predominate.

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