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REVIEW

Water-Casting Ultrathin-Film Composite Membranes for Air Separation

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ABSTRACT

The water-casting method is one of the most important techniques for the preparation of pinhole-free ultrathin film for air separation. Strong interest exists in the optimizations of preparing routes of the ultrathin film and of the fabrication of the ultrathin-film composite membranes with a variety of polymers. A number of water-casting solvents with high spreadability over water are offered in the present review. Progress made in the inconsecutive and continuous preparations of ultrathin films is reviewed in detail. The oxygen permselectivity, air separation performance, and the stability of ultrathin-film composite membranes are discussed with a detailed citation of references. This review also compares the performances through ultrathin-film composite membranes fabricated by the water-casting method with other methods.

Key Words. Water-casting method; Spreading solvent on water; Ultrathin polymer film; Composite membrane; Laminated membrane; Oxygen permselectivity; Air separation; Performance stability

INTRODUCTION

A recent technological success with many intriguing dimensions is the invention of the preparation method of pinhole-free ultra-thin polymer

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films, which were defined as a layer of less than 5 μm in thickness (1). It became possible to fabricate composite membranes with a combination of high permselectivity, high stability, and good mechanical strength because composite membranes allow the structure and properties of the thin separating layer and the thick porous support layer to be optimized individually to a great extent (2). The utilization of composite membranes can also offer a means of minimizing membrane cost by reducing the content of expensive high performance polymers. A successful fabrication of ultrathin-film composite membranes is one of the most important breakthroughs in the area of functional membranes. The techniques used for the preparation of ultrathin-film composite membranes may be finely grouped into seven types (3).

1. Immerse glass plate into a polymer solution (or cast a polymer solution onto a glass plate), peel off an ultrathin film, and then laminate it to a porous support (4–8)

A film as thin as 60 nm has been reproducibly prepared with this procedure. However, only a glassy polymer film could be made, and the peeling of a larger area ultrathin film off the glass plate is a problem, especially when the film thickness is less than 1 μm.

2. Dip-coat a prepolymer or polymer solution onto a porous support, followed by curing or drying with heat or radiation (9)

An ultrathin film with a thickness of about 50 nm can be formed on the porous support. This technique requires that the support must have higher thermostability and be insoluble in the film-forming solvent. Only water, lower alcohols, and aliphatic hydrocarbons can be used as coating solvents. A second problem is that the coating solution must be dilute so as to form an ultrathin film. However, dilute solutions with low viscosity tend to migrate upon drying to form a defective or discontinuous coating.

3. Deposit monomer vapors onto a porous support, followed by polymerizing with heat (10)

Chemical vapor deposition on a porous support in a vacuum and polymerization by heating at 200–300°C for 3 hours have recently been employed to prepare a PI ultrathin-film composite membrane. The PI layer with a thickness of about 200 nm can be easily obtained. This method is very useful for the preparation of a solvent-resistant or solventless ultrathin-film composite membrane in a completely dry process. However, to form collision-free molecular beams and to prevent the influence of trace amounts of water on the polymerization, an extremely high vacuum of lower than 10^{-6} torr is requisite. Only a few studies have been performed for the purpose of pervaporation. There seems to be no work aimed at applying this technique to the preparation of air-separation composite membranes.

4. Plasma deposit of an ultrathin film onto a porous support (11–14)

Gas-phase deposition on a porous support by plasma polymerization was successfully used for the preparation of ultrathin-film composite membranes with a film thickness between 150 and 600 nm, but the plasma reactions are rather heterogeneous, not only involving polymerization but depolymerization and modification of functional groups, resulting in poor reproducibility.

5. Interfacially polymerize reactive monomers on the surface of a porous support (1, 15–20)

The interfacial polycondensation technique is applied for the preparation of polyamide thin-film composite membrane which is the most interesting for reverse osmosis but is less interesting for air separation because the pores of the support are filled with the water-swellen hydrogel. When the membrane is dried for air separation, the hydrogel becomes a low permeable rigid glass. More recently, electrochemically or photochemically initiated interfacial polymerization of an ultrathin film with thicknesses ranging from 50 to 3000 nm at the surface of a porous support has been reported (1, 18–20). Unfortunately, the ultrathin-film composite membranes appear to be poor in oxygen permeation.

6. Spin-coat a polymer solution onto a porous support (17, 21–23)

By spin-coating a dilute solution of polymer directly onto a porous support in the spinning speed range from 250 to 6000 rpm, 13–20 nm-thick-ultrathin-film composite membranes can be prepared. This spin-coating method can be especially employed if limited polymer solubility dictates the use of a high boiling point solvent. However, these composite membranes do not seem to be available for large-scale commercial use at this time.

7. Cast a polymer solution onto a water surface, then laminate the ultrathin-film to a porous support (24–31)

A dilute polymer solution in a volatile solvent exhibiting slight water solubility is spread on the surface of water. The free-floating ultrathin film with a thickness as thin as 6 nm which forms on the water surface is then picked up on a finely porous support. This water-casting method or water surface floating-casting method has been developed into a semicontinuous process (27–29). The adhesion between the ultrathin film and the porous support is sometimes a problem. An approach to overcome the problem would be to add an adhesive rubber layer, followed by heat treatment (30, 31).

Obviously, among these seven methods, the water-casting method is especially useful because an ultrathin film with a larger area and an order of magnitude thinner can be continuously obtained on a large scale. Furthermore, the water-casting method could be applicable to nearly all water-insoluble or hydrophobic polymers. It has been applied mostly for ultrathin-film composite membranes for air separation (32, 33).

Considerable work is presently underway in academic and industrial studies in order to optimize the preparative conditions of ultrathin film by the water-casting method as well as the fabrication of the ultrathin-film composite membranes that have both a higher oxygen permeate flux and a higher oxygen over nitrogen selectivity. Nishimura et al. and Masutani et al. reviewed the preparation of an ultrathin polymer film through the water-casting method and briefly mentioned the use of an ultrathin film as the selective top layer of the composite membranes for gas separation, but without a detailed citation of references (32, 33). Recent reviews by Koros and Fleming, Stern, Robeson et al., and Mazid and Matsuura are concerned with membrane engineering and materials for gas separation and with the mechanisms in membrane gas separation, and cited a large number of references, but have little information on ultrathin-film composite membranes (2, 34–36).

The aim of this paper is to describe the characteristics of solvents exhibiting high spreadability over the surface of water, to review some of research in the field of the preparation of pinhole-free ultrathin films from a variety of polymers via the water-casting technique and of their composite membranes for air separation with a detailed citation of references published in recent years, and to summarize the key developments in the area and to comment on their significance.

SOLVENTS FOR WATER-CASTING METHOD

The solvents employed for the water-casting method must spread spontaneously on the surface of water. The spontaneous spreading depends on both the individual surface tensions of the solvents and water and the interfacial tensions between them (37–40). On the basis of an interface in the equilibrium state without dissolution and evaporation, the spreading ability could be quantified with the spreading coefficient ($S_{o/w}$) as follows:

$$S_{o/w} = r_w - r_o - r_{o/w} \qquad (1)$$

where r_w is the surface tension of water
r_o is the surface tension of solvent
$r_{o/w}$ is the interfacial tension between solvent and water

Theoretically, only solvents with a positive $S_{o/w}$ value can spread automatically over water to produce a thin solvent layer (37–40). The larger the $S_{o/w}$ value, the higher is the spreading ability of the solvent on water. It should be pointed out that the spreading rate of the solvent depends on the size of the solvent drop, the viscosity and temperature of the solvent, and the available capillary pressure. Generally, hotter, less viscous or smaller drops spread faster on water. Note that the retraction of some water-miscible solvent drops may occur after a fast initial spreading (37).

In the formation of a ultrathin polymer film with a larger area but without any pinhole or defect, the moderate spreading coefficient and the volatility of a solution on the water surface are the key factors. The most suitable

TABLE 1

Boiling Point, Solubility in Water, and Spreading Coefficient ($S_{o/w}$) over Water for Some Solvents in the Temperature Range from 20 to 30°C

Solvent (abbreviation)	Boiling point (°C)	Solubility (wt%)	$S_{o/w}$ (dyne/cm)	Solvent (abbreviation)	Boiling point (°C)	Solubility (wt%)	$S_{o/w}$ (dyne/cm)
Dipropylamine	109	4.0	49.1	Ethyl nonylate	227	0.002	20.9
Isobutanol	108	8.5	48.0	Bromoethane	38	0.91	17.5
Cyclohexene (CHE)	83	0.03	46.0[a]	Benzadehyde	180	0.3	17.3
Butanol	118	7.8	45.8	Dichloromethane (DCM)	40	2.0	16.4
Isovaleric acid	177	4.1	45.0	Chloroform ($CHCl_3$)	61	0.82	14.7
Ethyl ether	35	4.6	44.7	Ethylbenzene	136	0.02	12.4
Isoamyl alcohol	131	2.4	44.0	Anisole	154	0.5	12.0
Ethyl acetate	77	8.1	41.9	*p*-Cymene	177	0.03	10.1
Pentanol	138	1.7	41.6	Benzene (BZ)	80	0.07	8.8
2-Pentanone	102	5.9	41.5	Toluene (PhMe)	111	0.05	8.0
Hexanol	157	0.58	41.0	*o*-Xylene	144	Insoluble	7.2
Heptanol	174	0.18	40.0	Isopentane	28	0.02	6.4
Acetic anhydride	140	12.0	36.6	Hexane (HX)	69	0.01	3.4
Pentyl acetate	150	0.17	36.2	Ethylene dichloride	84	0.87	3.3
Octanol	195	0.01	35.7	Heptane	98	0.01	2.1
Cyclohexane (CHA)	81	0.01	35.4[b]	Tetrachloromethane	77	0.08	1.0
2-Hexanone	127	1.75	35.2	Cyclohexanone (CHON)	156	2.3	31[c]
n-Butyronitrile	118	3.3	35.1	*sym*-Trichloropropane (TCP)	157	0.09	>1
Diethyl carbonate	127	Insoluble	33.9				
Cyclohexanol (CHAL)	161	3.6	33.6	Trichloroethylene (TrCE)	87	0.11	>1
Heptaldehyde	153	0.02	32.2	Tetrachloroethylene (TeCE)	121	0.02	>1
t-Butylchloride	51	0.1	29.0	*o*-Dichlorobenzene (DCB)	181	0.01	>1
Benzyl alcohol	205	3.8	28.9				
Nitromethane	101	9.7	26.3				
Diisobutyl ketone	168	0.04	25.9				
Aniline	183	3.6	24.0				
Acetophenone (APON)	202	0.55	21.7				

[a] The spreading coefficient of a cyclohexene solution containing 5 wt% PMP and 4.75 wt% cyclohexenyl hydroperoxide (47).

[b] The spreading coefficient of a cyclohexane solution containing 1 wt% PMP and 0.25 wt% polyolefin polyol (48).

[c] Calculated value according to $S_{o/w} = r_w - r_o - (r_w^{0.5} - r_o^{0.5})^2$.

$S_{o/w}$ values of the solvents for producing polymer solution are in the range from 25 to 47 dyne/cm. Solvents with $S_{o/w}$ values less than 25 dyne/cm are difficult to spread on water. On the contrary, very high $S_{o/w}$ values may result in the formation of pinholes in the film formed. Additionally, solvents with boiling points lower than 35°C or higher than 200°C may not be appropriate for the water-casting method. Exceptionally high volatility will result in too fast evaporation which prevents the spread the solution over water and the formation of a continuous thin layer with a large area. In contrast, low volatility demands long evaporation times. During an elongated evaporation period, the cast film might absorb sufficient water to precipitate the polymer and produce a mottled, hazy, and porous surface. This suggests that solvents possessing high solubility in water are unsuitable for the water-casting technique. Only a slight water solubility and a specific gravity of less than 1.0 g/mL for the solvents are required to produce a defect-free ultrathin film. The boiling point (bp), solubility in water, and spreading coefficient $S_{o/w}$ (calculated values from Eq. 1) over water for 48 polymer solvents are compiled in Table 1 (42–48).

The spreading coefficient of solvents over water can be regulated by using solvent mixtures or introducing only a small amount of surfactants. Thus, the solvents showing $S_{o/w}$ values of less than 25 dyne/cm can also be employed for the preparation of pinhole-free ultrathin films by the water-casting technique after adding ethoxylated siloxane, ethoxylated fluoroalcohols (38), or cyclohexenyl hydroperoxide (27–29). Such water-soluble solvents as methanol, ethanol, butanol, acetone, butanone, ethyl acetate, acetic anhydride, tetrahydrofuran (THF), dimethylacetamide (DMAc), and dimethylsulfoxide (DMSO) could also serve as additives for adjusting the $S_{o/w}$ values of water-insoluble solvents because they usually exhibit high spreadability over water (also see Table 1). To sum up, cyclohexanone (CHON), cyclohexene (CHE), and 1,2,3-*sym*-trichloropropane (TCP) are broadly useful for the water-casting method, although various other solvents and mixtures are also used.

PREPARATION OF ULTRATHIN FILM BY WATER-CASTING METHOD

The successful preparation of water-casting ultrathin films depends on the spreadability and concentration of polymer solutions, the temperatures of the water surface and the solutions, as well as the polymer molecular weight. The preparation conditions for a number of ultrathin polymer films via an inconsecutive water-casting method are collected in Table 2 (2, 24, 30, 49–69). In order to increase the spreading ability of the solutions

TABLE 2
Preparation of Ultrathin Film via Inconsecutive Water-Casting Technique

			Solution		Ultrathin film		
Polymer	Solvent	Water temperature (°C)	Concentration (wt%)	Temperature (°C)	Area (cm^2)	Thickness (nm)	Ref.
CDA or CN	CHON/acetone	—	2–10	—	—	100	1, 49
CTA	TCP/DCM/CH_3OH	—	4.7	—	—	16	50
DMPCC	Styrene	—	1	—	—	100	51
EC	TCP/PhMe	—	8	—	—	1200	52
EVA	DMAc	10–30	10	60	340	2400	53
EVAAA	DMAc or DMSO	0–30	10	60	180	5000	54
PBD	BZ or CHE	—	2–8	—	—	100–200	55, 56
PDMS–PC	TCP or TrCE	5	1–10	—	160–900	15–90	24, 57, 58
DMS–HST–PMP	CHA/CHE	—	1–10	—	>25	23	59
PI	TCP/DCB	—	7.4	—	—	23	60
PMP/PDMS–PC	TeCE	50	1.5	75	400	20	61
PPO	$CHCl_3$	20	4	20	40	330	62
PSF	DCM	13	2.5	15	40	500	63
PST	CHON	20	1	20	—	19	41
PTMSP	Hexane	20	1	20	250	10–50	30, 64
PVC/EBBA	THF/PhMe or CHON	10	8–12	—	—	20–30	65–67
TMSP–PMDSP	PhMe	—	2–3	—	>25	10–35	68

over water, the water is generally controlled at lower temperatures (0–50°C, preferably 5–20°C). In contrast, the solutions should be controlled at higher temperatures such as 15–75°C (preferably 30–40°C) which depend on the boiling points of the solvents. The concentration of polymer solutions usually ranges from 1 to 12 wt%, preferably 2 to 5 wt%. By using a microsyringe for the inconsecutive process, only a drop (0.005–1 mL, preferably 0.05–0.08 mL) of the polymer solutions can quickly spread over water, be desolvated, and then form a solid film (48, 54, 57, 62, 69–71). The area of the ultrathin film thus formed ranges approximately from 25 to 1000 cm^2, usually 160 to 390 cm^2. The thickness of the film is in the range of about 10 to 5000 nm, ordinarily 20 to 100 nm. On the other hand, the effect of polymer molecular weight on the critical concentration above which uniform dense films can be formed is shown in Table 3 (41, 72). It is apparent that the critical concentration decreases with an increase in the polymer molecular weight. Hence, a polymer with a higher molecular weight may be beneficial for the formation of an extremely thin pinhole-free film.

TABLE 3
Critical Concentration above Which Pinhole-Free/Dense Ultrathin Film Can Be Formed

Polymer	Weight-average molecular weight	Solvent	Critical concentration (wt%)	Ref.
DMS–SF–HST	150,000	Benzene	2.0	72
PST	233,000	Cyclohexanone	0.4	41
PST	233,000	Isopentylchloride	0.6	41
PST	1,450,000	Cyclohexanone	0.1	41
PST	1,450,000	Isopentylchloride	0.3	41
PST	6,390,000	Cyclohexanone	0.05	41

Effect of Solvent on the Formation of Ultrathin Film

The spreading coefficient of solvents should generally correspond to the spreadability of polymer dilute solutions in the case of moderate volatility and slight water solubility of the solvents. However, there is no correlation between the spreading coefficient of the solvents and the spreading ability of the polymer solution (41) if the dissipation speed of the spreading solvents into both air and water is higher than the magnitude of the spreadability of the solutions during the water-casting process. Shuto et al. suggested that PST/butanone solution can spread rapidly, disappears immediately, with no PST film left on the surface of water due to the high volatility (bp = 80°C and vapor pressure = 90.6 mmHg at 25°C) and high water solubility (22.6 wt%) of butanone irrespective of its higher spreading coefficient (higher than 41 dyne/cm) (41). But PST/CHON and PST/isopentylchloride solutions can spread uniformly over water and remain stable for a few seconds and then an homogeneous dense PST film can be obtained, which may be attributed to their moderate volatility (bp = 156°C and vapor pressure = 5 mmHg at 26°C for CHON; bp = 108°C and vapor pressure = 31 mmHg at 25°C for isopentylchloride) and slight water solubility (2.3 wt% for CHON and 0.02 wt% for isopentylchloride). Uniform dense PMP ultrathin films can easily be formed by using various spreading solvents including CHA, CHE, OCHE, TrCE, CHE/CHAL, and CHA/CHON which exhibit moderate volatility, slight water solubility, and a fitter spreading coefficient (Table 1), as shown in Table 4. Especially in the case of CHA/CHON or TrCE as a spreading solvent, PMP films as thin as 10–25 nm can be prepared.

TABLE 4

Preparation and Oxygen Permselectivity through Composite Membranes Comprising a Porous PP Support and a Dense Ultrathin PMP Film via the Water-Casting Method

		Solution					
Solvent	Water temperature (°C)	Concentration (wt%)	Temperature (°C)	PMP film[a] thickness (nm)	Oxygen flow rate ($cm^3/cm^2 \cdot s \cdot cmHg$)	Oxygen nitrogen separation factor	Ref.
CHA	—	1	—	930	$1.2–18 \times 10^{-5}$	2.9–3.2	73
CHA	—	1–10	—	75	4.46×10^{-5}	3.8	74
CHA	15	5	40	89	1.20×10^{-3}	2.8	75
CHA	2	3	40	1200	—	—	75
CHE	—	5	—	—	1.58×10^{-4}	—	47
CHE	4–5	5	30	120	2.51×10^{-4}	4.0	76
OCHE[b]	40	5	—	—	1.62×10^{-4}	3.12	77
OCHE[c]	40	5	—	—	1.72×10^{-4}	2.1	77
CHE/CHAL	10	5	40	52	—	—	70
CHA/CHON	17	2	60	10–25	5.00×10^{-5}	2.9	78
TrCE	25	2	72	16	—	—	69

[a] PMP film areas are larger than 150 cm^2.

[b] OCHE means the oxidized cyclohexane with a refractive index of 1.4494.

[c] OCHE means the oxidized cyclohexane with a refractive index of 1.4483.

Additionally, variation of the spreading solvent would result in a structural difference of the ultrathin films formed. The structure of ultrathin films is either dense or porous, depending on the volatility of the solvent in air and the solubility of the solvent in water (49, 79). In the case of a volatile water-immiscible solvent as the spreading solvent, the solvent in a polymer solution over water evaporates rapidly from the spreading surface of the solution, and the film structure is mainly determined by the evaporation rate of the solvent. Thus, the ultrathin films formed are dense and pinhole-free, and exhibit high oxygen permselectivity (see Table 4). In the case of a water-miscible and volatile solvent as the spreading solvent, the film structure is determined by both the coagulation rate of the polymer solution next to the water side and the evaporation rate of the solvent next to the air side. Therefore, the surface structure on the air side of a film is more dense than that on the water side (49). In the case of a water-containing polymer solution having a low evaporation rate and a low diffusion rate in water, coagulation of hydrophilic polymer begins on water and then gelation occurs. Hence, only a relatively porous ultrathin film can be formed (33, 53, 54, 79).

Effect of Forming Conditions on Thickness/Area of Ultrathin Film

The data listed in Table 4 clearly demonstrate that even minor variations of forming conditions will lead to dramatic changes in the thickness of the PMP films. Consequently, the thickness of ultrathin films can be readily controlled by changing the forming conditions such as the concentration and temperature of the polymer solutions and the temperature of the water. Table 5 shows the influence of the preparative conditions on the thickness and area of ultrathin polymer films (41, 79). The thickness decreases with decreasing polymer concentration and increases with polymer solution temperature, whereas the film area increases with an increased temperature of the polymer solution. These all result substantially from the enhancement of the spreading capability of polymer solutions.

Evaluation of the Thickness of Water-Casting Ultrathin Film

The thickness of a water-casting ultrathin film is difficult to evaluate exactly by a micrometer screw gauge due to its extreme thinness. But film thicknesses can be determined by measurements of absorption peak intensities in infrared spectra of films (80). The average thickness is often evaluated from the weight of a known area and of the density a film (81). In addition, film thickness could be exactly confirmed by means of a scanning electron microscopy observation (62, 80, 82), an x-ray diffraction method (83), or an interferometric technique. A simple mechanical stylus method is also good enough for rapid and accurate thickness measurements of ultrathin films (83). The thickness can be determined with a stylus instrument when the stylus force is extrapolated to zero. On the

TABLE 5
Effect of Solution Concentration and Temperature on the Thickness and Area of an Ultrathin Film by the Water-Casting Technique (41, 79)

Concentration of PST in CHON at 20°C (wt%)		0.3	0.5	1.0	2.0
PST film thickness (nm)		11	14	19	29
Solution temperature of 10 wt% EVA in isopropanol/water (2/3) (°C)	0	15	20	40	60
EVA film thickness (μm)	15	—	9	6	5
EVA film area (cm^2)	196	340	395	400	400

other hand, the specific light interference coloring exhibited by ultrathin films floating on water can be used as a general visual guide for film thickness. Although low-quality ultrathin films with heterogeneous thicknesses show "rainbow-like" optical diffraction patterns, high-quality uniform polymer films, which are hundred of nanometers thick, show only one color (1). A blue interference color is indicative of a thickness of about 200 nm for a cellulose acetate film, and a gold color is thinner, but green and red colors are thicker (82). For better visualization of the light interference colors, a black-colored casting tray is preferred (80).

CONTINUOUS PREPARATION OF WATER-CASTING ULTRATHIN-FILM COMPOSITE MEMBRANES

An ultrathin film can also be prepared continuously by supplying polymer solutions at a constant feed rate (18–600 mL/h, preferably 60 mL/h) from an inclined guidance disk onto the surface of water flowing slowly at 6 to 900 m/h (32). After stabilization of the process of continuous formation of an ultrathin film, the film is continuously taken up at a constant winding rate (30–600 m/h, preferably ranging from 98 to 150 m/h) from the water surface by a moving porous support on a roller to give a composite membrane (32). Table 6 lists some important preparative parameters that have been employed for continuously producing ultrathin film composite membranes (27–29, 72, 84–86). Comparing Table 6 with Table 2, it is found that there is a marked similarity in the thickness and area of ultrathin

TABLE 6

Preparation of Ultrathin Film via a Continuous Water-Casting Technique

			Solution			Continuous film		
Polymer	Solvent	Water temperature (°C)	Concentration (wt%)	Feed rate (mL/h)	Winding rate (m/h)	Thickness (nm)	Width (cm)	Ref.
DMS–SF–HST	BZ	—	2	60[a]	98	6	40	72
PDMS	BZ	—	10	—	1 rpm	95–200	30	84
PDMS–PC	TrCE	5	10	60	—	90	—	72
PDMS–PC/PPO	TCP/TrCE	—	2	—	—	50	30	85
PMP	CHE	4–5[b]	5[c]	61[d]	150	120	38	27–29
PPO	$CHCl_3$	25	10	60	120	95	—	86

[a] The distance between the solution feed point and the winding roll is 30 cm.

[b] Water flow rate is 12 m/h.

[c] Spreading solution temperature is 30°C.

[d] The distance between the solution feed point and the winding roll is 20 cm.

films prepared by the inconsecutive and continuous water-casting techniques. The difference between the two techniques is that the continuous addition of a casting solution with mechanical drawing off of the solidified film or by varying other preparation variables can be used to control the thickness of a film (82). The thickness of PI film decreases from 250 to 150 to 50 nm with an increasing fraction (from 0 to 10 to 50 wt%) of APON having a higher spreading coefficient in a DMAc/APON mixture (33). Zhang et al. also suggested that the spreading capability of PMP solution in a CHA/CHON mixture on water increased and the thickness of the PMP film formed decreased from 25 to 18 to 10 nm with an increasing CHON fraction having a higher spreading coefficient from 0.5 to 3 to 20 wt%; on the contrary, the PMP film area increased from 380 to 540 to 1000 cm^2 (78). The film thickness also decreases when the distance between the feed point of the spreading solution and the winding roll is lengthened or by increasing the winding rate due to enlargement of the spreadable water surface. These results are summarized in Table 7 (33). It should be noted that the lower concentration of polymer solution or higher winding rate might result in the formation of pinholes or defects in the film (72). It is interesting that a 95-nm-thick PDMS film prepared by the water-casting method was pinhole-free, whereas a directly coated pinhole-free PDMS/porous PSF composite membrane must have a PDMS thickness of more than 500 nm (87), otherwise a pinhole will form. The data in Table 8 reveal that a 25 nm-thick PTMSP film prepared by the water-casting method can effectively cover the pores (450 nm diameter) of a porous CN support surface, but a thickness of greater than 3000 nm for a directly cast polyaniline film onto a porous alumina membrane surface is required to bridge the pores (20 nm diameter) at the surface of the porous membrane (104). It is likely the water-casting method is superior to the directly coating method on a porous support for the preparation of ultrathin-film composite

TABLE 7
Effect of the Distance Between the Feed Point of the Spreading Solution and the Winding Roll as Well as the Winding Rate on the Thickness of the Ultrathin PI Film by the Continuous Water-Casting Technique (33)

Distance between feed point and winding roll (cm)	18	20	22	28	30	35	42–80
PI film thickness (nm)	47	48	37	25	20	15	13
Winding rate of roll (m/min)	5	7		10	12	15	20
PI film thickness (nm)	30	24		20	15	13	10

membranes. In closing, the water-casting method is a promising technique for the fabrication of pinhole-free ultrathin-film composite membranes from an enormous number of polymer materials.

OXYGEN PERMSELECTIVITY THROUGH WATER-CASTING ULTRATHIN-FILM COMPOSITE MEMBRANES

Oxygen permselectivity through water-casting ultrathin film composite membranes is summarized in Tables 4 and 8. The oxygen over nitrogen separation factor through composite membranes comprising both a top layer and an elastomeric interlayer is higher than that through composite membranes having only a top layer. Composite membranes containing a

TABLE 8

Oxygen Permselectivity through Composite Membranes Comprising a Porous Support Laminated with Ultrathin Polymer Films Formed by the Water-Casting Method

Ultrathin film					
Top/interlayer	Thickness (nm)	Porous support	Oxygen flow rate ($cm^3/cm^2 \cdot s \cdot cmHg$)	O_2/N_2 separation factor	Ref.
PADMSP/no	100/-	PP	3.20×10^{-2}	1.6	88
PDMS/PPO/PDMS	—	PP	1.60×10^{-2}	4.0	89
PDMS/no	95–500/-	PP	$6.6\text{–}9.14 \times 10^{-3}$	1.9–2.1	84, 90, 91
PTMSP/PMS	10/-	PSF	9.60×10^{-3}	2.8	30, 31
PTMSP/no	25/-	CN	3.88×10^{-3}	1.8	64
PTMSP/DMS–SF–HST	200	PP	3.82×10^{-3}	2.79	92
PMP/HST–DMS	—	PP	1.80×10^{-3}	3.1	93
PDMS–PC/no	100/-	PE or PC	1.80×10^{-3}	2.3	24, 58
PTMSP–MS–DMS–HST/ MMA–MS	50/50	PES	1.70×10^{-3}	2.7	94
PMP/SP–DMS	200/100	FP	1.02×10^{-3}	3.89	95
VPPMA/no	—	—	$3.7\text{–}6.4 \times 10^{-4}$	2.8–3.8	96
ATMS–MHP/no	—	PP	5.40×10^{-4}	3.7	77
DMS–HST–PMP/PDMS	90/-	PP	3.43×10^{-4}	2.52	59
PPO–PDMS/no	100/-	PP	$3.0\text{–}7.5 \times 10^{-4}$	1.9–2.84	97
PMP/no	100/-	PSF	2.60×10^{-4}	4.1	98
Porous PP/PMP	—	PP	1.62×10^{-4}	3.12	99
PDMS/PMP	—	PP	1.60×10^{-4}	3.8	100
PDIPF/no	—	PP	1.59×10^{-4}	4.05	101
DMS–SF–HST/no	50/-	PP	1.09×10^{-4}	2.15	72
PMMA/PDMS–PC	-/500	PP	8.90×10^{-5}	2.7	102
Fluorocarbon/no	>350	PP	6.30×10^{-5}	3.2	103
PPO/no	95–1000/-	PP or PSF	4.40×10^{-5}	4.0–4.2	62, 86
PMP/PDMS–PC	160	PC	3.78×10^{-5}	4.05	61
PDB/no	100–1000/-	PC	1.30×10^{-5}	2.4–4.0	55, 56

glassy top layer and an elastomeric interlayer exhibit both a high oxygen flow rate and a high oxygen over nitrogen separation factor. PDMS/PPO/PDMS/porous PP four-layer composite membrane has the highest oxygen permselectivity (89), which is much higher than that through a solution-deposited PPO/PAS/porous PSF three-layer composite membrane (62). Moreover, the PDMS/PP and PMP/SP-DMS/FP composite membranes listed in Table 8 exhibit 10 and 50 times as high an oxygen flow rate as directly coated 1000 nm-thick PDMS/PSF and PMP(1200 nm thick)/PDMS(1000 nm thick)/PSF composite membranes, respectively, while they exhibit essentially the same oxygen/nitrogen separation factors (105). The oxygen permselectivity across water-casting ultrathin PMP film/porous PP membranes shown in Table 4 also appears to be higher than that across spin-coating ultrathin PMP film/porous PSF membranes (21). It is worth noting that the PDMS/PP composite membrane listed in Table 8 has a 500 times greater oxygen flow rate than a plasma-coated hexamethyldisiloxane thin film/porous PC composite membrane, but the oxygen against nitrogen separation factor through the former is somewhat lower than that through the latter (106). It follows that, in one sense, ultrathin-film composite membranes fabricated by the water-casting method exhibit a higher oxygen permselectivity than composite membranes fabricated by the above-mentioned other methods.

Effect of Preparative Parameters on Oxygen Permselectivity

Oxygen permselectivity across ultrathin-film composite membranes fabricated by the water-casting method has a strong dependence on the preparative parameters of the ultrathin film. During the continuous manufacturing of PMP ultrathin films, with an increasing guidance disk radius from 8 to 30 cm while the other conditions are fined, the oxygen/nitrogen separation factor across the PMP ultrathin-film composite membranes increases from 1.2–2.2 to 2.5–2.6 (27). At a given guidance disk radius of 30 cm, the composite membranes laminated with the PMP ultrathin film formed over an quiescent water surface has the oxygen/nitrogen separation factor of 2.4–2.5 (or 1.0–1.4) at 5 minutes (or 8 minutes) after the takeup began, compared with 2.6–2.7 (or 2.6–2.8) over a water flow of 12 m/h (29).

The oxygen permselectivity through ultrathin-film composite membranes also depends strongly on the film-forming solution concentration, water temperature, the thickness of the ultrathin film, and the pore size in the support. Asakawa and coauthors reported that the oxygen flow rate through DMS–SF–HST/PP composite membranes increased from 5.69 ×

TABLE 9

Effect of Spreading Solution Concentration (with Hexane as the Spreading Solvent) and Water Temperature on Oxygen Enrichment Through the PTMSP Ultrathin Film/Porous CN Composite Membranes with Air as the Feed Gas (64)

PTMSP concentration (wt%)	0.01	0.025	0.1	0.5	1.0	2.0
OEA flux ($cm^3/s{\cdot}cm^2$)	0.128	0.15	0.205	0.313	0.375	0.450
Oxygen concentration (%)	28.5	28.0	27.4	26.8	26.4	25.6
Water temperature (°C)	10	20	30	40		
OEA flux ($cm^3/s{\cdot}cm^2$)	0.155	0.313	0.40	0.45		
Oxygen concentration (%)	28.0	26.8	26.0	25.5		

10^{-5} to 1.09×10^{-4} $cm^3/cm^2{\cdot}s{\cdot}cmHg$ with a decrease in DMS–SF–HST concentration from 4 to 2 wt% in benzene, but that both membranes have the same oxygen/nitrogen selectivity factor of 2.15 (72). It is interesting that the oxygen-enriched air (OEA) flux through a PTMSP/CN composite membrane decreases and the oxygen concentration in the OEA increases with decreasing PTMSP concentration in hexane or water temperature (Table 9) because lower water temperature can reduce the evaporation

TABLE 10

Effect of Ultrathin-Film Thickness on Oxygen Enrichment through Composite Membranes (56, 64, 72)

Thickness of PTMSP film (nm)	25	30	100	250	350	1500	6500
OEA flux ($cm^3/s{\cdot}cm^2$)	0.155	0.155	0.150	0.125	0.105	0.1	0.0475
Oxygen concentration[a] (%)	32.0	31.5	31.0	31.0	31.0	27.5	27.0
Thickness of DMS–SF–HST film (nm)	17	22	28	33	39		
Oxygen flow rate ($cm^3/cm^2{\cdot}s{\cdot}cmHg$) × 10^4	2.98	1.55	1.27	1.16	1.09		
O_2/N_2 separation factor	1.3	1.7	2.0	2.15	2.15		
Thickness of PBD film (nm)	100	200	500	700	1000	1500	
Oxygen flow rate ($cm^3/cm^2{\cdot}s{\cdot}cmHg$) × 10^4	2.5	1.1	0.2	0.15	0.13	0.095	
O_2/N_2 separation factor	1	1	2	2.2	2.4	2.7	

[a] Air containing 21% oxygen was used as the feed gas.

rate of the hexane, thus resulting in a denser structure of the PTMSP film (64). The effect of PTMSP concentration cannot be explained at present.

It is seen from Table 10 that the oxygen flow rate increases and the oxygen/nitrogen separation factor decreases with a decrease in the thickness of ultrathin films of rubbery DMS–SF–HST and PBD, but the OEA flux increases simultaneously with the oxygen concentration in OEA enriched by a glassy PTMSP thin-film composite membrane with a decrease of the PTMSP thickness from 6500 to 25 nm, probably due to the more uniform and denser structure in a thinner film than in a thicker film (41, 56, 64, 72). The OEA flux through PTMSP ultrathin-film composite membranes shows an opposing tendency against the oxygen concentration with varying microporosity of the support, as listed in Table 11 (64, 107, 108). Because of the extreme thinness of the selective top layer, the demand on the surface characteristics of the support used is extremely critical (109). The presence of large pores may result in pinholes upon pressurization, but too low a pore size or porosity may also bring about an excessive reduction of oxygen flux across composite membranes. The pore size usually ranges from 25 to 3000 nm (preferably less than 200 nm) and the porosity ranges from 38 to 80% for the porous support, and the values are suitable for the fabrication of an ultrathin-film composite for air separation (24, 32, 64). Note that a pore size of 100 nm in the porous support represents an upper limit for adequate support of an ultrathin-film layer for reverse osmosis (80). The requirement of a smaller pore size limit in a porous support for reverse osmosis than for air separation might be due to a higher operating pressure difference through the reverse osmosis membrane than through the air-separation membrane.

TABLE 11
Effect of Support Structure on the Initial Oxygen Enrichment through PTMSP Ultrathin-Film Composite Membranes in the Case of Air as the Testing Gas (64, 107, 108)

Support	CN	CN	Cell	PP	PP	PVC
Pore size in support (nm)	450	100	200	200 × 20	400 × 20	400
OEA flux (cm^3/s·cm^2)	0.313	0.113	0.0025	0.0125	0.01	0.0375
Oxygen concentration (%)	26.8	28.0	29.8	29.5	29.0	29.0

Support	PPCA	PPCA	PPCA	PPCA	PPCA	PPCA	PTMSP	PTMSP
Air flux through support (cm^3/s·cm^2)	0.75	1.75	2.13	2.63	3.50	3.75	0.25	1.5
OEA flux (cm^3/s·cm^2)	0.0375	0.0375	0.05	0.07	0.085	0.0975	0.0775	0.143
Oxygen concentration (%)	29.2	29.1	29.1	29.3	29.0	29.0	26.1	25.9

AIR-SEPARATION PERFORMANCE THROUGH WATER-CASTING ULTRATHIN-FILM COMPOSITE MEMBRANES

Most monolayer and multilayer ultrathin-film composite membranes fabricated by the water-casting technique exhibit a superior air-separation capability at transmembrane pressure differences between 533 and 947 Pa, as shown in Table 12. Among them, 25–100 nm-thick PTMSP, PTMSP/PDMS, and PDMS-PC film composite membranes are of most interest due to their exceptionally high OEA flux of up to 0.114–0.155 cm^3(STP)/s·cm^2, which appears to be much higher than those [0.0001–0.0142 cm^3(STP)/s·cm^2] across 15–695 nm-thick plasma-polymerized ultrathin-film composite membranes within the transmembrane pressure difference range from 71 to 690 kPa (11–14). The other six composite membranes in Table 12 have an oxygen concentration higher than 40% in a single step.

Water-casting ultrathin-film composite membranes have been incorporated into small plate/frame modules as portable oxygen enrichers for use by people suffering from respiratory problems (36, 114). Ultrathin-film composite membranes have also been incorporated into a leaf-type module. A larger oxygen enricher consisting of six 50-cell leaf-type modules has an initial OEA output of 1300 L/min at an oxygen concentration of 33% (109).

TABLE 12

Air-Separation Capability through Composite Membranes Fabricated by Laminating an Ultrathin Film on a Porous Support

Ultrathin film						
Top/interlayer	Thickness (nm)	Porous support	Operating pressure difference (Pa)	Oxygen enriched air flux (cm^3/s·cm^2)	Oxygen concentration (%)	Ref.
PTMSP/no	25/-	CN	533	0.155	32.0	64
PTMSP/PDMS	7.5/50	PSF	—	0.144	28.2	110
PDMS–PC/no	100/-	PC	912	0.114	35.0	109
PPCA/PTMSP/PDMS	7.5/7.5/50	PSF	—	0.05	33.1	110
PPO/no	40/-	PC	912	0.0259	50	109
ATMS/DMS–BD/ATMS	14/97/14	PSF	947	0.016	42.1	111
PMP/PDMS–PC	80/-	PSF	—	0.00652	41.3	112
PPO/PDMS–PC	-/100	PSF	—	0.00571	40.1	113
PMP/no	150/-	PP	—	0.00333	41.7	74
PMP–PDMS–PC/no	160/-	PC	912	0.00258	43.0	61

PERFORMANCE STABILITY OF WATER-CASTING ULTRATHIN-FILM COMPOSITE MEMBRANES

As shown in Tables 9, 11, and 12, PTMSP thin-film composite membranes have an exceptionally high initial OEA flux but a very low performance stability (64). An obvious decline in OEA flux across PTMSP ultrathin-film composite membranes after a short time has been confirmed by Takada et al. (64, 107, 108), as listed in Table 13. The performance deterioration of composite membranes depends slightly on the porosity of the support and the thickness of the PTMSP film. The deterioration rate

TABLE 13

Stability of Oxygen Enrichment Performances Through Water-Casting Ultrathin-Film Composite Membranes or Oxygen Enricher

Composite membrane				
Top/interlayer/support	Initial performance[a]	Testing time (h)	Performance retention (%)	Ref.
PTMSP/no/CN	$Q_{\mathrm{OEA}} = 17$ mL/s $Y_{\mathrm{O_2}} = 27.0\%$	1	36.5	64
PTMSP/no/PTMSP	$Q_{\mathrm{OEA}} = 3.1$ mL/s $Y_{\mathrm{O_2}} = 26.1\%$	16.7	41.9	108
PTMSP/no/PPCA	$Q_{\mathrm{OEA}} = 2.8$ mL/s $Y_{\mathrm{O_2}} = 29.3\%$	16.7	53.6	107
UV irradiated crosslinked PTMSP/no/PP	$P_{\mathrm{O_2}} = 5800$ Barrer $\alpha_{\mathrm{O_2/N_2}} = 2.0$	2400	84.5	26
Electron beam irradiated crosslinked PTMSP/no/PP	$P_{\mathrm{O_2}} = 7100$ Barrer $\alpha_{\mathrm{O_2/N_2}} = 2.0$	2400	84.5	25
Electron beam irradiated PTMSP-TMPTA/no/PP	$P_{\mathrm{O_2}} = 7100$ Barrer	2400	91.5	115
PTMSP/PMS/PSF	$J_{\mathrm{O_2}} = 0/00789$ Barrer/cm $\alpha_{\mathrm{O_2/N_2}} = 2.6$	1000	90/80 (25/60°C)	30
PTMSP/DMS-SF-HST/PP	$J_{\mathrm{O_2}} = 0.00382$ Barrer/cm $\alpha_{\mathrm{O_2/N_2}} = 2.79$	120	100	92
PMP-MS-ST/no/PES	$Q_{\mathrm{O_2}} = 1.3$ mL/s $\alpha_{\mathrm{O_2/N_2}} = 3.2$	1000	92	116
PMP/no/PSF	$J_{\mathrm{O_2}} = 0.000192$ Barrer/cm	2100	100	98
PMP/PDMS-PC/PSF	$Q_{\mathrm{OEA}} = 0.00652$ cm^3/s·cm^2 $Y_{\mathrm{O_2}} = 41.3\%$	6000	100	113
PDMS-PC/no/PC	$Q_{\mathrm{OEA}} = 22667$ mL/s $Y_{\mathrm{O_2}} = 31.0\%$	2150	100	109

[a] 1 Barrer = 10^{-10} cm^3(STP)·cm/cm^2·s·cmHg. Q_{OEA} (or $Q_{\mathrm{O_2}}$) means oxygen-enriched air (or oxygen) flux. $Y_{\mathrm{O_2}}$ means oxygen concentration in the oxygen-enriched air. $J_{\mathrm{O_2}}$ means oxygen flow rate. $P_{\mathrm{O_2}}$ means oxygen permeability coefficient. $\alpha_{\mathrm{O_2/N_2}}$ means oxygen against nitrogen separation factor.

seems to increase when the pore size of the support or the film thickness increases. This performance deterioration or instability is mainly attributed to a slow collapse of the structure (e.g., free volume collapse and molecular conformational changes of PTMSP with time) and also to the interface interaction between the film and the support (e.g., an anchoring effect of the film onto the support (64, 107). As a result, there is a large reduction of the effective permeated area. Additionally, even minor levels of contamination, including compressor oil and migrating oil from rubber gaskets, can significantly decrease the permeability (35). Thinner PTMSP films are more affected by contamination than thicker PTMSP films because the pores in thinner films are more easily sealed. If hexane vapor is charged into PTMSP ultrathin-film composite membranes, the performance values can be recovered to some extent (107). With the evaporation of the hexane charged, the membrane performance deteriorates again. Note that the measured permeability of a PTMSP film soaked in a nonsolvent such as methanol or ethanol for 30 minutes is initially very high but rapidly decreases with time, approaching the original intrinsic value of the PTMSP after 1 month because the devolatilization rapidly occurs in minutes (35). Moreover, plasma-coating tetrafluoroethylene or hexamethyl-disiloxane modifying thick dense PTMSP membranes can retain their initial oxygen permeability of only 68–77% after 2400 hours (117, 118). Apparently the performance stabilities of PTMSP homogeneous membrane, PTMSP asymmetric membrane (108), and PTMSP ultrathin-film composite membrane are all low.

Recently, high stable PTMSP ultrathin-film composite membranes have been fabricated by an irradiating/crosslinking method. When a PTMSP film floating on water is irradiated and then crosslinked with UV light or an electron beam at 30 Mrad, the crosslinked ultrathin-film composite membranes can retain their initial oxygen permeability of 84.5% after 2400 hours (25, 26). If 10 wt% TMPTA comonomer is added to the PTMSP film-forming solution, the laminated composite membrane of a PTMSP–TMPTA ultrathin film irradiated over water and crosslinked with an electron beam at 200 kV and 30 Mrad can maintain its initial oxygen permeability of 91.5% after 2400 hours (115). It is worth noting that the mechanical properties of PTMSP membranes are not affected after being irradiated with 230–280 nm UV-light at 183 mW/cm^2 for 5 seconds (119).

Another method for increasing performance stability is by adding an adhesive rubbery layer between the ultrathin film and the support. The rubbery layer might serve as a resilient manifold interlayer to prevent the ultrathin film from intruding into the surface pores on the support (2), averting the failure of the laminated ultrathin film. In addition, the rubbery layer might act as a gutter layer to channel gas from the glassy dense layer into the pores of the support (105). Without the rubbery layer, the effective permeated fraction of the glassy selective layer would be strongly limited by the surface porosity of the support. Thus, this kind of three-layer composite membrane shows a higher stability and can tolerate a higher transmembrane pressure differential (8, 62, 92, 113). It can be found from Table 13 that the three-layer composite membrane PTMSP/PMS/PSF as the glassy top layer/rubbery interlayer/porous support layer, respectively, exhibits permeability retentions of 90 and 80% after 1000 hours, respectively, at room temperature and at 60°C/95% humidity (30) versus 10 and 3%, respectively, without the rubbery PMS interlayer. Similarly, a PTMSP/DMS–SF–HST/PP three-layer composite membrane was used for over 120 hours without reduction in the oxygen flow rate, whereas a composite membrane without the DMS–SF–HST interlayer showed a fast reduction in the oxygen flow rate (92). The air-separation performance through a PMP/PDMS–PC/PSF three-layer composite membrane remained stable after 6000 hours of service (113), which is more stable than a fluorinated layer(25 nm)/PMP(1600 nm)/PDMS(1000 nm)/porous PSF four-layer composite membrane (105, 120). Three-layer composite membranes maximize gas flux/separation factor/stability/mechanical strength simultaneously. However, note in Table 13 that two-layer composite membranes (PMP–MS–ST/PES, PMP/PSF and PDMS–PC/PC) also show better performance stabilities.

CONCLUSIONS

A number of water-immiscible solvents having moderate volatility and a spreading coefficient of higher than 25 dyne/cm over water are suggested to be suitable for the preparation of pinhole-free ultrathin polymer film with a large area via a simple water-casting method. The film thickness is easily controlled in a wide range from 6 to 15000 nm through variation of solvent composition and solution concentration/temperature, and also through stretching of the water-borne film while it is still in the liquid state. Water-casting ultrathin-film composite membranes are easily handled and show both a higher oxygen permselectivity and a higher performance stability. The oxygen-enriched air produced with an oxygen enricher comprising ultrathin-film composite membranes is appropriate for medical and industrial applications. The same composite membranes can also be incorporated into a nitrogen enricher for producing nitrogen-enriched air to provide inert atmospheres for the long-term storage of fresh foods and for annealing, sintering, and brazing operations.

POLYMER ABBREVIATION

ATMS	allyltrimethylsilane polymer
ATMS–MHP	allyltrimethylsilane–4-methylheptene copolymer
CDA	cellulose diacetate
Cell	regenerated cellulose
CN	cellulose nitrate
CTA	cellulose triacetate
DMS–BD	dimethylsiloxane–butadiene copolymer
DMS–HST–PMP	dimethylsiloxane–hydroxystyrene–methylpentene copolymer
DMS–SF–HST	dimethylsiloxane–sulfone–hydroxystyrene copolymer
EC	ethyl cellulose
EVA	ethylene–vinyl alcohol copolymer
EVAAA	ethylene–vinyl alcohol–acrylic acid copolymer
FP	fluoropolymer
HST–DMS	hydroxystyrene–dimethylsiloxane copolymer
MMA–MS	methyl methylacrylate–methylsiloxane copolymer
PADMSP	poly(1-monoalkyldimethylsilylpropyne)
PAS	poly(aminosiloxanes)
PBD	polybutadiene
PC	polycarbonate
PDIPF	poly(diisopropylfumarate)
PDMS	polydimethylsiloxane
PDMS–PC	polydimethylsiloxane–polycarbonate block copolymer
PE	polyethylene
PES	polyether sulfone
PI	polyimide
PMMA	poly(methyl methylacrylate)
PMP	poly(4-methylpentene)
PMP–DMS–PC	blend of polymethylpentene with copoly(dimethylsiloxane–carbonate)
PMP–MS–ST	blend of polymethylpentene with graft copoly(methylsiloxane–styrene)
PMS	polymethylsiloxane

PP	polypropylene
PPCA	poly(phenyl-1-chloroacetylene)
PPO	poly(2,6-dimethylphenylene oxide)
PPO–PDMS	poly(2,6-dimethylphenylene oxide)-*graft*-polydimethylsiloxane
PSF	polysulfone
PST	polystyrene
PTMSP	poly(1-(trimethylsilyl)-1-propyne)
PTMSP–MS–DMS–HST	trimethylsilylpropyne–methylsiloxane–dimethylsiloxane–hydroxystyrene copolymer
PTMSP–TMPTA	trimethylsilylpropyne–pentamethyldisilylpropyne
PVC	polyvinyl chloride
SP–DMS	silphenylene–dimethylsiloxane copolymer
TMSP–PMDSP	trimethylsilylpropyne–pentamethyldisilylpropyne copolymer
VPPMA	vinyl pivalate–polyethylene glycol–monomethacrylate copolymer

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