

Review on the Development of Defect-Free and Ultrathin-Skinned Asymmetric Membranes for Gas Separation through Manipulation of Phase Inversion and Rheological Factors

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ABSTRACT: Development of high-performance asymmetric membranes is a major breakthrough in membrane technology. A comprehensive study on original concepts and new advances in membrane formation process is necessary to generate defect-free and ultrathin-skinned asymmetric membranes with superior performance for gas separation process. Correlation of rheological factors with primary-phase inversion process is a novel approach in

membrane research that provides a potential platform to improve membrane performance. The former controls general morphology of membrane, whereas the latter further affects molecular orientation in membrane. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 442–451, 2003

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INTRODUCTION

Performance of membrane-based gas separation process strongly depends on permeability and selectivity of membrane. Membrane with higher permeability leads to higher productivity and lower capital costs, whereas membrane with higher selectivity leads to more efficient separations, higher recovery, and lower power costs; indeed, membranes that simultaneously possess high values of selectivity and permeability would lead to the most economical gas separation processes. Hence, numerous studies and efforts were centered on development of high-performance membranes for gas separation process.

In 1960, Loeb and Sourirajan successfully developed the first integrally skinned asymmetric membranes.^{1,2} An integrally skinned asymmetric membrane consists of a very thin and dense skin layer (0.1–1 μm) overlaying on a thick and highly porous sublayer (100–200 μm), with an average void size ranging from 0.01 to 1 μm), where both layers are composed of the same material and formed in a single operation.^{2–4} The skin represents the actual separating barrier that possesses selective properties, while the sublayer serves solely as a mechanical support for the skin, with negligible effects on separation.

In asymmetric membrane, density and mass transfer resistance of the skin layer is somewhat greater than that of the sublayer; therefore, permeability of asymmetric membrane does not depend on entire membrane thickness, but instead is inversely proportional to thickness of skin layer.^{2,5} Hence, a high value of permeability can be achieved in asymmetric membrane with very thin skin layer. Generally, asymmetric membrane with effective skin thickness of approximately 1,000–5,000 angstroms (\AA) is classified as ultrathin-skinned membrane, whereas hyperthin-skinned asymmetric membrane possesses a skin layer with thickness much less than that for ultrathins.⁶ Both of them are specifically designed to achieve permeability of practical interest.

However, development of thin-skinned asymmetric membranes would result in defects or pinholes on skin surface due to irregular packing of kinked polymer chains and incomplete coalescence of polymer molecules in skin layer.^{7,8} Solution-diffusion mechanism of permeation through membrane materials is very slow compared to Knudsen diffusion or viscous flow that occurs through nonselective pores in membrane; thus, a defective area plague on membrane surface can substantially cause a dramatic loss in selectivity and prevent the intrinsic selectivities (i.e., selectivities measured on dense homogeneous films) from being achieved in very thin membranes.⁹

Consequently, for any given separation, there is usually a trade-off between permeability (skin thickness) and selectivity (skin integrity), where both pa-

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rameters tend to exhibit a contradictory relation, representing a major problem in productions and applications of asymmetric membranes for gas separation process. At present, new challenges are directed toward development of defect-free and ultrathin-skinned asymmetric membranes for gas separation process, in which further insight and dramatic progress are being made.

EVOLUTION AND DEVELOPMENT

As early as 1950, Weller and Steiner demonstrated that membranes could theoretically separate gases.¹⁰ At that time, membranes for gas separations were made of polymeric materials. However, prior to 1965, membranes with attractive combinations of permeability and selectivity were hardly produced for any practical applications of commercial interest.¹¹ Most of the early membranes were limited for commercial applications due to a lack of productivity since membranes had to be relatively thick and dense to avoid irregularities on membrane surface that caused a dramatic loss in selectivity. Literally, the thinnest practical membranes were about tens of microns.¹² Consequently, membrane thickness became the greatest limitation for gas separation process using membrane.

Only in 1960 did Loeb and Sourirajan successfully develop the first integrally skinned asymmetric cellulose acetate membranes for reverse osmosis, which were finally applied to gas permeation in 1970.¹ Asymmetric membranes with a relatively thin separating layer could produce fluxes that were an order of magnitude greater than those for membranes available at that time, yet exhibiting comparable separation characteristics. Riley et al. examined cellulose acetate membranes developed by Loeb and Sourirajan in electron microscope and determined their effective thickness to be about $0.2 \mu\text{m}$.¹³

Phase inversion, which was developed by Loeb and Sourirajan, represents one of the most versatile, economical, and reproducible formation processes for polymeric asymmetric membranes.¹⁴ Typical structure and morphology of asymmetric membrane (skin and substructure) are formed as a result of the interplay of mass transfer and phase separation. Much of the early work focused on wet-phase inversion process to form asymmetric membranes (flat sheet or hollow fiber), which could produce essentially thin selective layers ($>2,000 \text{ \AA}$).¹⁵

Wet-phase inversion process always involves a quenching step, that is, immersion of a homogeneous multicomponent solution (consisting of either a binary mixture of polymer and solvent or a combination of polymers, solvents, and nonsolvents) in a coagulant (nonsolvent), which is miscible with solvents and nonsolvents but immiscible with polymer.¹¹ Phase instability of solution is induced exclusively by counterdif-

fusion between solvents and nonsolvents during quench step, which leads to wet-phase separation to form membrane with asymmetric structure. Therefore, choice of quench medium for a solution is of utmost importance, which would affect polymer precipitation and diffusion between solvents and nonsolvents and determine ultimate structures of asymmetric membranes.

Kesting et al. at Permea (now belongs to Air Products) hypothesized that a critical molar volume exists in dope formulation for asymmetric membranes with an ultrathin selective layer.¹⁶ They discovered a new class of integrally skinned asymmetric hollow fibers possessing ultrathin and graded-density skins by incorporating Lewis acid–Lewis base complexes (non-solvent–solvent) to spinning dopes.¹⁷ The Lewis base solvent sequesters the Lewis acid nonsolvent by formation of a complex and permits higher concentrations of nonsolvent to be included in the spinning dope than can be achieved in congener prepared from classical solvent–nonsolvent mixtures.

The complex acts as a transient template, which then dissociates rapidly into its constituent moieties on contact with coagulant, accelerating-phase inversion kinetics and facilitates the removal of dissociated moieties from hollow fibers. Sol-to-gel transition is so rapid that restricting polymer molecules to approach equilibrium by undergoing further packing or conformational rearrangement and fixing structural units of effective separating layer before concomitant compression and distortion can occur.^{18,19} Therefore, a high level of free volume is enhanced in skin layer.

Hollow fibers spun from Lewis acid–Lewis base complex also have a very thin effective separating layer and transition zone with a large gradient of increase in pore size and porosity.¹⁸ As a result, a multiple increase in gas transport rates can be obtained. However, skin layers of hollow fiber contain many defects, therefore coating is required to maintain selectivity. Aqueous quenched polysulfone hollow fibers spun from propionic acid:*N*-methylpyrrolidone complexes in molar ratio of 1.09–0.72 created an apparent skin thickness of approximately 230 \AA . The coated polysulfone hollow fibers could yield oxygen transport rates ranging from 41.3×10^{-6} to $50.7 \times 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$, which was a four- to fivefold increase as compared to those spun from 87:13 molar ratio of formylpiperidine–formamide, with comparable selectivities for oxygen–nitrogen (~ 5).²⁰

Subsequently, Chung et al. at Hoechst Celanese produced high-flux, ultrathin-skinned hollow fibers using mainly a binary (one polymer and one solvent) system by wet-phase inversion process. The newly developed hollow fibers were wet-spun from a 35:75 weight ratio of polyethersulfone–*N*-methylpyrrolidone dope using water as external coagulant and 80:20 weight ratio of

N-methylpyrrolidone–water as bore fluid. The coated polyethersulfone hollow fibers showed an oxygen : nitrogen selectivity of 5.8 with a permeance of $9.3 \times 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ for oxygen. The skin thickness of polyethersulfone hollow fibers was calculated to be 474 Å. This work implies that solvent/nonsolvent or multisolvent approach may not be a necessary precondition to form asymmetric membranes with an ultrathin skin layer, as previously suggested by the Permea research group.¹⁶

Recently, a new type of asymmetric membrane developed by Hachisuka et al. at Nitto Denko Corporation having an almost defect-free hyperthin skin layer (40–60 nm) was wet-cast from a solution with 18 wt % polyimide synthesized by 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2-bis(4-amino phenyl)hexafluoropropane (BAAF) in diethylene glycol dimethyl ether.^{16,21,22} Solvents such as diethylene glycol dimethyl ether are miscible in water, but a sharp interface exists between diethylene glycol dimethyl ether and water for a while. Therefore, hyperthin skin layer with hardly any defects is possibly formed by solidification at their sharp interface. Such solvent properties might depend on dielectric constant and dipole moment.²¹ After coating, oxygen:nitrogen selectivity of 6FDA–BAAF polyimide membranes was found to be 4.3 for $7.1 \times 10^{-5} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ of oxygen flux. Therefore, Hachisuka et al. emphasized that formation of asymmetric membranes with a hyperthin skin layers depends on the dissolution property between a dope solvent and coagulant as a solidification solvent.

Furthermore, Van't Hof at the University of Twente became the first to study and develop a dual-bath wet-phase inversion process by taking advantage of both delayed demixing and instantaneous demixing to prepare selective gas separation membranes.²³ Membranes are formed by contacting a polymer solution with two nonsolvent baths in series. They immerse a cast film or an extruded fiber in the first nonsolvent bath for a relatively short time, which may induce delayed demixing, followed by immersion in a second nonsolvent bath to induce instantaneous demixing. Therefore, selection of both nonsolvents strongly depends on the type of solvent present in polymer solution. Besides that, contact time in the first nonsolvent bath should preferably be shorter than delay time for demixing, so that only a thin and concentrated skin layer is formed at membrane interface, while the rest of the solution remains unchanged. The nascent membrane with anisotropic distribution is then immersed in the second nonsolvent bath to initiate instantaneous demixing, which is responsible for the actual coagulation (precipitation).

Although a combination of both mechanisms is very favorable to form defect-free selective layers, they are rather thick (more than 0.5 μm) for gas separation.^{24,25}

Polyethersulfone hollow fibers were wet-spun from a dope consisting of 35 wt % polyethersulfone and 10 wt % glycerol in *N*-methylpyrrolidone by using glycerol as the first nonsolvent and water as the second nonsolvent. For a feed gas of 25 vol % of carbon dioxide in methane, the intrinsic selectivity of polyethersulfone (50–55) was easily obtained without any necessity of coating. However, skin layer of the resultant fiber was relatively thick (1.6–2.0 μm), causing a low flux for carbon dioxide [$2.5 \times 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$].²⁶

Hence, high-flux asymmetric membranes with an ultrathin skin layer can be formed by wet-phase inversion process. However, they are highly defective because of stress-induced rupture of skin layer by intrusion of quench medium, as suggested by Strathmann and Kock. In recent years, a number of post-treatments, among which the coating or caulking technology developed by Henis and Tripodi in 1970, has been widely practiced in both academic and industry to plug defects on ultrathin-skinned asymmetric membranes with a highly permeable but nonselective material such as silicone rubber or polydimethylsiloxane to increase selectivity without decreasing permeability. Sometimes coated asymmetric membranes are also referred to as composite or multilayered membranes.⁹ Nevertheless, coating process is often time-consuming, inducing complexity and adding costs for continuous membrane production.²⁷ Furthermore, curing agent deposited on membrane surface may add significant resistance to the overall gas transport process and cause a moderate loss in productivity, which can limit one's ability to benefit from membrane materials having a relative high intrinsic permeability or membranes with a relatively thin-skinned form.¹⁷ Henis and Tripodi also noticed that coating could not work for asymmetric membranes with significant substructure resistance.

Alternatively, addition of a convective evaporation step in wet-phase inversion process (or dry/wet-phase inversion process) in combination with a well-developed polymer solution were later implemented by Pesek and Koros at the University of Texas as a new effort in developing defect-free and ultrathin-skinned asymmetric membranes without any necessity of coatings.¹⁷ A homogeneous multicomponent solution containing polymer, solvents (a more volatile solvent and a less volatile solvent), and nonsolvents, which is tailored to be close to the thermodynamic instability limit, undergoes forced-convective evaporation for a certain period to induce dry-phase inversion. A selective loss of highly volatile solvent from solution causes instantaneous destabilization at outermost surface of nascent membrane and results in a defect-free region with locally elevated polymer concentration. The nascent membrane is then immersed in a coagulant (nonsolvent) for wet-phase inversion,

where the bulk of the membrane structure is formed by counterdiffusion of solvents and nonsolvents and extraction of the remaining components occurs.¹⁷

According to Pesek and Koros, the addition of non-solvent additives in polymer solution can alter the thermodynamic and kinetic properties of solution. Solution components have to go through a series of rearrangement and conformation.²⁸ Initially, macromolecules in polymer solution may exist as extended chains, especially when a polymer is dissolved in a good solvent. By adding a nonsolvent additive into polymer solution, interaction of nonsolvent and solvent molecules leads to a reduction in compatibility and miscibility between polymer and solvent system. Therefore, aggregation of polymer molecules is promoted due to entanglement of polymer chains.²⁹ A tightly coiled conformation in polymer solution brings its composition close to precipitation point as much as possible in order to accelerate phase separation.³⁰

Dry/wet-phase inversion process had been applied by Pinnau and Koros in fabricating asymmetric membranes in flat-sheet geometry from a solution containing halogenated hydrocarbon solvents and aliphatic alcohol nonsolvents and an organic quench media.¹⁷ Asymmetric membranes made from 12.2 wt % polysulfone, 52.8 wt % methylene chloride, 20.3 wt % 1,1,2-trichloroethane, and 14.7 wt % 2-methyl-2-butanol, and quenched in a methanol bath, showed an ultrathin defect-free skin layer (180–700 Å) and an average oxygen : nitrogen selectivity of 5.4 for an oxygen permeability of about $31.8 \times 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$.³¹

Pesek and Koros also developed an aqueous quenched dry/wet system that was more attractive for commercial purpose.³² An optimum casting solution for preparing flat-sheet asymmetric polysulfone membranes consisted of 22.0 wt % polysulfone, 31.8 wt % dimethylacetamide, 31.8 wt % tetrahydrofuran, and 14.4 wt % ethanol, while water was used as a coagulation medium. Asymmetric polysulfone membranes with an ultrathin selective skin layer (450–1,000 Å) were produced, corresponding to an average oxygen:nitrogen selectivity of 6.0 for an approximate oxygen permeability of $19.3 \times 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$.¹⁷

Koros et al. then extended their original approach to a dry/wet spinning process.³³ Application of dry/wet-phase inversion process in hollow fiber geometry is more complicated than with simple flat sheets.^{27,34,35} The outer surface of hollow fiber experiences an evaporation-induced dry-phase inversion during residence time in air gap, which is extremely short and usually measured in tenths or even hundredths of a second, prior to coagulation for wet-phase inversion.³⁴ Meanwhile, the inner surface of hollow fiber is in contact with a bore fluid and only undergoes wet-phase inversion.

In recent reports, Clausi and Koros formed hollow fibers by a dry-jet, wet-quench process using Matrimid 5218. Spin dope comprised of 26.2 wt % Matrimid, 55.9 wt % 1-methyl-2-pyrrolidinone, 3.0 wt % tetrahydrofuran, and 14.9 wt % ethanol was coextruded with a bore fluid (with a composition of 96% : 4% 1-methyl-2-pyrrolidinone:water) through an air gap and was then coagulated in an aqueous quench bath. The resultant hollow fibers had not only shown a defect-free skin thickness of approximately 1,000 Å, but also exhibited an oxygen:nitrogen selectivity of 7.1 with $12.2 \times 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ of oxygen flux.³⁴

Optimized protocols in dry/wet-phase inversion process have been successfully applied to form essentially defect-free and ultrathin-skinned asymmetric membranes for gas separation, which is a tremendous contribution in membrane technology. However, under suboptimal conditions, samples containing minor defects would be produced, and again coatings are required to render asymmetric membranes gas-selective.³⁶ Nevertheless, research on membrane formation process is mainly focused on the nature of phase inversion. Indeed, new advances are necessary to generate defect-free and ultrathin-skinned asymmetric membranes with superior performance for gas separation process.

Recently, Ismail et al. have recognized that manipulation of rheological factors in membrane formation process would lead to a considerable effect on morphology, physical properties, and separation performance of final product. Asymmetric membranes produced by phase inversion process usually involve casting of a polymer solution during which shear is subjected prior to a rapid coagulation. Membrane-forming polymer solution is often shear-thinning and viscoelastic, suggesting a progressive alignment of polymer molecules under shear in flow direction.^{37–40} Coagulation is most rapid at outermost surface of as-cast membrane; therefore, instantaneous sol-to-gel transition tends to take place, which limits conformational and configurational rearrangement in nascent membrane, causing oriented polymer molecules to be frozen into skin region.^{38,41} Further coagulation of membrane substructure results in differing morphology between skin and sublayer.⁴²

According to results determined by Shilton et al. using polarized reflection infrared spectroscopy and gas permeation tests, molecular orientation is found to be intensified in high-sheared membranes, which has a favorable effect on membrane permeability and selectivity.⁴³ Ismail even produced superselective polysulfone hollow fibers for gas separation with an optimized dope proposed by Pesek and Koros using a dry/wet spinning process in combination with a high extrusion rate and a bore fluid with reduced water activity. The selectivity of polysulfone hollow fibers

was heightened by increasing dope extrusion rates, with some even reaching about three times of the intrinsic value, while skin thickness of high-shear polysulfone hollow fibers was found to be around 900 Å.^{39,40}

The structures and properties of membrane are intimately tied to the mechanism of membrane formation process. Slight variations either in formulation recipes or fabrication parameters can greatly influence membrane performance. Inherently, the combination of a novel rheology approach with primary-phase inversion process provides a potential platform to form defect-free and ultrathin-skinned asymmetric membranes with superior gas separation performance. The former controls the general morphology of membrane, whereas the latter further affects molecular orientation in membrane. Therefore, the present work focused on formation mechanism of high-performance asymmetric membranes for gas separation process by correlating dry/wet-phase inversion and rheological factors.

MEMBRANE FORMATION PROCESS

Basic procedures of asymmetric membrane formation process are shown schematically in Figure 1. Asymmetric membrane formation process involves the formulation of a homogeneous multicomponent solution that consists of a polymer, solvents (a less volatile solvent and a more volatile solvent), and a nonvolatile nonsolvent, which is tailored to be close to the thermodynamic instability limit and approaching cloud point curve. The membrane is cast at an appropriate shear, followed by a forced-convective evaporation for dry-phase separation. A nascent skin layer is formed from a region with locally elevated polymer concentration due to a selective loss of highly volatile solvent from the outermost surface of freshly cast membrane. The underlying region beneath the nascent skin layer remains in a fluid state. The nascent membrane is then immersed in a coagulation bath for wet-phase separation, where the bulk of the membrane structure is formed by counterdiffusion of solvents and nonsolvents and extraction of the remaining components occurs.¹⁷

Nevertheless, the nascent skin layer, which is formed during dry-phase inversion, acts as a resistive barrier between the coagulation bath and the interior region of the membrane. Strathmann et al. have determined that the diffusion coefficients of skin layer are much lower (<100 times) than the bulk structure of sublayer.⁴⁴ The top layer directly influences the sub-

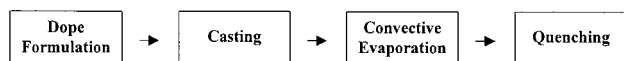


Figure 1 Schematic diagram of asymmetric membrane formation process.

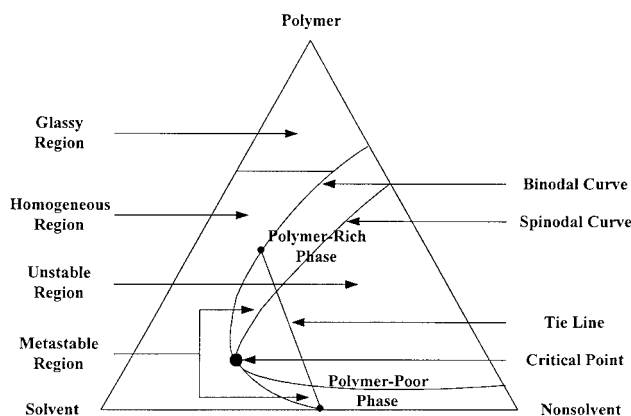


Figure 2 Ternary-phase diagram of polymer-solvent-nonsolvent system.

sequent layers by controlling the counterdiffusion rate of solvents and nonsolvents through membrane during wet-phase inversion. Variation of the second layer is thus governed mainly by the top layer structure, while variation of the third layer would be influenced by composite properties of the top layer and the second layer. The following layers are eventually formed by a similar mechanism. Each layer has different demixing and precipitation kinetics due to mass transfer resistance created by the layers above, therefore leading to different morphologies.^{45,46}

As a result, an integrally skinned asymmetric membrane can be produced, which consists of a very thin and dense skin layer with a highly porous sublayer. Furthermore, asymmetric membrane formation process involves a complicated relationship between thermodynamic and kinetic factors of a ternary system (polymer-solvent-nonsolvent). The morphology and performance of membrane strongly depend on their effects, which are closely related to fabrication parameters of the membrane formation process. From a thermodynamic point of view, study on polymer-solvent-nonsolvent system can be well depicted in a ternary-phase diagram, as illustrated in Figures 2 and 3.⁴⁷

In a ternary-phase diagram, corners of the triangle represent pure components (polymer, solvent, and nonsolvent), axes of the triangle represent binary combinations of two components, and any point within the triangle represents a ternary mixture of three components.⁴⁸ Mixtures of solvents and nonsolvent additives are conveniently treated as one effective component in ternary-phase diagrams.³⁴ Essential elements of ternary-phase diagram consist of binodal and spinodal curves, a critical point, tie lines, and a glassy region. In homogeneous region of ternary-phase diagram, all three components are miscible. A primary envelope (binodal curve) and a secondary envelope (spinodal curve) enclose demixing boundary. Both curves coincide at the critical point.

The region between binodal and spinodal corresponds to metastable state. Phase separation by nucle-

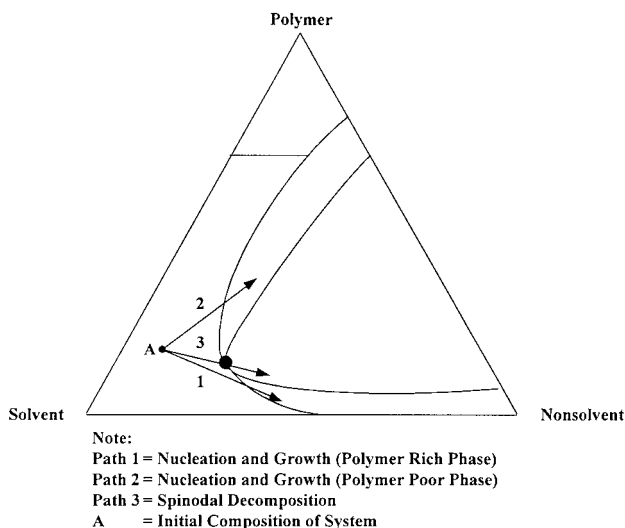


Figure 3 Schematic representation of phase separation process.

ation and growth takes place, in which minor phase is nucleating and growing in continuous matrix of major phase.^{45,49} Both phases are in equilibrium with each other as connected by tie lines. They are identical at the critical point. Two types of nucleation and growth can be envisioned to arise from phase separation process. When demixing is started somewhere below the critical point, nucleation and growth of concentrated phase (polymer-rich phase) occur. Polymer-rich phase is nucleating and growing in polymer-poor phase. Therefore, low-integrity powdery agglomerates would be produced. However, nucleation and growth of concentrated phase (polymer-rich phase) are not practical in membrane formation.

On the other hand, when demixing is started somewhere above the critical point, nucleation and growth of diluted phase (polymer-poor phase) occur. Polymer-poor phase is nucleating and growing in polymer-rich phase. The former forms porous structure while the latter results in solid matrix of membrane. Occasionally, nucleated droplets of polymer-poor phase would grow into macrovoids if the diffusional flow of solvents from the surrounding polymer solution into the nuclei is larger than the diffusional flow of nonsolvents from the nuclei to the surrounding polymer solution.⁵⁰ As long as surroundings around the nuclei remain stable (no new nuclei is being generated in front of the existing ones and no gelation takes place in the freshly formed nuclei), nuclei growth continues.³⁰ Macrovoids are conical or spherical voids (with cavity diameter of 20–100 μm) embedded within the membrane.¹⁹ They are undesirable sites of mechanical weakness. Possible failures such as compaction or collapse of membranes would occur when being applied to high-pressure operation for gas separation process.^{51,52}

Spinodal decomposition occurs in the unstable region of spinodal envelope that leads to a bicontinuous and interconnected network structures.¹⁵ Eventually, solidification of concentrated phase occurs in the glassy region by phenomena such as vitrification, gelation, or crystallization that interrupts phase separation process. Hence, the ultimate structure of membrane is completely formed. A coagulation path in the ternary-phase diagram can represent changes in state and composition of a ternary system during membrane formation, which depend on interaction parameters between components, size and location of miscibility gap, as well as boundary between demixing regions.⁵³

A qualitative treatment of membrane formation process combines kinetic and thermodynamic parameters. As a result of the complex interplay between thermodynamic and kinetic factors, membrane-demixing process can be broadly divided into two categories, denoted as instantaneous demixing and delayed demixing. Qualitatively, asymmetric membrane with an ultrathin microporous skin layer and an open-cell substructure is often obtained under instantaneous demixing process.⁵³ Asymmetric membrane having a relatively thick and dense skin layer with a closed-cell substructure is always formed by delayed demixing process.⁵³

Recently, new emphases are directed toward development of high-performance asymmetric membranes for gas separation, in which further insight and dramatic progress are being made. According to earlier studies, the formation of ultrathin and defect-free skin structure has been performed through manipulation of phase inversion and rheological factors. The former controls general morphology of membrane, whereas the latter further affects molecular orientation in membrane. Therefore, the combination of a novel rheology approach with primary-phase inversion process provides a potential platform to form high-performance asymmetric membranes for gas separation.

Phase inversion factors

The formation of asymmetric membrane involves numerous phase inversion factors. Phase inversion factors control general morphology of membrane and hence determine basic capability of membrane for gas separation. Phase inversion factors, including forced-convective evaporation time, polymer concentration, and solvent ratio, have been identified as dominating fabrication factors in controlling skin thickness and skin integrity, and thus have substantial effects on separation properties of resultant membranes.

Recent investigations by the Koros group have demonstrated that physical events occurring during dry-phase inversion induced by forced-convective evaporation may considerably affect the membrane forma-

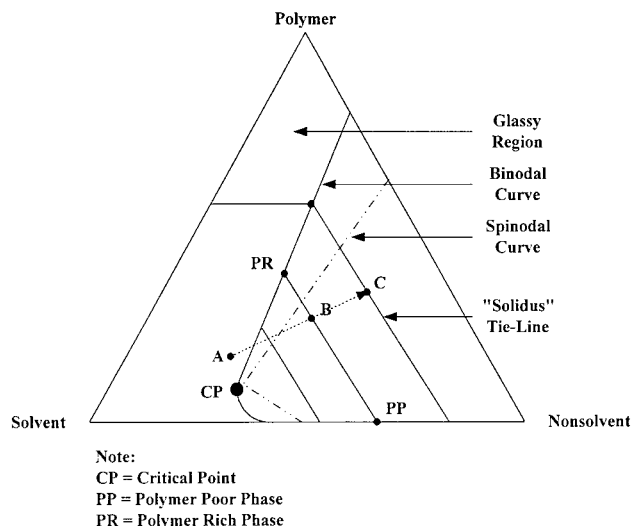


Figure 4 Ternary-phase diagram of physical events occurring during dry-phase inversion process induced by forced-convective evaporation.

tion process. Basically, the skin layer of asymmetric membrane is formed during dry-phase inversion.^{15,17,54} Therefore, structures and properties of the skin layer for asymmetric membrane are predominantly controlled by forced-convective evaporation. Dry-phase inversion induced by forced-convective evaporation for a ternary system can be illustrated in a ternary-phase diagram, as shown in Figure 4.⁵⁴

Initially, a polymer solution must be properly formulated, having a starting composition given by point A. During forced-convective evaporation, a convective stream (inert gas) removes predominantly the most volatile solvent from membrane surface and results in a region with locally elevated polymer concentration. The outermost region of membrane with an average composition B resides deep in the unstable region of spinodal curve. Therefore, dry-phase separation by spinodal decomposition is instantaneously induced at the outermost region of membrane. Instantaneous destabilizations such as formation of fine haze and onset of turbidity can be apparently observed at the topmost surface of membrane.⁴⁹

As pointed out by Cahn's pioneering work on spinodal decomposition, a finely mazed three-dimensional network of polymer-rich phase and polymer-poor phase evolves during the initial stage of phase separation process.¹⁵ Coarsening of bicontinuous structure occurs at a later stage of phase separation process to form spherical nodules.¹⁵ Furthermore, Pinnau and Koros have proposed an additional physical process that leads to coalescence of highly plasticized nodular network into an essentially homogeneous nascent skin layer.⁵⁴ Basic principles involved in this process are similar to but more rapid than those occurring during the drying of a latex to produce a

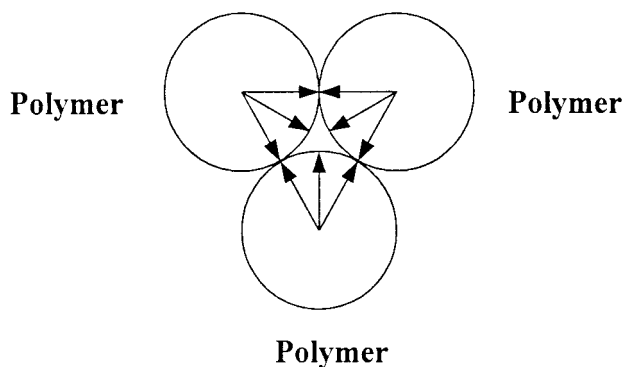


Figure 5 Contracting forces of polymer particles resulting from capillary pressure in interstitial spaces of film.

consolidated nonporous film, as previously analyzed by Brown and others.¹⁵

In the case of a spinodal network, there are two interpenetrating continuous media comprised of polymer-poor phases pervading void spaces between polymer-rich phases. Capillary pressures arise from the curvature of interface of polymer-poor phase contacting with an external gas phase. Capillary pressure acting normal at membrane interface would tend to deform the dispersed polymer-rich phase and pull them together.⁵⁴ Interstitial surface voids are eliminated to generate a defect-free gel-like surface layer. Therefore, a condition for skin formation requires the force resulting from capillary pressure to exceed the resistance of polymer particle to deformation (Fig. 5).¹⁵

Capillary pressure diminishes upon the completion of coalescing spinodal network in the outermost region of membrane. Adhesion between neighboring polymer-rich domains may continue to evolve by interdiffusion of polymer chain segments through a reptation mechanism.¹⁵ A homogeneous nascent skin layer with a compact and three-dimensionally connected nodular transition layer is finally formed.¹⁷ The underlying region of nascent membrane tends to redissolve and remains in a fluid state. A schematic diagram of hypothetical physical events occurring during dry-phase inversion induced by forced-convective evaporation is outlined in Figure 6.^{17,54}

Furthermore, properties of skin layer are intimately related to polymer concentration of casting solution. Nowadays, polymeric materials are widely used as

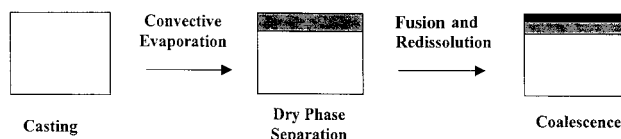


Figure 6 Schematic diagram of hypothetical physical events occurring during dry-phase inversion induced by forced-convective evaporation.

membrane materials because of their unique properties. Optimum polymer concentration of casting solution has to be determined in order to achieve defect-free and ultrathin-skinned asymmetric membranes for gas separation. Solution viscosity increases with increasing polymer concentration. According to Chung et al.,^{16,55} dopes that exhibit a sign of significant chain entanglement were essential to yield a useful gas separation membrane with minimum defects. Therefore, casting asymmetric membranes from a concentrated polymer solution results in an increase in skin thickness and a decrease in mean pore size and surface porosity of asymmetric membrane. Consequently, a relatively high degree of selectivity is accompanied by a low value of permeability for gas separation, and vice versa.^{16,17,56}

The membrane formation process involves a solution-processing method that includes certain solvents as well as nonsolvent additives (if necessary), which attribute to a considerable effect on membrane structures and properties. Solvating power, diffusivity, and volatility characteristics of solvents and nonsolvents are critical for membrane formation. Solution that contains a primary, more volatile solvent and a secondary, less volatile solvent allows finer adjustment of solvent evaporation and polymer coagulation. Since skin layer is generated during solvent evaporation, the ratio of less volatile solvent to more volatile solvent or solvent ratio (mass ratio) in solution becomes a paramount parameter for the development of defect-free and ultrathin-skinned asymmetric membrane for gas separation. Decreasing solvent ratio of casting solution results in a higher evaporation rate and a lower coagulation rate. A relatively thick skin layer with a decrease in mean pore size and surface porosity of asymmetric membrane is produced, thus increasing selectivity but decreasing permeability for gas separation, and vice versa.^{17,53,56}

Rheological factors

Manipulation of rheological factors in membrane formation process is a novel approach in membrane technology, which provides a potential platform to develop defect-free and ultrathin-skinned asymmetric membranes for gas separation. Rheological factors would affect the morphology, physical properties, and separation performance of asymmetric membrane. Recently, rheological factors in membrane formation process have been extensively investigated.^{37–40,43,57–59}

The membrane formation process involves the casting of a homogeneous multicomponent solution. Solution behavior under shear is described by response to tangential stress, which is related to molecular orientation or preferential alignment of randomly coiled chain molecules.³⁷ If the relationship is linear, then the fluid is said to be Newtonian:

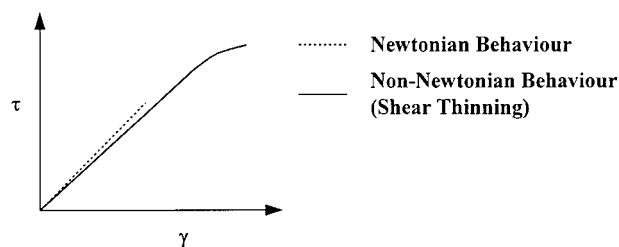


Figure 7 Shear stress versus shear rate curve for shear-thinning fluid.

$$\tau = \eta \dot{\gamma} \quad (1)$$

where τ is the shear stress, η the viscosity, and $\dot{\gamma}$ the shear rate. If the relationship is nonlinear, the fluid is said to be non-Newtonian:

$$\tau = k \dot{\gamma}^n \quad (2)$$

where k and n are constants for the particular fluid. k is a measure of the consistency of the fluid; a high value of k indicates a more viscous fluid. n is a measure of the degree of non-Newtonian behavior; if $n > 1$, the fluid is said to be shear-thickening, whereas if $n < 1$, the fluid is shear-thinning. This empirical relationship is known as the power law proposed by de Waele and Ostward.³⁷ Polymer solution is often shear-thinning, suggesting a progressive alignment of polymer molecules under shear in flow direction.^{37,38} Rheological tests were carried out using a rheometer, and a typical behavior of a shear-thinning solution is shown in Figure 7.³⁷ The dashed line represents Newtonian behavior and the solid line represents non-Newtonian behavior (shear-thinning) under shear. Stretching of polymer chains between entanglement junctions leads to a decrease in solution viscosity.³⁷

This is the cause of viscoelasticity. A substance is viscoelastic if it exhibits both energy dissipation and energy storage in its mechanical behavior. A viscoelastic fluid will exhibit a Trouton ratio (the ratio of shear viscosity to elongational viscosity) of greater than 3.³⁷ A higher value of Trouton ratio indicates greater viscoelasticity. Viscoelasticity relates to the relaxation time of the solution, which is the characteristic time of the exponential stress decay curve. The relaxation time can be determined by conducting a creep test, whereby a viscoelastic fluid will respond in the manner depicted in Figure 8.³⁷

After an instantaneously imposed stress, the strain of the sample is monitored with time. The stress is then released and the relaxation, reflected in negative strain or recoil, is observed with time. After any instantaneous yield, the nonlinear region of the curve, C_1 , relates to strain growth, which is controlled by combined viscous and elastic effects. This region is called the retardation period. After all elastic yield is

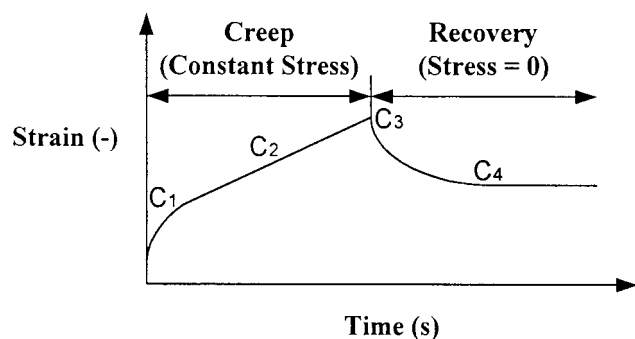


Figure 8 Ideal shear creep and creep recovery from small shear stresses.

exhausted, pure viscous flow prevails. This is reflected in the linear (constant shear rate) region depicted by curve C_2 , which corresponds to a steady shear viscosity. When the stress is released (point C_3), elastic recovery will occur. Combined viscous and elastic effects again control the rate of recovery. This is the relaxation period and corresponds to curve C_3 to C_4 . In this period, the fluid recoils due to polymer chain relaxation and eventually reaches equilibrium. The strain is not recovered completely because of the viscous flow in region C_2 . Relaxation relates to a number of separate strain increments, each decaying exponentially with time. Each increment is governed by elastic and viscous influences working together analogous to a spring and dashpot system. The total relaxation time of the fluid is the summation of the characteristic decay times of each strain increment. Analysis of the relaxation region of the creep curve, C_3 to C_4 , allows the relaxation time to be calculated.

The relaxation time is significant in membrane fabrication. As phase separation progresses, the relaxation time will actually increase due to the onset of solidification. As long as phase separation occurs quickly, the material has no chance of relaxing and hence orientation will be frozen into the membrane. In fact, relaxation times become progressively longer at lower levels of residual strain and thus some level of orientation would still be likely even if phase inversion is delayed. The relaxation time indicates the level of viscoelasticity in polymer solutions and hence the level of molecular orientation induced under shear.

While casting a shear-thinning and viscoelastic solution, polymer molecules are maintained in an oriented (partially) conformation by castline deformation. After casting, polymer molecules would relax to some preferred state. However, they recover only a portion of their total deformation.⁶⁰ The as-cast membrane is then going through forced-convective evaporation. Dry-phase separation progresses instantaneously and limits conformational and configurational rearrangement especially in the nascent skin region. Polymeric material has no chance of relaxing and

therefore shear-induced molecular orientation will be frozen into the nascent skin layer of membrane.^{37,38,41,54} Besides that, dope formulation is tailored to be close to the thermodynamic instability limit and approaching cloud point curve. Nonsolvent is added into the polymer solution in order to speed up preprecipitation of phase-separated structures and reduce relaxation effects on molecular orientation.⁵⁸ In addition, shear fields (over a certain value) can distort phase diagram and hence alter phase stability, demixing, and precipitation kinetics of membrane formation process.⁵⁹ The nascent membrane is then immersed in a coagulation bath for wet-phase separation. The nascent skin layer with sufficiently rigid structures is solidified immediately to form a well-defined skin layer with enhanced molecular orientation.⁴³ Serkov and Khanchich also postulated that shear-induced orientation is frozen into the skin layer during formation.³⁷

Structural organization is well documented in textile and fiber industries. However, only recently have a number of investigators recognized the importance of rheological perspective in membrane fabrication and performance and some of them have systematically investigated these rheological effects with regard to gas separation membranes. According to results determined by using polarized reflection infrared spectroscopy and gas permeation tests, molecular orientation is enhanced in high-sheared membranes, which has a favorable effect on membrane properties.^{38-40,43} Permeability and selectivity of membrane are found to increase with increasing shear; some selectivities even surpass the generally recognized intrinsic selectivity.^{38,39}

CONCLUSIONS

Asymmetric membranes with optimum permeation and separation properties often should exhibit extremely thin yet defect-free skins and negligible substructure resistance. Many previous investigations have been made so far to indicate that properties and gas separation performance of asymmetric membrane are mainly controlled by forced-convective evaporation and rheological factors. However, most of their studies have neglected the exact interaction effects between those parameters due to the complex natures of membrane formation process. Indeed, interdependencies of parameters actually play a significant role in the formation of high-performance asymmetric membranes. Therefore, systematic work is essential to clarify the relationship and interdependency between these factors in order to optimize and generalize the membrane formation process. A detail investigation of this study is under way and will be reported in due course.

NOMENCLATURE

- k constant (a measure of fluid consistency)
 n constant (a measure of degree of non-Newtonian behavior)
 $\dot{\gamma}$ shear rate (s^{-1})
 η viscosity (Pas)
 τ shear stress (Pa)

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