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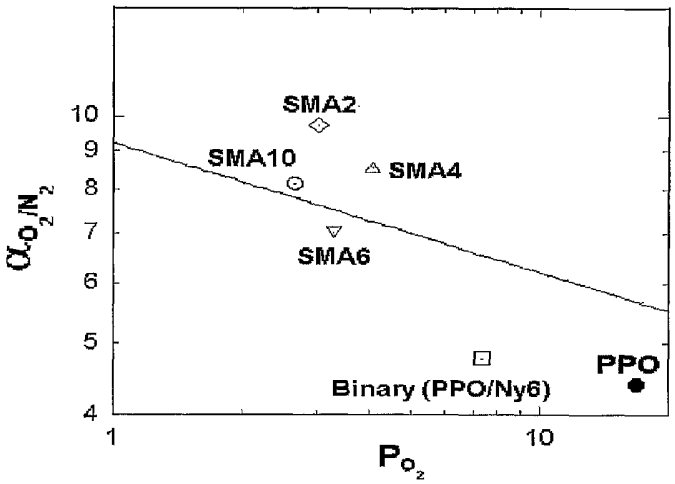
(54) Title: POLYMERIC COMPOSITE SEPARATION MEMBRANE



(57) Abstract: Semi-crystalline polymer blended gas or chemical separation membranes are obtained by melting and processing 50-99 wt % of a thermoplastic resin, 1-50 wt% of a semi-crystalline polymer and 0.1-10 wt % of a compatibilizer. A method for fabricating semi-crystalline polymer blended gas or chemical separation membrane includes the steps of: mixing 50-99 wt % of thermoplastic resin, 1-50 wt% of semi-crystalline polymer and 0.1-10 wt % of compatibilizer; and axially drawing the resulting blend melt coming from an extrusion die. The separation membrane exhibits high selectivity when applied in a gas separation process exceeding the limit value which has been seldom overcome by the existing separation membranes as well as high permeability enough to be applied in real gas separation processes. This enhanced selectivity is ascribed to the morphology of the ternary blends and different interaction between the compatibilizer and diffusing molecules. The membrane prepared by this method can be used for chemical separation processes (such as reverse osmosis, artificial kidney, artificial lung, drug delivery, drug release, to name a few) as well as liquids and gas separation processes.

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Description

POLYMERIC COMPOSITE SEPARATION MEMBRANE

Technical Field

[1] The present invention relates to a polymeric composite separation membrane and its preparation method. The separation membrane of the present invention which is produced by blending an amorphous thermoplastic resin, a semi-crystalline polymer and a compatibilizer which controls the dispersion state of the semi-crystalline polymer in the thermoplastic resin and adhesion at the interface, and then by preparation of a thin film of the blended mixture which is capable of increasing a selective permeation rate in such a manner that the dispersed semi-crystalline polymer is morphologically altered to serve as an obstacle to permeation, by which the permeation distance of the chemicals (liquid or gases) is extended. When applied to a gas separation process, this enhances the selective permeability over the so-called trade-off limit. More particularly, a semi-crystalline polymer which is hardly permeable to a gas or chemicals is dispersed in an amorphous thermoplastic resin, and at this time, an appropriate amount of compatibilizer is added so as for the semi-crystalline polymer to have a uniform size and well dispersed state, and then, the mixture obtained from the extruder is passed through a die as a thin film, whereby, the semi-crystalline polymer phase evenly dispersed and morphologically controlled in the film works as an obstacle to diffusion of chemicals or gases, to thereby morphologically altering path length of permeants. The chemicals or gases are separated according to interaction difference between the compatibilizer and permeant mole cules, which induces diffusion time difference during which they pass the deformed path by the diffusion constant difference depending on the size of the chemicals or gas molecule and the interaction with the compatibilizer, thereby exhibiting a highly superior selectivity.

Background Art

[2] Polymeric separation membranes are used for various separation processes which are technologically important such as liquids separation, drug delivery, drug release, artificial kidney and lung, separation of air, separation of carbon dioxide from a natural gas, or separation of nitrogen and oxygen or separation of hydrocarbon and hydrogen in a petrochemical process.

[3] In the gas separation process, the basic factors determining the separation performance of polymeric gas separation membranes for a pair of gases (i.e., oxygen/nitrogen, carbon dioxide/methane or hydrogen/nitrogen, etc.) are permeability constant and selectivity. Permeability constant is typically obtained by dividing the multiplied

value of a gas concentration difference and the thickness of separation membrane by a pressure difference of both sides of the separation membrane. Selectivity is a ratio of permeability of two gases. That is, when the selectivity ratio is represented by A/B, 'A' is the permeability of high permeable gas and 'B' is the permeability of low permeable gas.

[4] High performance separation membranes are desired to have a high permeability and a high selectivity, because a high permeability allows to reduce an area of separation membranes required for separating a certain amount of gas or chemicals and a high selectivity allows to enhance the purity of a product.

[5] However, generally, if the separation membranes have a high permeability, it has a low selectivity, whereas if a separation membrane has a high selectivity, it has a low permeability.

[6] According to Robeson's observation, as to separation of several pairs of gases, most polymer separation membranes have a negative slope in the correlation between the selectivity and the permeability (Journal of Membrane Science, Vol. 62, 165, 1991, USA). That means the selectivity is reduced as the permeability is increased.

[7] In addition, upon observation of performance of numerous polymer separation membranes, it has been revealed that most of the polymer separation membranes do not exhibit a performance higher than a certain level. That is, for each permeability, there exists an upper limit of the selectivity, along which an inversely proportional relation exists between the selectivity and the permeability all the time. The reason why such an upper limit exists is a natural result as the hard chains of a glass phase polymer substance screen the gas molecules. The slope of the upper limit has no relation to a chemical structure of the polymer separation membranes.

[8] For the past 30 years, in order to simultaneously increase the selectivity and the permeability, most researchers in the separation membrane industrial field have exerted their energy on synthesizing novel polymers (for example, US Patent No. 5,725,633). However, though many researches have been conducted, there has been no report on polymeric gas-separation membranes having a performance exceeding the existing upper limit. Very recently, we could make a polymeric- composite gas-separation membrane that has a selectivity going over the upper limit(U.S. Patent 6,517,606B2). In that case, the permeability of the prepared composite membrane was rather low to be practically used for the gas separation process, though.

[9] The present invention is directed to a fabrication process of a polymeric gas (or chemicals) separation membrane that can overcome the upper limit on the basis of a novel concept of a polymer composite instead of synthesizing a new polymeric material. Prepared membrane has the permeability high enough to be applied for real processes.

Disclosure of Invention

Technical Problem

[10] Therefore, an object of the present invention is to provide a process for fabricating a blend allowing a uniform dispersion and having an improved interface adhesion by adding a semi-crystalline polymer to an amorphous thermoplastic resin and at the same time, adding a compatibilizer so that the compatibilizer works at the interface of the semi-crystalline polymer and the thermoplastic resin to lower the interfacial tension, to provide a process for fabricating membranes with a desired thickness by performing extrusion and drawing, and to produce polymeric gas- or chemical separation mem branes exhibiting a high selectivity in such a manner that almost impermeable semi-crystalline polymer uniformly dispersed in the film is formed in a thin and long plate type, working as an obstacle to a chemical or gas permeation to change a curvature for a diffusing molecules so that they pass through the channel at the interface where the compatibilizer is located and the mixed molecules are separated because of the interaction difference with the compatibilizer.

[11] Another object of the present invention is to optimize dispersion of a semi-crystalline polymer by using an optimum amount of the compatibilizer.

[12] Still another object of the present invention is to utilize a drawing process, for fabricating thin film membranes to let the dispersed phase have a different axial ratio.

[13] Yet another object of the present invention is to provide a method for fabricating a semi-crystalline polymer blended high-selective gas separation membranes.

[14] Still yet another object of the present invention is to provide a method for separating a gas or chemicals in liquid state by using the semi-crystalline polymer blended high selective separation membranes. For liquids separation process, the liquids do not dissolve the membrane or its components.

Technical Solution

[15] To achieve these and other advantages and in accordance with the purpose of the present invention, as embodied and broadly described herein, there is provided a semi-crystalline polymer blended gas separation membrane obtained by melting and processing a 50~99 wt % of thermoplastic resin, 0.9~50 wt % a semi-crystalline polymer and 0.1~10 wt % of compatibilizer for the semi- crystalline polymer and the amorphous (or very low crystalline) matrix polymer.

[16] To achieve the above objects, the method for fabricating semi-crystalline polymer blended separation membranes is provided, including the steps of : mixing a 50~99 wt % of thermoplastic resin, 0.9~50 wt % semi-crystalline polymer and 0.1~10 wt % of compatibilizer; and injecting the resulting mixture in an extrusion die and extend coming out film to fabricate an axially oriented film.

[17] The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when the accompanying drawings are taken into consideration.

Advantageous Effects

[18] As will be described below, the thin semi-crystalline polymer blended gas separation membranes fabricated in accordance with the present invention have many advantages.

[19] For example, first, it exhibits the high selectivity exceeding the limit value, which has been hardly overcome by the existing separation membranes. Also, the permeability is high enough to be used in practical gas separation process.

[20] Secondly, as a separation membrane fabricating technique with a novel concept combining a physical method and a chemical method, since the whole process is performed in the extruder, it does not require a complicated process such as a solution casting method, a post-treatment process such as a solvent recovery and processing is not necessary, and it is also possible to make separation membranes in large scale.

[21] Thirdly, since it can be used between every crystalline polymer and thermoplastic resin as long as a suitable compatibilizer is available, it can be used to separate gases having different permeation rate from mixtures. It can also be used to separate liquid chemicals as long as they do not dissolve the membrane components.

Brief Description of the Drawings

[22] The accompanying drawings, which are included to provide a further understanding of the invention and constitute a part of this specification, illustrate embodiments of the invention and together with the description serve to explain the principles of the invention.

[23] In the drawings:

[24] Top row in Figure 1 includes photographs of a scanning electron microscope (SEM) of a section of a membrane generated in accordance with a preferred embodiment of the present invention, of which Figure 1A is a SEM figure of a membrane section generated by binary blend system of semi-crystalline polymer (nylon6, 20 wt%)/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO); Figure 1B is a SEM figure of a membrane section generated by ternary blend system of a semi-crystalline polymer (nylon6,20 wt%)/PPO/compatibilizer (2 wt%); Figure 1C is a SEM figure of a membrane section generated by ternary blend system of a semi-crystalline polymer (nylon6, 20 wt%)/PPO/compatibilizer (6wt%); and Figure 1D is a SEM figure of a membrane section generated by ternary blend system of a semi-crystalline polymer (nylon6, 20 wt%)/PPO/compatibilizer (10wt%)

[25] Bottom row in Figure 1 is a photograph of a transmission scanning electron

microscope (TEM) of a section of a membrane generated in accordance with a preferred embodiment of the present invention, of which Figure 1A is a TEM figure of a membrane section generated by binary blend of a semi-crystalline polymer(20 wt%)/PPO; Figure 1B is a TEM figure of a membrane section generated by ternary blend of a liquid crystalline polymer (20wt%)/ PPO/compatibilizer (2 wt%); Figure 1C is a TEM figure of a membrane section generated by a ternary blend of a liquid crystalline polymer (20wt%)/PPO/compatibilizer (6wt%); Figure 1D is a TEM figure of a membrane section generated by a ternary blend of a liquid crystalline polymer (20 wt%)/PPO/compatibilizer (10wt%)

[26] Figure 2 shows the relationship of oxygen permeability and the N_2/O_2 selectivity of the membranes prepared by using the present invention method.

Best Mode for Carrying Out the Invention

[27] Reference will now be made in detail to the preferred embodiments of the present invention, examples of which are illustrated in the accompanying drawings.

[28] A semi-crystalline polymer blended high selective gas separation membrane of the present invention comprises a semi-crystalline polymer, an amorphous (or very low crystalline)thermoplastic resin and a compatibilizer.

[29] In the present invention, the semi-crystalline polymer is used in the amount of 0.9~50 wt %, preferably 5~25 wt %. All polymers containing some parts of crystalline phase can be used for the present invention, but the one having a high portion of crystalline phase, low melting point (preferably lower than 300°C), a lower melt viscosity than that of the matrix polymer (amorphous resin) at the processing temperature and conditions is more preferable.

[30] In the present invention, the amorphous thermoplastic resin is used in an amount of 50~99 wt %, and preferably, 75~95 wt % and it is preferred that it does not decompose at a process temperature not lower than the melting temperature of the semi-crystalline polymer. In this respect, a melt viscosity is preferred to be higher than that of the semi-crystalline polymer for better deformation of the dispersed phase, though not necessarily required. In the present invention, any commercial thermoplastic resin can be used. In this respect, according to a preferred embodiment of the present invention, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (a product of G.E. of USA), provided a favorable result.

[31] In the present invention, the compatibilizer is used in an amount of 0.1~10 wt %, preferably 0.1~5 wt %, and most preferably 1~2 wt %. The compatibilizer is positioned at the interface of the matrix resin and the semi-crystalline polymer, lowering the interfacial tension between the crystalline polymer and the matrix resin, improving dispersion, and strengthening the interfacial adhesion.

[32] Especially, it is preferred not to be decomposed at a process temperature of the semi-crystalline polymer and the matrix resin, to be positioned at the interface of the dispersed phase to lower the interfacial tension and accordingly evenly disperse the dispersed phase, and to improve the adhesion at the interface.

[33] A compatibilizer used in the present invention can be any compound giving compatibility to the matrix thermoplastic resin and the semi-crystalline polymer. For example, it can be a block copolymer, a graft polymer or a copolymer generated by interfacial reaction. According to the preferred embodiment of the present invention, as the compatibilizer, poly(styrene-co-maleic anhydride), provided a favorable result. It is well known that polystyrene forms a miscible blend with PPO and the amine end group of nylon 6 reacts with maleic anhydride. Thus the compatibilizer has a graft copolymer structure.

[34] A process for preparing the semi-crystalline polymer blended high selective gas separation membrane includes the steps of: a) mixing 50~99 wt % of an amorphous thermoplastic resin, 0.9~50 wt % of a semi- crystalline polymer, and 0.1~10 wt % of compatibilizer based on the thermotropic liquid crystalline polymer; b) after passing through the extrusion die, the flim was uni-(or bi-)axially drawn to produce an oriented composite film.

[35] The semi-crystalline polymer blended in a high-selective gas-separation membrane produced by the present invention works as an obstacle against the gas permeation, so that the gas molecules should pass around the dispersed crystalline phase where the compatibilizer resides, and accordingly, the gas molecules interact with the compatibilizer, and the distance for the gas molecules to diffuse out is considerably increased.

[36] The gas molecules are normally diffused through the path of a free volume of the amorphous thermoplastic resin. In this respect, the diffusion coefficient is different depending on the size of the gas molecules, and thus, the diffusion flux becomes different. As the distance along which the gas molecules pass is long, the diffusion flux between the gas molecules are differentiated, and due to the interaction with the compatibilizer, there is a difference in the distance that the gas molecules are diffused for the same time, resulting in a high selectivity.

[37] In the preparation method of the present invention, the mixing step may be performed by a general method, such as by using a twin screw extruder, single screw extruder and an internal mixer.

[38] The drawing step in the preparation method of the present invention is conducted in a tensile apparatus connected to the extrusion die. The drawing can be biaxial drawing using simultaneous extension or film blowing process, and the dispersed semi-crystalline phase has a stripe shape, of which a drawing ratio in the one axis direction

is higher than a drawing ratio in the other direction.

[39] When the film blowing process is applied, a dual mandrel of which outside and inside are rotated in the opposite direction may be used instead of the extrusion die so that the deformed semi-crystalline phase may be formed as a net shape. Or, a multilayer film composed of many layers may be fabricated by using a multilayer-co-extrusion die.

[40] The invention will be further illustrated by the following examples. It will be apparent to those having conventional knowledge in the field that these examples are presented only to explain the present invention more clearly, but the invention is not limited to the following examples.

Mode for the Invention

[41] As a semicrystalline polymer, a raw material, nylon 6 (Kolon 171, Korea) was used. As a matrix resin, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (a product of G.E. of USA) was used. As a compatibilizer, a random copolymer between styrene and maleic anhydride, poly(styrene-co-maleic anhydride), containing 7wt% of maleic anhydride was used.

[42] After nylon 6, PPO and the compatibilizer were dried in a vacuum oven at a temperature of 100℃ for more than 24 hours, they were premixed with the ratio in Table 1. The resulting mixture was then extruded at a process temperature of 240℃ in a Bravender twin screw extruder. It is well known that polystyrene is miscible with PPO and amine group of nylon 6 reacts with maleic anhydride group very well. Thus while mixed and blended in the extruder, the random block copolymer reacts with nylon 6 to form a graft copolymer. This graft copolymer should be located at the interface due to enthalpic and entropic interaction with the matrix (PPO) and the dispersed phase (nylon 6). Polystyrene section of the compatibilizer would be in the matrix side while grafted polyamide parts reside in the dispersed nylon 6 phase. Thus, interfacial adhesion is enhanced while the interfacial tension between those two phases is significantly reduced.

[43] A flat die was connected to an exit of the twin screw extruder and the blend was subjected to an extension with a drawing unit. The extension ratio was adjusted with the rate of the winding speed to obtain a thin film of a uniform thickness. After then the film was wound. A film with an even thickness of 100 mm having 3% error limit was used.

[44] After the film samples were installed in a testing container, and an absorption gas was discharged under a high vacuum (10^{-6} torr) before measuring a permeation rate. In the testing apparatus, an isometric method was used in which a pressure increase in the opposite side of a side where a pressure was not applied was measured. The related

process is described in detail in ASTM D1434-82.

[45] Experiment was performed for the separation of oxygen and nitrogen which are most difficult to separate among the gases. The reason for this is that kinetic diameters of oxygen molecule and nitrogen molecule are respectively 3.46 and 3.64Å having little difference each other. The feasibility of this mechanism can be confirmed by measuring the permeability of CO_2 (Pco_2) and the selectivity of $\alpha_{CO2/N2}$. In the experiment, the upstream pressure was 1 atm and the temperature was maintained at 35℃.

[46] In order to compare the separation capability of the three-component blend film of the present invention and a simple film (a test sample 2) made under the same condition but by mixing only two components, i.e., PPO and semi-crystalline polymer (nylon 6) without using the compatibilizer, the respective permeability and selectivity of ternary blend film were also measured. The results are shown as follows in Table 1.

[47] Table 1

Permeabilities and selectivities at 35℃						
No.	Films	P_{O2}(Barrer)[(a)]	P_{N2}(Barrer)	P_{CO2}(Barrer)	$\alpha(P_{O2}/P_{N2})$	$\alpha(P_{CO2}/P_{N2})$
1	PPO	16.8	4.1	61	4.4	14.4
2	PPO/NY(20%)	7.32	1.53	24.8	4.77	16.15
3	PPO/NY(20%) /PSMA(2%)	3.02	0.309	12.0	9.75	38.7
4	PPO/NY(20%) /PSMA(4%)	4.06	0.474	17.0	8.56	35.87
5	PPO/NY(20%) /PSMA(6%)	3.29	0.469	12.9	7.01	27.43
6	PPO/NY(20%) /PSMA(10%)	2.65	0.325	11.1	8.15	34.22

[48] (a) 1 Barrer=$10^{-10}$$cm^3$(STP)cm/($cm^2$s cmHg)

[49] In case that a film is fabricated by adding the semi-crystalline polymer into PPO, though the permeation rate was a little bit reduced due to the addition of the crystalline phase having less free volume, its selectivity was increased.

[50] The results of ternary blend system depend on the amount of the compatibilizer.

[51] When 2 wt % of compatibilizer was added (test sample 3), as shown in Figure 1B, the semi-crystalline polymer (nylon 6) was uniformly and finely dispersed in the

matrix resin, PPO. Its size was remarkably reduced. Though the permeation rate was reduced, the selectivity was significantly increased. The selectivity at this time exhibits a higher value than a limit value of the existing separation membranes (See Figure 2).

[52] Meanwhile, in case that an excessive amount of compatibilizer was added (test sample 4 and 5), the selectively was rather decreased. This difference results from the fact that, as shown in Figures 1B, in case that a suitable amount of compatibilizer is introduced, the size of the dispersion phase was rapidly reduced compared to the case of the binary system and was evenly dispersed, while, as shown in Figures 1C and 1D, if the compatibilizer is added in an excessive amount, it forms its own phase as well as surrounding the periphery of the dispersed phase, and accordingly, the dispersed phase is coagulated.

[53] In case of the three component blend (sample 3) showing the uniform dispersion, as aforementioned, the permeating gas molecules should pass the boundary portion of the impermeable semi-crystalline polymer, of which the distance is proportionate to the square root of the number of dispersed phase, being far more lengthened. The path around the semi-crystalline polymer is occupied by the compatibilizer, which interacts differently for different gas molecules (oxygen and nitrogen).

[54] Accordingly, the small difference of diffusion constant ends in a large difference of the permeation rate of oxygen and nitrogen while the gas molecules pass the long distance receiving different interactions from the compatibilizer, resulting in that oxygen comes easily, and thus, high permeation rate and selectivity of oxygen are obtained. This is similar to the separation principle of a gas chromatography.

[55] On the other hand, in case that an excessive amount of compatibilizer was introduced, the path length is reduced due to the coagulation of dispersed phase and the interaction with the compatibilizer also decreased, resulting in lowering of the selectivity. When excessive amount of the compatibilizer was added they form their own phase and the selectivity was increased slightly because the selectivity of the film made of solely compatibilizer for O_2/N_2 pair is relatively high.

[56] In the present invention, PPO was used as a matrix, mixed with a polyamide (nylon 6), to which a random block copolymer of styrene and maleic anhydride was added as the compatibilizer, thereby fabricating the extended film after die exit. In view of the morphology of the extended film, the dispersed phase and the interfacial adhesion were confirmed by the electronic microscopy. In addition, by separating oxygen and nitrogen, which are the most difficult to be separated as their molecular sizes are similar, the performance of the film was measured.

[57] The feasibility of this mechanism can be confirmed by measuring the permeability of CO_2 (Pco_2) and the selectivity of $\alpha_{CO2/N2}$. The results are shown in Table 1. The behavior of Pco_2 and $P_{CO2/N2}$ vs Pco_2 follows exactly that of Po_2 and $\alpha_{O2/N2}$. Addition of

the semi-crystalline Ny6 phase into PPO (binary blend film) decreases Pco_2 compared to that of PPO film whereas it increases the selectivity $\alpha_{O2/N2}$ a little bit. The selectivity of the ternary blend film containing 2wt% PSMA shows a remarkable increase. Though the permeability has been decreased a little bit, the selectivity increased more than twice of that of the binary blend film. Permeability of this film is high enough (12 Barrer) to be used for the removal of CO_2. Addition of more compatibilizer leads to coalescence of dispersed Ny6 phase(Fig.1). Then, the selectivity $\alpha_{O2/N2}$ decreased while the permeability Pco_2 increased. Further addition of PSMA results in the formation of PSMA own phase. High selectivity of PSMA ($\alpha_{O2/N2}$ of PSMA is 34.64) and low permeability compared to that of PPO (Pco_2 of PSMA is 10.8) bring in lower Pco_2 and high $\alpha_{O2/N2}$. After each passage through the compatibilizer around a dispersed phase, the concentration of CO_2 would go up and up and high selectivity is achieved. This result confirms the role of the compatibilizer acting as an organic molecular sieve for selection of gas molecules.

[58] As so far described, the thin semi-crystalline polymer blended gas separation membranes fabricated in accordance with the present invention have many advantages.

[59] For example, first, it exhibits the high selectivity exceeding the limit value, which has been hardly overcome by the existing separation membranes. Also, the permeability is high enough to be used in practical gas separation process.

[60] Secondly, as a separation membrane fabricating technique with a novel concept combining a physical method and a chemical method, since the whole process is performed in the extruder, it does not require a complicated process such as a solution casting method, a post-treatment process such as a solvent recovery and processing is not necessary, and it is also possible to make separation membranes in large scale.

[61] Thirdly, since it can be used between every crystalline polymer and thermoplastic resin as long as a suitable compatibilizer is available, it can be used to separate gases having different permeation rate from mixtures. It can also be used to separate liquid chemicals as long as they do not dissolve the membrane components.

[62] Through the present inventors used a single extruder for a monolayer film, it can be extended to multiple layer extruder. Also it can be easily modified to have a film-blowing die after extruder to produce a blown film. Also a pair of counter rotating mandrels for the extrusion die in the film blowing process can be adopted, hence to produce a membrane in which the dispersed crystalline phases are declined to 45° with each other (inside and outside).

[63] As the present invention may be embodied in several forms without departing from the spirit or essential characteristics thereof, it should also be understood that the above-described embodiments are not limited by any of the details of the foregoing description, unless otherwise specified, but rather should be construed broadly within its

spirit and scope as defined in the appended claims, and therefore all changes and modifications that fall within the metes and bounds of the claims, or equivalence of such metes and bounds are therefore intended to be embraced by the appended claims.

Industrial Applicability

[64] Here we applied the idea of present invention to prepare a polymer composite film for the gas separation. However, it can be easily applied to any membranes used in the chemical mixture separation process such as reverse osmosis, drug delivery, drug release, artificial kidney, and artificial lung to name a few as well as liquids separations. Thus any separation process using the composite polymer film of this invention should also be embraced by the appended claims.

Claims

[1] Polymer blended mixture comprising
50~99 wt% of an amorphous (or low crystalline) thermoplastic resin selected from the group consisting of polyethylenepropylendienterpolymer, poly(1-(trimethylsilyl)-1-propyne), amorphous nylon, polystyrene and polycarbonate;
0.9~50 wt% of a semi-crystalline polymer selected from the group consisting of polyamide(nylons), polyethylene terephtalate, polybuthylene terephtalate, polyethylene, polypropylene, polyetheretherketone, polyvinylidene flouride, polytetraflouroethylene, polyphenylene sufide and thermotropic or lyotropic liquid crystal polymer; and
0.1~10 wt% of a compatibilizer consisting of block copolymer or graft copolymer having compatibility or gererated by interfacial reaction.

[2] Polymer blended mixute according to the claim 1, wherein the compatibilizer is selected from the group consisting of poly(styrene-co-maleic anhydride), random or block copolymer of styrene and maleic, polystyrene whose oxazoline group is substituted, amorphous polymer added with maleic anhydride group, and polycarbonate and polystyrene having reaction group.

[3] Polymer blended mixture according to the claim 1 or 2, the amount of the amorphous thermoplastic resin is 75-95wt%, the amount of the semi-crystalline polymer is 4.9-25wt% and the amount of the compatibilizer is 0.1-5wt%.

[4] Polymer blended mixture according to the claim 1 or 2, wherein the semi-crystalline polymer has low gas permeability irrespective of degree of crystallinity and is selected from the group consistng of polyamide(nylons), polyethylene terephtalate, polyethylene, polypropylene, polyetheretherketone, polyvinylidene flouride, polytetraflouroethylene, polyphenylene sulfide and thermotropic or lyotropic liquid crystal polymer.

[5] Polymer blended mixture according to the claim 1 or 2, wherein the compatibilizer is positioned at the interface between the thermoplastic resin and the semi-crystalline polymer, to lower an interfacial tension between the semi-crystalline polymer and the thermoplastic resin, improves the dispersion and strengthens the interfacial adhesion as well as interacts differently for different diffusing gas molecules, hence, changes the diffusion rate of each gas.

[6] A method for preparing a film from the polymer blended mixture claimed in claim 1 or 2 comprising the step of
forming a melt blend by mixing the theremoplastic resin, the semi-crystalline polymer and the compatibilizer and

axially drawing the melt blend obtained from step a) using an extension apparatus or film blowing apparatus connected to an extrusion die to fabricate a film

wherein a phase of the semi-crystalline polymer has a stripe shape in the film due to non-equal biaxial drawing, which means more extension in the vertical direction than in the horizontal direction.

[7] A film prepared by the method claimed in claim 6.

[8] A method according to claim 6, wherein dual mandrel of which inside and outside are rotated in the opposite direction is used as the extrusion die, so that a morphologically modified semi-crystalline phase is formed in a net shape.

[9] A film prepared by the method claimed in claim 8.

[10] A method according to claim 6, wherein multilayer film composed of many layer is fabricated by using a multiple coextrusion die.

[11] A film prepared by the method claimed in claim 10.

[12] A semi-crystalline polymer blended gas seperation membrane wherein the the compatibilizer positioned at the interface of the impermeable dispersed phase of the film claimed in claims 7, 9 or 11 has the different interaction with the different gases each other by which the permeability of the film is affected and thus the film has high seperation performance.

[13] A gas separation method using the separation membrane of the claim 12.

[14] Polymer blended mixture according to claim 1 or 2, amorphous crystalline polymer of the matrix resin has a high melting point than that of semi-crystalline polymer at the processing temperature.

[15] An oriented film prepared from the polymer blended mixture of the claim 14.

[16] Gas separation process using the film of the claim 15 as a seperation membrane.

[17] Polymer blended mixture according to claim 1 or 2, semi-crystalline polymer consists of one ingredient or one or more ingredients.

[18] One layer or multilayer thin film which is prepared from the polymer blended mixture of the claim 17.

[19] A method preparing the film of the claim 18 comprising the step of

forming a melt blend by mixing the theremoplastic resin, the semi-crystalline polymer and the compatibilizer and

axially drawing the melt blend obtained from step a) using an extension apparatus or film blowing apparatus connected to an extrusion die to fabricate a film

wherein a phase of the semi-crystalline polymer has a stripe shape in the film due to non-equal biaxial drawing, which means more extension in the vertical direction than in the horizontal direction.

[20] A method according to the claim 19, wherein dual mandrel of which inside and outside are rotated in the opposite direction is used as the extrusion die, so that a morphologically modified semi-crystalline phase is formed in a net shape.

[21] Polymer blended mixture according to the claim 17, amorphous crystalline polymer of the matrix resin has a high melting point than that of semi-crystalline polymer at the processing temperature.

[22] An oriented film prepared by the method of claim 17.

[23] A semi-crystalline polymer blended gas seperation membrane wherein the the compatibilizer positioned at the interface of the dispersed phase of the film claimed in claim 22 has the different interaction with the different gases each other by which the permeability of the film is affected and thus the film has high seperation performance.

[24] Gas seperation process using the film of the claim 23 as a seperation membrane.

[25] A polymer composite film for gas seperation wherein the semi-crystalline polymer of claim 1 or 2 has a thicness of nanometer.

[26] A film according to claim 7 or 15, wherein the dispersed phase is composed of inorganic materials (such as clay) and the film includes a compatibilizer for the matrix and the dispersed phase.

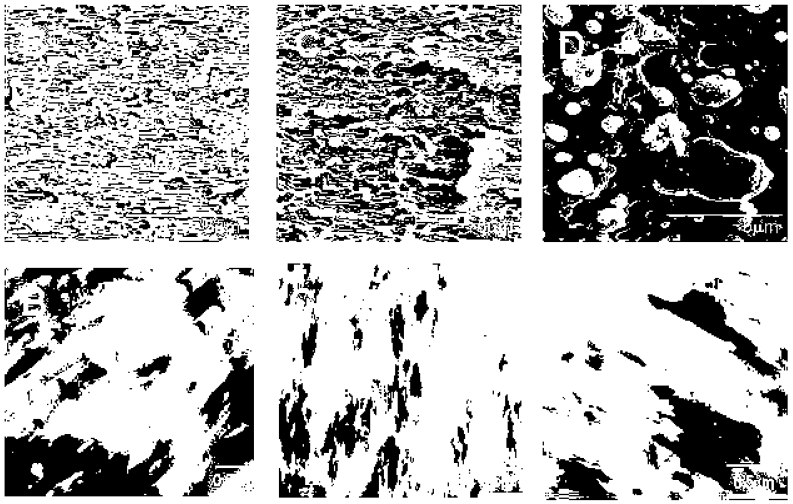
[27] Gas separation process using the film of the claim 26.

[28] Polymer blended mixture according to claims 1, 2 or 3, wherein the compatibilizer is positioned at the interface by reactiong with the matrix resin or the dispersed phase to form a copolymer.

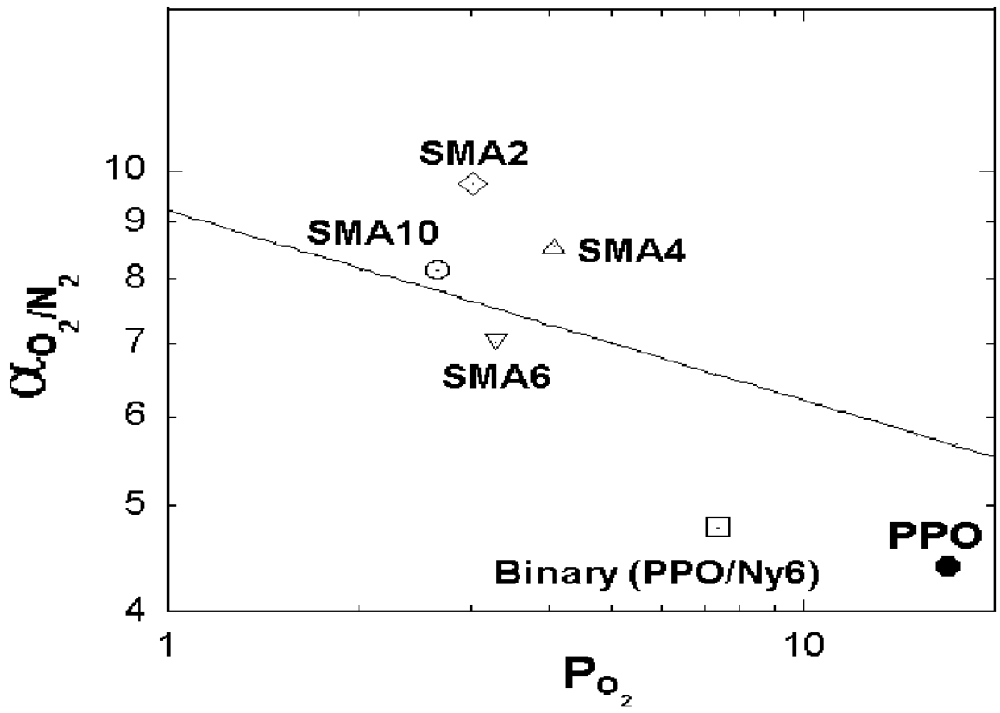
[29] A semi-crystalline polymer blended gas seperation membrane according to the claim 12, wherein the compatibilizer is positioned at the interface by reactiong with the matrix resin or the dispersed phase to form a copolymer.

[30] A film according to claim 21 or 26, wherein in case the matrix resin is PPO(poly(2,6-dimethyl-1,4-phenylene oxide) and the dispersed phase is polyamides, a random copolymer or a block copolymer of styrene and maleic anhydride is used.

[Fig. 1]



[Fig. 2]


SMA2
SMA10
SMA4
SMA6
Binary (PPO/Ny6)
PPO
10
9
8
7
6
5
4
1
10
α_{O_2/N_2}
P_{O_2}

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2005/000425

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C08J 5/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC7 C08J 5/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)
eKIPASS, SCOPUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6517606 B2 (Korea Institute of Science and Technology; Bionast Co. Ltd.) 11 Feb. 2003 See the whole document	1, 3-24, 28, 29
X	Chiang C. et al., "Polymer blends of polyamide-6 (PA6) and poly(phenylene oxide) (PPO) compatibilized by styrene-maleic anhydirde (SMA) copolymer", Polymer, 38(19), pp 4807-4817. 30 Sep. 1997 See the whole document	1, 2, 4, 5, 14, 17, 21, 28, 30
X	Wu D. et al., "Toughening of poly(2,6-dimethyl-1,4-phenylene oxide)/nylon 6 alloys with functionalized elastomer via reactive compatibilization: morphology, mechanical properties, and rheology", European Polymer Journal, 40, pp 1223-1232. 04 Feb. 2004 See the whole document	1, 2, 4, 5, 14, 17, 21, 28
A	Kelnar I. et al., "Compatibilization of PA6/PPO blend with carboxylated poly(styrene) compounds", Journal of Applied Polymer Science, 80(12), pp 2273-2280. 20 Jun. 2001 See abstract	1
A	JP 2000-2124347 A (Kuraray Co. Ltd.) 02 Aug. 2000 See abstract	1

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 JUNE 2005 (28.06.2005)	**28 JUNE 2005 (28.06.2005)**
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