

THIN FILM COMPOSITE MEMBRANES FOR PERVAPORATION

BACKGROUND OF THE INVENTION

Pervaporation (or pervaporative separation) is a process for separating a mixture of liquids by vaporization through a non-porous membrane. Typically, an asymmetric membrane, e.g., a thin film composite (TFC) membrane, is employed for pervaporation dehydration applications. Dehydration of industrial solvents (e.g., ethanol and isopropanol) by pervaporation is more economical than conventional distillation.

During pervaporation, a TFC membrane formed of a thin film layer and a porous support is typically exposed to a high temperature and various chemicals. Swelling of the porous support resulting from the exposure damages the thin film layer and undermines its pervaporation performance. Thus, it is critical that a porous support be rigid, thermal stable, and chemical resistant.

Ceramic materials are well suited for making porous supports for their excellent properties, e.g., strong mechanical strength, thermal stability, and high chemical resistance. Yet, a TFC membrane made of a ceramic support has a thick thin film layer, resulting in poor pervaporation performance.

There is a need to develop a high-performance TFC membrane having a ceramic support for use in pervaporation of industrial solvents.

SUMMARY OF THE INVENTION

This invention provides a TFC membrane including a ceramic support that swells minimally. The membrane has an unexpectedly high separation performance. In other words, it possesses an unexpectedly high flux rate and separation factor, even at an elevated temperature. As such, it is suitable for use in a pervaporation process.

One aspect of this invention relates to a TFC membrane that includes a ceramic support, a polymeric gutter layer bonding covalently or non-covalently onto the ceramic support, and a thin film layer bonding covalently onto the polymeric gutter layer.

The ceramic support has a thickness of 1 to 10000 μm (preferably, 50-1000 μm , and, more preferably, 100-300 μm) and a pore size of 1 to 200 nm (preferably, 5-100 nm, and, more preferably, 10-40 nm). Examples of the ceramic support include, but are not limited to, α -alumina, titania, zirconia, and a combination thereof.

The polymeric gutter layer has a thickness of 1 to 10000 nm (preferably, 20-1000 nm, and, more preferably, 50-500 nm) and can be made of polydopamine (PDA) or a polyelectrolyte having an amine functional group, e.g., polyethyleneimine (PEI). Examples of a polyelectrolyte can be found in Krasemann et al., Self-assembled polyelectrolyte multilayer membranes with highly improved pervaporation separation of ethanol/water mixtures, J. Membr. Sci. 181 (2001) 221–228.

The thin film layer, having a thickness of 10 to 1000 nm (preferably, 20-500 nm, and, more preferably, 50-100 nm), can be made of a polyamide covalently bonding to the polymeric gutter layer via an ester bond or an amide bond.

In one embodiment, the TFC membrane includes a ceramic support made of α -alumina, a polymeric gutter layer made of PEI, and a thin film layer made of poly(m-phenylenediamine trimesoyl amide) covalently bonding to the polymeric gutter layer via an amide bond.

In another embodiment of the TFC membrane, the ceramic support is a tube that has an outer diameter of 0.1 to 100 mm and an inner diameter of 0.05 to 95 mm, the polymeric gutter layer bonding onto the inner surface of the tube.

Optionally, the TFC membrane of this invention further includes a sealing layer that bonds to the thin film layer. The sealing layer, which can be made of polydimethylsiloxane (PDMS), has a thickness of 1 to 250 nm (preferably, 5-100 nm, and, more preferably, 10-40 nm).

Another aspect of this invention relates to a method of preparing the above-described TFC membrane. The method includes the following steps: (i) providing a ceramic support having a thickness of 1 to 10000 μm and a pore size of 1 to 200 nm, (ii) coating a polymer on a surface of the ceramic support to form a polymeric gutter layer having a thickness of 1 to 10000 nm, and (iii) forming by interfacial

polymerization a thin film layer having a thickness of 10 to 1000 nm and bonding covalently onto the polymeric gutter layer. The TFC membrane thus formed has a ceramic support, a polymeric gutter layer, and a thin film layer.

As disclosed above, the ceramic support can be made of α -alumina, titania, zirconia, or a combination thereof; the polymeric gutter layer can be made of PDA or a polyelectrolyte having an amine functional group; and the thin film layer can be made of a polyamide. Poly(m-phenylenediamine trimesoyl amide), an example of a polyamide, is typically formed via interfacial polymerization between phenylenediamine (MPD) and trimesoyl chloride (TMC).

The above-described method can include a step of coating a sealing layer onto the thin film layer. Examples of the polymer used for the sealing layer are enumerated above.

The details of the invention are set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description and from the claims.

DETAILED DESCRIPTION

The TFC membrane of this invention includes a ceramic support, which swells minimally and maintains the stability of the membrane in a pervaporation process. It has a flux rate of $6.0 \text{ kgm}^{-2}\text{h}^{-1}$ and a separation factor of greater than 1000 at 80 °C for pervaporation dehydration of isopropyl alcohol (IPA).

Both the flux rate and the separation factor of a TFC membrane can be measured in a laboratory scale pervaporation study described in Shi *et al.*, Dual-layer PBI/P84 hollow fibers for pervaporation dehydration of acetone, AIChE J., 58 (2012) 1133-1145.

The flux rate J is determined by the following equation:

$$J = \frac{Q}{AT},$$

wherein Q is the total mass transferred over time t and A is the membrane area. The mass of permeate is weighed by using a Mettler Toledo balance.

The separation factor β is defined as follows:

$$\beta_{ij} = \frac{y_{wi}/y_{wj}}{x_{wi}/x_{wj}},$$

wherein subscripts i and j refer to water (i.e., component i) and IPA (i.e., component j), respectively; y_w and x_w are the weight fractions of a component in the permeate and feed, respectively. They are analyzed using a Hewlett-Packard GC 7890 with a HP-INNOWAX column and a TCD detector.

The permeance P_i/l of a membranes, expressed in GPU ($1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3 (\text{STP})/\text{cm}^2 \text{ s cm Hg}$), is determined as follows:

$$\frac{P_i}{l} = J_i / (x_i \gamma_i P_i^{sat} - y_i P^p)$$

wherein P_i and J_i are the membrane permeability and flux rate of component i , respectively, l is the membrane thickness, y_i and x_i are the permeate mole fraction and the feed mole fraction of component i , respectively, P^p is the total pressure at the permeate side, P_i^{sat} is the partial vapor pressure of component i at the feed side, and γ_i is the activity coefficient. Both P_i^{sat} and γ_i are obtained from the AspenTech Process Modeling V7.2.

The permeance P_i/l is determined in the same manner.

The membrane selectivity α_{ij} is defined by the equation below:

$$\alpha_{ij} = \frac{P_i/l}{P_j/l}$$

Described below is an exemplary procedure for preparing a TFC membrane of this invention.

First, a ceramic tube made of α -alumina is prepared to serve as a ceramic support. To ensure that the subsequent coating only occurs on the inner surface of each tube, the outside of the tube is wrapped with tape.

Next, the inner surface of the tube is coated with either PDA or a polyelectrolyte having an amine functional group to form a polymeric gutter layer.

After a PDA coating solution is prepared, the PDA coating is conducted under ambient conditions for 24 h.

The polyelectrolyte coating is performed by dipping a ceramic tube in a polyelectrolyte coating solution for 1 min, followed by blowing air into the ceramic tube to remove excess polyelectrolyte coating solution. The dip-coating process is repeated once to ensure the formation of a polyelectrolyte layer on the inner surface of the ceramic tube. Afterwards, the tube having a polymeric gutter layer bonded onto its inner surface is dried in a vacuum oven at 100 °C for 10 min.

Finally, a polyamide thin film layer is coated onto the polymeric gutter layer via the interfacial polymerization reaction between MPD and TMC. The PDA- or polyelectrolyte-coated ceramic tube is first immersed in an MPD solution for 10 min, followed by blowing air into the tube to remove excess MPD solution. The tube is then immersed in a TMC solution for 2 min, followed by heating at 65 °C for 10 min to facilitate interfacial polymerization between MPD and TMC to form a polyamide thin film layer.

The TFC membrane thus prepared has a ceramic support, a polymeric gutter layer bonding covalently or non-covalently onto the ceramic support, and a thin film layer bonding covalently onto the polymeric gutter layer.

Further, the TFC membrane can be immersed in a PDMS solution for 3 min to form a sealing layer bonded to the thin film layer.

The specific examples below are to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever. Without further elaboration, it is believed that one skilled in the art can, based on the description herein, utilize the present invention to its fullest extent. All publications cited herein are incorporated by reference in their entirety.

EXAMPLE 1: Preparation of TFC membranes having a ceramic support

Ceramic tubes purchased from Inocep® α -alumina tube M20 (outside diameter 3.7 mm, inside diameter 2.7 ± 0.1 mm, and average pore size 20 nm, supplied by Hyflux SIP Pte Ltd.) were cut into shorter tubes each having a length of about 15 cm. These shorter tubes, each used as a ceramic support, were

ultrasonically washed in deionized (DI) water for 20 min before coating either PDA or PEI on their inner surfaces to form a polymeric gutter layer.

Prior to the coating process, each of the ceramic tubes was wrapped with Teflon tape to ensure that only the inner surface of the tubes was coated.

5 After a PDA coating solution (2 g/L) was prepared by dissolving dopamine hydrochloride (Sigma-Aldrich) in tris-buffer at PH = 8.5, the PDA coating was conducted under ambient conditions for 24 h.

On the other hand, the PEI coating was performed by dipping a ceramic tube for 1 min in a PEI coating solution (10 g/L), which was prepared by
10 dissolving hyperbranched PEI (Sigma-Aldrich molecular weight 60,000 g/mol) in DI water, followed by blowing air into the tube to remove excess PEI solution. The dip-coating process was repeated once to ensure the formation of a PEI film on the inner surface of the ceramic tube.

After the PDA or PEI coating, the ceramic tubes, each having a polymeric gutter layer bonded onto its inner surface, were dried in a vacuum oven at 100 °C
15 for 10 min.

A polyamide thin film layer was then coated onto the polymeric gutter layer via the interfacial polymerization reaction between MPD and TMC. First, the PDA- or PEI-coated ceramic tube was immersed in an MPD (Sigma-Aldrich)
20 2 wt% solution for 10 min, followed by blowing air into the tube to remove the excess MPD solution. Next, the tube was immersed in a TMC (Sigma-Aldrich) 0.1 wt% solution for 2 min and then subjected to heat treatment at 65 °C for 10 min, thereby forming a polyamide thin film layer covalently bonding to the polymeric gutter layer via an amide bond.

25 The TFC membranes having the PDA coating thus prepared were designated as "PDA-IP" and those having the PEI coating were designated as "PEI-IP." Finally, PDA-IP and PEI-IP membranes were immersed in a PDMS (Sylgard® 184) n-hexane solution for 3 min to form a sealing layer bonded to the thin film layer and they were stored for at least 24 h for the sealing layers to cure.
30 The PDA-IP and PEI-IP membranes coated with PDMS were designated as "PDA-IP-PDMS" and "PEI-IP-PDMS," respectively.

EXAMPLE 2: Characterization of TFC membranes having a ceramic support

The membrane morphology of the TFC membranes, i.e., PDA-IP-PDMS and PEI-IP-PDMS membranes prepared in Example 1, was observed by using a JSM-6700F field emission scanning electron microscope (FESEM). The FESEM images show that the TFC membranes had a ridge-and-valley structure, which is a typical morphology for those prepared by interfacial polymerization. Also, the images show a continuous polyamide thin film layer with a thickness of about 100 nm, but not a polymeric gutter layer made of PDA or PEI.

To evaluate the roughness and topology of the surface of the membranes, an atomic force microscope (AFM, Agilent Technology, USA) in contact mode was employed. The AFM images indicated that the polymeric gutter layers made of PEI yielded a much smoother surface than that made of PDA. Note that a smoother surface of the polymeric gutter layer leads to less defects in the polyamide thin film layer later formed. As confirmed by pervaporation performance below, PEI-IP-PDMS membranes had higher flux rates than PDA-IP-PDMS membranes.

In addition, an X-ray photoelectron spectrometer (XPS, Kratos XPS System-AXIS His-165 Ultra) was utilized to assess the surface roughness of layers in the TFC membranes, the results of which show that the polymeric gutter layer made of PDA or PEI was not continuous owing to the rough inner surface of original ceramic tubes.

EXAMPLE 3: Pervaporation performances of TFC membranes have a ceramic support

A study was conducted to assess the pervaporation performances of TFC membranes PDA-IP, PEI-IP, PDA-IP-PDMS, and PEI-IP-PDMS prepared in Example 1. Ceramic-IP, a TFC membrane which only included a ceramic support and a thin film layer, was used as a control in the study.

A feed solution of IPA/water (85/15 wt %) was used, which was maintained at 20 l/h for each membrane. The permeate pressure was maintained at < 2 mbar by a vacuum pump. Retentate and permeate samples were collected after the membranes were kept under these conditions for at least 2 h. The flux rate and

separation factor were determined for each membrane following the equations described above. Table 1 below lists the results.

Table 1. Pervaporation performances of TFC membranes (Feed: IPA/Water 85/15 wt% at 50°C).

Membrane	Flux rate (kgm ⁻² h ⁻¹)	Water in permeate (wt%)	Separation factor (water/IPA)
Ceramic-IP	3.40	76.0	27.8
PDA-IP	2.85	95.4	110
PEI-IP	2.70	97.5	220
PDA-IP-PDMS	2.55	97.6	233
PEI-IP-PDMS	2.19	99.7	2800

The results show that, when used for dehydration of IPA at 50 °C, both PDA-IP and PEI-IP membranes exhibited unexpectedly higher separation factors than that of the Ceramic-IP membrane (110 and 220 vs. 27.8) while they had about the same flux rates (2.70 – 3.40). The gain in pervaporation performance of PDA-IP and PEI-IP over Ceramic-IP was clearly attributed to a polymeric gutter layer which was missing from Ceramic-IP. Having a polymeric gutter layer bonded onto the ceramic support, both PDA-IP and PEI-IP had a polyamide thin film layer bonding covalently on the polymeric gutter layer, thus contributing to high-performance in pervaporation.

Note that PEI-IP had a higher separation factor than that of PDA-PI (220 vs. 110), which is consistent with the observations with the AFM images that the

polymeric gutter layer made of PEI yielded a much smoother surface than that made of PDA

The results in Table 1 also show significant improvement in pervaporation performance for TFC membranes having a PDMS sealing layer. For example, compared to PEI-IP, PEI-IP-PDMS exhibited a much higher separation factor (2800 vs. 220) and only a less than 20% drop in the flux rate (2.19 vs. 2.7), implicating that the PDMS sealing layer effectively sealed defects of a TFC membrane. However, the PDA-IP-PDMS did not exhibit much improvement over PDA-IP possibly due to too many surface defects (observed with the AEM images) that could not be effectively sealed by PDMS.

EXAMPLE 4: Temperature effects on the pervaporation performances of various TFC membranes

A study was conducted to assess the performances of PDA-IP-PDMS and PEI-IP-PDMS membranes when pervaporation was carried out at 40, 50, 60, and 80°C. The results are shown in Table 2 below.

Table 2. Temperature effects on the pervaporation performances of TFC membranes (Feed: IPA/Water 85/15 wt%)

TFC membrane	Feed temp. (°C)	Flux Rate (kg m ⁻² h ⁻¹)	Separation factor (water/IPA)	Water permeance (GPU)	IPA permeance (GPU)	Selectivity (water/IPA)
PDA-IP	40	1.68	414	13,416	29.5	454.6
-PDMS	50	2.55	233	12,289	47.0	261.3
	60	3.70	90	10,810	105.3	102.7
	80	6.40	71	9755	118.1	82.62
PEI-IP	40	1.31	3350	10,561	2.87	3678
-PDMS	50	2.19	2800	10,768	3.43	3140
	60	3.10	2000	9595	4.20	2282
	80	6.05	1396	9917	6.10	1625

The results indicate that, with the increase in temperature, the separation factors decreased significantly while the flux rates increased also significantly for both PDA-IP-PDMS and PEI-IP-PDMS membranes. At 80 °C, the flux rate of the PEI-IP-PDMS membrane was unexpectedly high, i.e., $6.05 \text{ kgm}^{-2}\text{h}^{-1}$, and its separation factor remained unexpectedly high, i.e., 1396.

Note that a flux rate of $6.05 \text{ kgm}^{-2}\text{h}^{-1}$ is higher than that of eight reported TFC membranes that exhibited satisfying separation factors, i.e., 160 or higher. See Table 3 below. This superior performance of the PEI-IP-PDMS membrane in a pervaporation process can be attributed to having (i) a ceramic support that resists temperature or chemical-induced swelling, (ii) a polymeric gutter layer, (iii) a polyamide thin film layer, and (iv) a sealing layer.

The results demonstrate that the TFC membranes having a ceramic support thus prepared are most suitable for dehydration of industrial solvents in a pervaporation process.

Table 3. Literature comparison of pervaporation performances of TFC
Membranes known to have a polymeric support

Membrane	Feed compositions (wt%/wt%)	Temperature (°C)	Flux rate (kg/m ² h)	Separation factor	Reference
IP/polyacrylonitrile	Ethanol/water (90/10)	25	~1.75	~600	[1]
IP/Torlon	IPA/water (85/15)	50	1.28	624	[2]
IP/polyetherimide	IPA/water (85/15)	50	3.5	278	[3]
Polyvinyl alcohol (PVA)/alumina	Ethyl acetate /water (95/5)	60	1.05	633	[4]
Polyimide P84 / γ -alumina	n-butanol/water (95/5)	95	~1.20	~1000	[5]
PVA–chitosan/alumina	Ethyl acetate /water (92/8)	50	2.22	500	[6]
PVA/ γ -alumina	IPA/water (95/5)	80	~1.00	~160	[7]
poly(acrylic acid)/alumina	Ethanol/water (95/5)	30	0.54	1168	[8]
Polyelectrolyte /alumina	Ethanol/water (94/6)	65	18.40	8.2	[9]
IP/ α -alumina	IPA/water (85/15)	80	6.05	1396	This study

5 References listed in Table 3:

- [1] Huang et al., Interfacially polymerized thin-film composite polyamide membranes: Effects of annealing processes on pervaporative dehydration of aqueous alcohol solutions, *Sep. Purif. Technol* 72 (2010) 40–47.
- [2] Zuo et al., Molecular design of thin film composite (TFC) hollow fiber
10 membranes for isopropanol dehydration via pervaporation, *J. Membr. Sci.*, 405-406 (2012) 123-133.
- [3] Zuo et al, Novel organic-inorganic thin film composite membranes with separation performance surpassing ceramic membranes for isopropanol dehydration, *J. Membr. Sci.*, 433 (2013) 60-71.
- 15 [4] Xia et al., Dehydration of ethyl acetate-water mixtures using PVA/ceramic composite pervaporation membrane, *Sep. Purif. Technol.*, 77 (2011) 53-59.

- [5] Kreiter et al., Hightemperature pervaporation performance of ceramic-supported polyimide membranes in the dehydration of alcohols, J. Membr. Sci., 319 (2008) 126-132.
- [6] Zhu et al., Preparation of ceramic-supported poly(vinyl alcohol)-chitosan composite membranes and their applications in pervaporation dehydration of organic/water mixtures, J. Membr. Sci., 349 (2010) 341-348.
- [7] Petes et al., Ceramic-supported thin PVA pervaporation membranes combining high flux and high selectivity; contradicting the flux-selectivity paradigm, J. Membr. Sci., 276 (2006) 42-50.
- [8] Cao et al., A novel hydrophilic polymer-ceramic composite membrane 1 Acrylic acid grafting membrane, J. Membr. Sci., 312 (2008) 15-22.
- [9] Chen et al., Organic-inorganic composite pervaporation membranes prepared by self-assembly of polyelectrolyte multilayers on macroporous ceramic supports, J. Membr. Sci., 302 (2007).

OTHER EMBODIMENTS

All of the features disclosed in this specification may be combined in any combination. Each feature disclosed in this specification may be replaced by an alternative feature serving the same, equivalent, or similar purpose. Thus, unless expressly stated otherwise, each feature disclosed is only an example of a generic series of equivalent or similar features.

Further, from the above description, one skilled in the art can easily ascertain the essential characteristics of the present invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions. Thus, other embodiments are also within the claims.

What is claimed is:

1. A thin film composite (TFC) membrane comprising
a ceramic support having a thickness of 1 to 10000 μm and a pore size of 1 to 200 nm,
a polymeric gutter layer having a thickness of 1 to 10000 nm, and
a thin film layer having a thickness of 10 to 1000 nm,
wherein the polymeric gutter layer bonds covalently or non-covalently onto the ceramic support and the thin film layer bonds covalently onto the polymeric gutter layer.
2. The TFC membrane of claim 1, wherein the ceramic support is made of α -alumina, titania, zirconia, or a combination thereof.
3. The TFC membrane of claim 2, wherein the ceramic support is made of α -alumina.
4. The TFC membrane of claim 1, wherein the polymeric gutter layer is made of polydopamine or a polyelectrolyte having an amine functional group.
5. The TFC membrane of claim 4, wherein the polymeric gutter layer is made of polyethyleneimine.
6. The TFC membrane of claim 1, wherein the thin film layer is made of a polyamide covalently bonding to the polymeric gutter layer via an ester bond or an amide bond.
7. The TFC membrane of claim 6, wherein the thin film layer is made of poly(m-phenylenediamine trimesoyl amide) covalently bonding to the polymeric gutter layer via an amide bond.
8. The TFC membrane of claim 7, wherein the ceramic support is made of α -alumina, the polymeric gutter layer is made of polyethyleneimine.

9. The TFC membrane of claims 1, wherein the ceramic support is a tube that has an outer diameter of 0.1 to 100 mm, an inner diameter of 0.05 to 95 mm, and an inner surface, the polymeric gutter layer bonding onto the inner surface.

10. The TFC membrane of claim 9, wherein the ceramic support is made of α -alumina, titania, zirconia, or a combination thereof, the polymeric gutter layer is made of polydopamine or a polyelectrolyte having an amine functional group, and the thin film layer is made of a polyamide covalently bonding to the polymeric gutter layer via an ester bond or an amide bond.

11. The TFC membrane of claim 10, wherein the ceramic support is made of α -alumina, the polymeric gutter layer is made of polyethyleneimine, and the thin film layer is made of poly(m-phenylenediamine trimesoyl amide) covalently bonding to the polymeric gutter layer via an amide bond.

12. The TFC membrane of claim 1, further comprising a sealing layer that bonds to the thin film layer, the sealing layer having a thickness of 1 nm to 250 nm.

13. The TFC membrane of claim 12, wherein the ceramic support is made of α -alumina, titania, zirconia, or a combination thereof, the polymeric gutter layer is made of polydopamine or a polyelectrolyte having an amine functional group, and the thin film layer is made of a polyamide covalently bonding to the polymeric gutter layer via an ester bond or an amide bond.

14. The TFC membrane of claim 12, wherein the sealing layer is made of polydimethylsiloxane.

15. The TFC membrane of claim 14, wherein the ceramic support is made of α -alumina, the polymeric gutter layer is made of polyethyleneimine, and the thin film layer is made of poly(m-phenylenediamine trimesoyl amide) covalently bonding to the polymeric gutter layer via an amide bond.

16. A method of preparing a TFC membrane of claim 1, the method comprising:
providing a ceramic support having a thickness of 1 to 10000 μm and a pore size of 1 to 200 nm,
coating a polymer on a surface of the ceramic support to form a polymeric gutter layer having a thickness of 1 to 10000 nm, and
forming by interfacial polymerization a thin film layer bonding covalently onto the polymeric gutter layer, the thin film layer having a thickness of 10 to 1000 nm.

17. The method of claim 16, further comprising coating a sealing layer onto the thin film layer.

18. The method of claim 17, wherein the ceramic support is a tube that has an outer diameter of 0.1 to 100 mm, an inner diameter of 0.05 to 95 mm, an outer surface, and an inner surface, the polymeric gutter layer bonding onto the inner surface.

19. The method of claim 18, further comprising coating a sealing layer onto the thin film layer, wherein the ceramic support is made of α -alumina, titania, zirconia, or a combination thereof, the polymeric gutter layer is made of polydopamine or a polyelectrolyte having an amine functional group, and the thin film layer is made of a polyamide covalently bonding to the polymeric gutter layer via an ester bond or an amide bond.

20. The method of claim 19, wherein the ceramic support is made of α -alumina, the polymeric gutter layer is made of polyethyleneimine, the thin film layer is made of poly(m-phenylenediamine trimesoyl amide) covalently bonding to the polymeric gutter layer via an amide bond, and the sealing layer is made of polydimethylsiloxane.