

FLAT SHEET MEMBRANE FOR CARBON DIOXIDE SEPARATION AND PREPARATION METHOD THEREOF

TECHNICAL FIELD

5 Engineering related to a flat sheet membrane for carbon dioxide separation and a method for preparing said membrane

BACKGROUND OF THE INVENTION

Carbon dioxide is one of the components found in natural gas, in addition to hydrocarbon compounds such as methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and pentane
10 (C_5H_{12}). Before natural gas can be utilized, it is necessary to separate the hydrocarbon compounds from non-hydrocarbon substances, such as carbon dioxide. The separation or removal of carbon dioxide can be carried out using various methods. One method that has been implemented is a membrane separation. Generally, polymers are the materials commonly used to form commercial membranes. A search of patent databases reveals some developments related
15 to membranes for carbon dioxide separation.

US 10,874,980 B2, titled "INERT GAS GENERATING SYSTEM," discloses a device for carbon dioxide separation present in a gas inerting system. The membrane used in the separation process is made of polyether-polyamide block copolymer (PEBAX), polyphenylene oxide (PPO), polyimide, polydimethylphenylene oxide, polysulfone, polyethersulfone,
20 poly(4-vinylpyridine)/polyetherimide), polyacrylonitrile with poly(ethylene glycol), poly(amide-6-b-ethylene oxide), and poly-vinylidene fluoride (PVDF).

US 11,285,445 B2, titled "CO₂-PHILIC THIN FILM COMPOSITE MEMBRANES," discloses a thin film composite membrane for capturing or removing carbon dioxide (CO_2). The structure of this membrane comprises a porous polymer support layer, which is selected from
25 polyacrylonitrile, polysulfone, polyetherimide, and polyvinyl difluoride; and a selective layer coating on the support layer. Said selective layer is made of polyether-based copolymer.

US 10,232,322 B2, titled "COMPOSITE SEPARATION MEMBRANE INCLUDING GRAPHENE OXIDE COATING LAYER AND METHOD FOR MANUFACTURING THE SAME," discloses a composite separation membrane for separating carbon dioxide. Such
30 membrane comprises a porous polymer support layer, which is selected from polyethersulfone, polyimide, polyetherimide, polyamide, polyacrylonitrile, cellulose acetate, cellulose triacetate,

and polyvinylidene fluoride; and a graphene oxide coating layer coating on the porous polymer support layer.

There is also a development of membranes for carbon dioxide separation comprising a polymer layer, a selective layer, and a crosslinking agent, as exemplified below.

5 WO 2021/236220 A1, titled "CROSSLINKED FACILITATED TRANSPORT MEMBRANE FOR HYDROGEN PURIFICATION FROM COAL-DERIVED SYNGAS," discloses a membrane for purifying hydrogen gas. The membrane structure comprises a support layer and a selective layer. The selective layer comprises hydrophilic polymer crosslinked with aminosilane cross-linking agent.

10 US 9,718,031 B2, titled "COMPOSITE HOLLOW FIBER MEMBRANES USEFUL FOR CO₂ REMOVAL FROM NATURAL GAS," discloses a membrane for removing carbon dioxide (CO₂) from natural gas. The composite hollow fiber polymer comprises a porous core layer made of polyamide-imide polymer or polyetherimide polymer, and a selective sheath layer made of polyimide polymer. Covalent ester crosslinks are also used.

15 Although there are mentions of composite membranes for carbon dioxide separation whose membrane structures contain polymer components in both the support layer and the selective layer, no prior art with the same composition and properties as this invention has been found. The flat sheet composite membrane for carbon dioxide separation according to the present invention comprises a support layer made of thermoplastic polymer and a selective layer made
20 of a block copolymer and is suitable for removing carbon dioxide from natural gas. The membrane of the present invention can provide a carbon dioxide gas permeability greater than 6 Barrer and a CO₂/CH₄ separation factor greater than 20. It can also be used under conditions with a CO₂ partial pressure above 18 barg, from a total pressure of 45 barg. This type of membrane is resistant to water vapor up to 1,700 ppm at a test temperature of 35°C. It has been
25 tested and shown to maintain a stable CO₂/CH₄ separation factor, even when the feed gas contains benzene or toluene at concentrations of 4,000 ppm and 1,160 ppm, respectively.

SUMMARY OF THE INVENTION

The present invention relates to a composition for forming a flat sheet composite membrane for carbon dioxide separation. Said membrane comprises a thermoplastic polymer
30 support layer having a porous structure. The surface of the support layer is coated with a block copolymer selective layer, to which an inorganic filler may be added. Said selective layer is crosslinked with 2,4-toluene diisocyanate (TDI) solution in hexane. A method for preparing said

membrane comprises preparing carbon dioxide-selective layer by dissolving a block copolymer in a mixture of ethanol and water and mixing until the solution becomes homogeneous. The obtained solution is then coated onto the support layer, dried, crosslinked, and then immersed in 2,4-toluene diisocyanate solution in hexane. The membrane is then washed with water, immersed
5 in water, and dried.

An object of the present invention is to produce a flat sheet membrane for carbon dioxide separation which is suitable for removing carbon dioxide from natural gas in conditions with high carbon dioxide content and demonstrates resistance to water vapor and heavy hydrocarbons, which are common impurities in natural gas. This reduces maintenance issues, particularly the
10 removal of water or heavy metals from the membrane, thereby lowering costs and extending the membrane's service life.

DETAILED DESCRIPTION

The present invention relates to a flat sheet membrane for carbon dioxide separation and a method for preparing said membrane. The embodiments of the invention will now be described
15 hereinafter.

Any aspects shown herein shall encompass application to other aspects of the present invention, unless stated otherwise.

Technical or scientific terms used herein have the meanings as understood by those skilled in the art, unless stated otherwise.

Any tools, equipment, methods, or chemicals mentioned herein shall refer to tools, equipment, methods, or chemicals commonly practiced or used by those skilled in the art, unless
20 expressly stated to be special or specific tools, equipment, methods, or chemicals for the present invention.

The following illustrates the detailed description without an intention to limit the scope
25 of the invention.

The present invention relates to the flat sheet membrane for carbon dioxide separation and the method for preparing said membrane. The membrane for carbon dioxide separation comprises a thermoplastic polymer support layer coated with a carbon dioxide-selective layer, which is a block copolymer with a concentration between 5-15% by weight which is crosslinked
30 with 2,4-toluene diisocyanate (TDI) in 2-3% by volume of hexane.

In an aspect, the thermoplastic polymer is selected from any one of polyetherimide, polyimide, or a mixture thereof.

In another aspect, the block copolymer is selected from polyether-polyamide block copolymer with a weight ratio of polyethylene oxide to polyamide of 60:40 in a polymer structure. The trade name of the block copolymer is Pebax 1657.

5 In another aspect, the carbon dioxide-selective layer comprises an inorganic filler to enhance its strength and separation capability. The inorganic filler is selected from any one of layered double hydroxides (LDH), graphene oxide (GO), or a mixture thereof.

The method for preparing the flat sheet membrane for carbon dioxide separation comprises the following steps:

- 10 a. preparing a thermoplastic polymer support layer, which is polyetherimide, by dissolving polyetherimide in a polymer solvent, 1-methyl-2-pyrrolidinone, at a concentration of 10-30% by weight, by mixing and heating at a temperature of 50-70°C for 12-24 hours until the solution becomes homogeneous.
- b. degassing the solution obtained in step a. using an ultrasonic cleaner for 15-30 minutes.
- 15 c. placing a polyester non-woven fabric on a glass plate to serve as a support layer in a formation of the support layer before coating the polyester non-woven fabric with the solution from step b. using an automatic film coater with a thickness of 0.2-0.3 mm and a coating speed of 1.6-1.7 cm/s.
- d. after coating the film in step c., allowing the film to rest for 2-5 minutes before
20 immersing it in water for 12-24 hours and then drying the film at a temperature of 50-70°C for 12-24 hours to obtain a support layer with a thickness of 150-250 μm .
- e. preparing a carbon dioxide-selective layer by dissolving a block copolymer in a mixture of ethanol and water to obtain a block copolymer solution with a concentration of 5-15% by weight, and mixing and heating the solution at a
25 temperature of 50-70°C until it becomes homogeneous.

In another aspect, the block copolymer is polyether-polyamide block copolymer with a weight ratio of polyethylene oxide to polyamide of 60:40 in a polymer structure. The trade name of the block copolymer is Pebax 1657.

In another aspect, a ratio of the mixture of ethanol and water is 60-80 to 20-40.

- 30 f. coating the solution obtained from step e. onto the support layer from step d., which is thermoplastic polymer, and drying it at a temperature of 50-70°C for 12-24 hours to obtain a membrane for carbon dioxide separation.

In an aspect, the thermoplastic polymer is selected from any one of polyetherimide, polyimide, or a mixture thereof.

- g. crosslinking the product obtained from step f. by immersing it in 2,4-toluene diisocyanate in 2-3% by volume of hexane for 30-60 minutes.
- h. washing the crosslinked membrane from step g. with water for 10-20 minutes and immersing it in water for 1-2 hours and drying it at a temperature of 50-70°C for 12-24 hours to obtain a membrane for carbon dioxide separation with a thickness of 200-300 μm .

The invention will be described hereinafter by way of examples for a clearer understanding. However, the flat sheet membrane for carbon dioxide separation which will be mentioned hereinafter is merely an example, which is intended to facilitate understanding of the invention and is not to be construed as limiting the scope of the invention to the examples.

Example 1: Test results of gas separation performance

For the separation of carbon dioxide in a molar ratio of methane to carbon dioxide of 60:40, the crosslinked membrane can be used at a temperature of 35°C under a high pressure of 45 bar, with a separation factor of carbon dioxide to methane in the range of 20-30 and a carbon dioxide permeability through the membrane in the range of 6-10 Barrer. This type of membrane is resistant to water vapor up to 1,700 ppm and is resistant to conditions where gases are contaminated with benzene or toluene at 4,000 ppm and 1,160 ppm. The details are shown in Tables 1-4.

Table 1 shows the crosslinking conditions and the results of the carbon dioxide separation test, conducted with a molar ratio of methane to carbon dioxide gas of 60:40 at a temperature of 35°C under a high pressure of 45 bar.

Membrane code	Crosslinking condition		Test result	
	Concentration by volume of crosslinking agent	Crosslinking time (min)	Separation factor	Carbon dioxide permeability (Barrer)
Pebax	-	-	17.79 $\pm$ 0.03	137.45 $\pm$ 0.04
CL-Pebax-3.00-60	3.00	60.00	28.17 $\pm$ 0.44	6.55 $\pm$ 0.01
CL-Pebax-2.21-38	2.21	38.40	20.30 $\pm$ 0.98	10.02 $\pm$ 0.30
CL-Pebax-2.17-60	2.17	60.00	22.20 $\pm$ 3.13	8.33 $\pm$ 1.77

Table 2 shows the crosslinking conditions and the results of the carbon dioxide separation test, conducted with a molar ratio of methane to carbon dioxide of 60:40 and a water vapor concentration of 1,680 ppm at a temperature of 35°C under a pressure of 25 bar.

Membrane code	Separation factor		Carbon dioxide permeability (Barrer)	
	Without water vapor	Water vapor*	Without water vapor	Water vapor*
Pebax	18.34±0.02	18.20±0.08	125.09±0.23	122.78±0.43
CL-Pebax-3.00-60	32.62±0.45	29.4±0.01	6.92±0.01	5.38±0.00
CL-Pebax-2.21-38	27.36±0.33	25.59±0.05	12.26±0.01	7.71±0.02
CL-Pebax-2.17-60	27.96±0.29	28.74±0.01	10.14±0.01	7.52±0.02

*Saturated water vapor at a pressure of 25 bar, temperature of 30°C, and a concentration of 1,680 ppm

Table 3 shows the crosslinking conditions and the results of the carbon dioxide separation test, conducted with a molar ratio of methane to carbon dioxide gas of 60:40 and a benzene-contaminated gas with a concentration of 4,000 ppm at a temperature of 35°C under a pressure of 25 bar.

Membrane code	Separation factor		Carbon dioxide permeability (Barrer)	
	Without benzene	Benzene*	Without benzene	Benzene*
Pebax	22.07±0.86	17.07±0.16	94.47±0.53	165.22±0.36
CL-Pebax-3.00-60	32.45±0.24	26.64±0.03	17.00±0.01	19.40±0.02
CL-Pebax-2.21-38	23.52±0.16	19.51±0.05	9.91±0.05	21.93±0.14
CL-Pebax-2.17-60	26.27±4.45	21.20±0.48	8.86±0.05	17.58±0.03

*Saturated benzene at a pressure of 25 bar, temperature of 20°C, and a concentration of 4,000 ppm

Table 4 shows the crosslinking conditions and the results of the carbon dioxide separation test, conducted with a molar ratio of methane to carbon dioxide gas of 60:40 and a toluene-contaminated gas with a concentration of 1,160 ppm at a temperature of 35°C under a pressure of 25 bar.

Membrane code	Separation factor		Carbon dioxide permeability (Barrer)	
	Without toluene	Toluene*	Without toluene	Toluene*
Pebax	20.62±0.01	15.80±0.06	66.65±0.07	118.05±0.28
CL-Pebax-3.00-60	30.22±0.87	25.92±0.32	23.80±0.09	24.02±0.16
CL-Pebax-2.21-38	24.21±0.29	21.73±0.25	8.79±0.03	23.88±0.02
CL-Pebax-2.17-60	27.58±1.29	26.88±0.71	12.57±0.04	15.61±0.07

*Saturated toluene at a pressure of 25 bar, temperature of 20°C, and a concentration 1,160 ppm

In addition, the method for preparing the flat sheet membrane for carbon dioxide separation further comprises an addition of an inorganic filler to the carbon dioxide-selective layer. The inorganic filler is selected from any one of layered double hydroxide (LDH) or graphene oxide (GO), with the amount limited to no more than 2.5% for LDH and 1.5% for GO by mass of the filler content in Pebax. The results of the separation capability are shown in Table 5.

Table 5 shows the results of the carbon dioxide separation test, conducted with a molar ratio of methane to carbon dioxide gas of 60:40 at a temperature of 35°C under a pressure of 25-45 bar, for a membrane containing layered double hydroxide (LDH) or graphene oxide (GO).

Membrane code	Separation factor			Carbon dioxide permeability (Barrer)		
	25 bars	35 bars	45 bars	25 bars	35 bars	45 bars
Pebax	19.81±0.19	18.26±0.20	16.84±0.09	61.62±0.16	68.84±0.19	66.70±0.16
1.5% GO/Pebax	19.03±0.10	17.40±0.17	15.97±0.02	88.67±0.21	94.43±0.10	93.21±0.02
2.5% LDH/Pebax	19.10±0.09	17.02±0.07	15.21±0.00	57.78±0.10	56.47±0.14	58.95±0.12
CL-Pebax*	32.45±0.24	-	28.17±0.44	23.80±0.09		6.55±0.01
CL-1.5%GO/Pebax*	-	-	23.82±0.06	-	-	6.40±0.00
CL-2.5%LDH/Pebax*	-		21.10±0.06	-	-	3.05±0.00

*Crosslinked with a crosslinking agent concentration of 3% by volume for 60 minutes

The addition of the filler has been found to effectively enhance separation efficiency under low-pressure conditions (< 20 bar). For example, a composite membrane made of Pebax with added inorganic filler, prepared using a polysulfone support layer and tested at 10 bar, exhibited a 6.70% increase in the separation factor of carbon dioxide to methane and a 19.95% increase in the permeability of carbon dioxide through the membrane compared to a membrane

without inorganic filler. However, under high-pressure conditions, it was found that polymer crosslinking is required to obtain a separation factor of carbon dioxide to methane in the range of 20-25, but the carbon dioxide permeability through the membrane decreased to a range of 3-10 Barrer.

5 Any modification or change may be clearly understood and can be carried out by those skilled in the art within the scope and spirit of the present invention as shown in the appended claims.

BEST MODE OF THE INVENTION

Best mode of the invention is as described in the detailed description of the invention.

WHAT IS CLAIMED IS:

1. A flat sheet membrane for carbon dioxide separation, comprising a thermoplastic polymer support layer coated with a carbon dioxide-selective layer, which is a block copolymer with a concentration between 5-15% by weight which is crosslinked with 2,4-toluene diisocyanate (TDI) in 2-3% by volume of hexane.
2. The flat sheet membrane for carbon dioxide separation according to claim 1, wherein the thermoplastic polymer is selected from any one of polyetherimide, polyimide, or a mixture thereof.
3. The flat sheet membrane for carbon dioxide separation according to claim 1, wherein the block copolymer is a polyether-polyamide block copolymer with a weight ratio of polyethylene oxide to polyamide of 60:40 in a polymer structure.
4. The flat sheet membrane for carbon dioxide separation according to claim 1, wherein the carbon dioxide gas-selective layer further comprises an inorganic filler.
5. The flat sheet membrane for carbon dioxide separation according to claim 4, wherein the inorganic filler is selected from any one of layered double hydroxide, graphene oxide, or a mixture thereof.
6. A method for preparing a flat sheet membrane for carbon dioxide separation comprising the steps of:
 - a. preparing a thermoplastic polymer support layer, which is polyetherimide, by dissolving polyetherimide in a polymer solvent, 1-methyl-2-pyrrolidinone, at a concentration of 10-30% by weight, by mixing and heating at a temperature of 50-70°C for 12-24 hours until the solution becomes homogeneous;
 - b. degassing the solution obtained in step a. using an ultrasonic cleaner for 15-30 minutes;
 - c. placing a polyester non-woven fabric on a glass plate to serve as a support layer in a formation of the support layer before coating the polyester

- non-woven fabric with the solution from step b. using an automatic film coater with a thickness of 0.2-0.3 mm and a coating speed of 1.6-1.7 cm/s;
- d. after coating the film in step c., allowing the film to rest for 2-5 minutes before immersing it in water for 12-24 hours and then drying the film at a temperature of 50-70°C for 12-24 hours to obtain the support layer with a thickness of 150-250 μm;
- e. preparing a carbon dioxide-selective layer by dissolving a block copolymer in a mixture of ethanol and water to obtain a block copolymer solution with a concentration of 5-15% by weight, and mixing and heating the solution at a temperature of 50-70°C until it becomes homogeneous;
- f. coating the solution obtained from step e. onto the support layer from step d., which is thermoplastic polymer, and drying it at a temperature of 50-70°C for 12-24 hours to obtain a membrane for carbon dioxide separation;
- g. crosslinking the product obtained from step f. by immersing it in 2,4-toluene diisocyanate in 2-3% by volume of hexane for 30-60 minutes; and
- h. washing the crosslinked membrane from step g. with water for 10-20 minutes and immersing it in water for 1-2 hours and drying it at a temperature of 50-70°C for 12-24 hours to obtain a membrane for carbon dioxide separation with a thickness of 200-300 μm.
7. The method for preparing a flat sheet membrane for carbon dioxide separation according to claim 6, wherein a ratio of the mixture of ethanol and water is 60-80 to 20-40.
8. The method for preparing a flat sheet membrane for carbon dioxide separation according to claim 6, wherein step a. further comprises adding an inorganic filler to the carbon dioxide-selective layer.
9. The method for preparing a flat sheet membrane for carbon dioxide separation according to claim 8, wherein the inorganic filler is selected from any one of layered double hydroxide, graphene oxide, or a mixture thereof.

10. The method for preparing a flat sheet membrane for carbon dioxide separation according to claim 6, wherein water in step d. is deionized water.