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(54) Title: ASYMMETRIC COMPOSITE MEMBRANES AND MODIFIED SUBSTRATES USED IN THEIR PREPARATION

(57) **Abstract:** Asymmetric composite membranes consisting of a film of partially cross-linked poly(ethenol) (polyvinyl alcohol (PVA)) adhered to a hydrophilicitized microporous sheet of grafted polyolefin are disclosed. The microporous sheet is made hydrophilic by grafting of the polyolefin, e.g. poly(ethylene), with a preformed polymer of ethenylbenzenesulfonic acid before adherence of the film of partially cross-linked poly(ethenol). The asymmetric composite membranes are chlorine tolerant with high levels of protein and salt rejection making them particularly suitable for use in the extraction or recovery of water from feed streams in the beverage and food industries, including dairy.

ASYMMETRIC COMPOSITE MEMBRANES AND MODIFIED SUBSTRATES USED IN THEIR PREPARATION

FIELD OF INVENTION

The invention relates to a durable water permeable asymmetric composite membrane with high levels of protein rejection, and substrates for use in their preparation. In particular, the invention relates to a durable water permeable asymmetric composite membrane consisting of a film of partially cross-linked poly(ethenol) adhered to a hydrophilicitized microporous sheet of poly(ethylene).

BACKGROUND ART

It is well-known to use grafting to modify the surface of films, sheets and moulded objects formed from polyolefins. For example, the publication of Tazuke and Kimura (1978) discloses photografting onto poly(propylene), poly(ethylene) and several other polymer films using benzophenone as a sensitizer. In this publication the choice of solvent and sensitizer was noted to be very important.

The publication of Ang *et al* (1980) discloses an irradiation procedure where the sensitizer is dissolved in the monomer solution and can be used for the photosensitized copolymerization in high yields of styrene, 4-vinyl pyridine and methyl methacrylate to poly(propylene). Again, this publication notes that the reaction was found to be very specific to certain types of sensitizers.

The publication of Ogiwara *et al* (1981) discloses the photografting on poly(propylene) and low-density poly(ethylene) (LDPE) films on which sensitizers were coated beforehand. The sensitizers coated on films enabled vinyl monomers, such as methyl methacrylate, acrylic acid and methacrylic acid to graft easily with high yields. The hydrophilic monomers acrylic acid and methacrylic acid were conveniently grafted using them in aqueous solution in a liquid phase system.

The publication of Allmer *et al* (1988) discloses the modification of surfaces of LDPE, high-density poly(ethylene) (HDPE) and polystyrene by grafting with acrylic acid. The grafting is performed in the vapor-phase and increased the wettability of the polymer. It was observed that acetone was able to initiate grafting and was found to promote and direct grafting to the surface. The later publication of Allmer *et al* (1989) discloses the grafting of the surface of LDPE with glycidyl acrylate and glycidyl

methacrylate by photoinitiation. Acetone and ethanol were used as solvents, with acetone yielding slightly more grafting at the surface.

The publications of Yao and Ranby (1990a, 1990b and 1990c) disclose *inter alia* a process for the continuous photoinitiated graft copolymerization of acrylamide and acrylic acid onto the surface of HDPE tape film. The process is performed under a nitrogen atmosphere using benzophenone as the photoinitiator. It was noted that pre-soaking was very important for efficient photographing within short irradiation times. The application of this pre-soaking photografting method to poly(ethylene terephthalate) (PET) was also disclosed. In this context acetone was found to be a somewhat better solvent than methylethylketone and methylpropylketone. When applied to a continuous process for the photochemically induced graft polymerization of acrylamide and acrylic acid of poly(propylene) (PP) fibre surface under a nitrogen atmosphere, optimal concentrations of monomer and initiator in the pre-soaking solution were determined.

The publications of Kubota and Hata (1990a and 1990b) disclose an investigation of the location of methacrylic acid chains introduced into poly(ethylene) film by liquid and vapor-phase photografting and a comparative examination of the photografting behaviours of benzil, benzophenone and benzoin ethyl ether as sensitizers. In these latter studies poly(methacrylic acid) was grafted onto initiator-coated LDPE film.

The publication of Edge *et al* (1993) discloses the photochemical grafting of 2-hydroxyethyl methacrylate (HEMA) onto LDPE film. A solution phase method is used to produce a material with increased wettability.

The publication of Singleton *et al* (1993) discloses a method of making a polymeric sheet wettable by aqueous solvents and useful as an electrode separator in an electrochemical device. The polymeric sheet is formed from fibres which comprise poly(propylene) alone and is distinguished from a membrane formed from a microporous polymer sheet.

The publication of Zhang and Ranby (1993) discloses the photochemically induced graft copolymerisation of acrylamide onto the surface of PP film. Acetone was shown to be the best solvent among the three aliphatic ketones tested.

The publications of Yang and Ranby (1996a and 1996b) disclose factors affecting the photografting process, including the role of far UV radiation (200 to 300 nm). In these studies benzophenone was used as the photoinitiator and LDPE film as the substrate. Added water was shown to favour the photografting polymerisation of acrylic acid on the surface of

polyolefins, but acetone was shown to have a negative effect due to the different solvation of poly(acrylic acid) (PAA).

The publication of Hirooka and Kawazu (1997) discloses alkaline separators prepared from unsaturated carboxylic acid grafted poly(ethylene)-poly(propylene) fibre sheets. Again, the sheets used as a substrate in these studies are distinguished from a membrane formed from a microporous polymer sheet.

The publication of Xu and Yang (2000) discloses a study on the mechanism of vapor-phase photografting of acrylic acid onto LDPE.

The publication of Shentu *et al* (2002) discloses a study of the factors, including the concentration of monomer, affecting photo-grafting on LDPE.

The publication of El Kholdi *et al* (2004) discloses a continuous process for the graft polymerisation of acrylic acid from monomer solutions in water onto LDPE. The publication of Bai *et al* (2011) discloses the preparation of a hot melt adhesive of grafted low-density poly(ethylene) (LDPE). The adhesive is prepared by surface UV photografting of acrylic acid onto the LDPE with benzophenone as the photoinitiator.

The publication of Choi *et al* (2001) states that graft polymerisation is considered as a general method for modifying the chemical and physical properties of polymer materials.

The publication of Choi (2002) discloses a method for producing an acrylic graft polymer on the surface of a polyolefin article comprising the steps of immersing the article in a solution of an initiator in a volatile solvent, allowing the solvent to evaporate, and then immersing the article in a solution of an acrylic monomer before subjecting the article to ultraviolet irradiation in air or an inert atmosphere. Acrylic acid is used as the acrylic monomer in each one of the Examples disclosed in the publication, although the use of equivalent amounts of methacrylic acid, acrylamide and other acrylic monomers is anticipated.

The publication of Choi (2004) discloses the use of "ethylenically unsaturated monomers" in graft polymerisation. These other monomers are disclosed as monomers that are polymerizable by addition polymerisation to a thermoplastic polymer and are hydrophilic as a consequence of containing carboxyl (-COOH), hydroxyl (-OH), sulfonyl (SO_3), sulfonic acid ($-SO_3H$) or carbonyl (-CO) groups. No experimental results concerning the chemical and physical properties of graft polymers prepared by a method using these other monomers is disclosed.

The publication of Choi (2005) discloses a non-woven sheet of polyolefin fibres where opposed surfaces of the sheet are hydrophilic as a consequence of an acrylic graft polymerisation. The properties of the sheet are asymmetric, the ion exchange coefficient of the two surfaces being different. The method used to prepare these asymmetric acrylic graft polymerised non-woven polyolefin sheets comprises the steps of immersing the substrates in a solution of benzophenone (a photoinitiator), drying and then immersing the substrate in a solution of acrylic acid prior to subjecting to ultraviolet (UV) irradiation. The irradiation may be performed when the surfaces are in contact with either air or an inert atmosphere.

The publication of Gao *et al* (2013) discloses a method of preparing a radiation cross-linked lithium-ion battery separator. In an example, a porous polyethylene membrane is immersed in a solution of benzophenone and triallyl cyanurate in dichloromethane. The immersed membrane is dried at room temperature before being immersed in a water bath at 30°C and irradiated on both sides using a high-pressure mercury lamp for three minutes.

The publication of Jaber and Gjoka (2016) discloses the grafting of ultra-high molecular weight polyethylene microporous membranes using monomers having one or more anionic, cationic or neutral groups. The publication states that the authors have discovered that molecules can be grafted on the surface of an asymmetric, porous ultra-high molecular weight polyethylene membrane using an ultraviolet radiation energy source. The grafted membranes are proposed for use in removing charged contaminants from liquids.

The objective of the majority of these prior art methods is to improve the adhesion, biocompatibility, printability or wettability of the surface of a substrate using photoinitiated polymerisation. These methods are to be distinguished from the use of UV-initiated grafting with an exogenously prepared preformed polymer to modify the permeability to water of a hydrophobic microporous polyolefin substrate.

The publication of Bolto *et al* (2009) reviews what is disclosed in publications concerning the cross-linking of poly(ethenol), i.e. PVA. These publications include those concerning cross-linking methods and the grafting of PVA onto support membranes, including porous hydrophobic membranes such as poly(ethylene) and poly(propylene).

The publication of Linder *et al* (1988) discloses semipermeable composite membranes comprising a film of modified PVA or PVA-copolymers on a porous support. Suitable support materials are required to be water insoluble and may be chosen, e.g. from polyacrylonitriles, polysulfones, polyamides, polyolefins such as poly(ethylenes) and poly(propylenes), or cellulosics.

The publication of Exley (2016) discloses an asymmetric composite membrane consisting of a film of cross-linked poly(ether ether ketone) adhered to a sheet of grafted microporous poly(ethylene). The microporous poly(ethylene) is obtained by photoinitiated grafting with an ethenyl monomer to provide a hydrophilic sheet.

The publication of Craft *et al* (2017) discloses improvements in the asymmetric composite membranes disclosed in the publication of Exley (2016). The improved asymmetric composite membranes comprise of poly(vinyl alcohol) polymer crosslinked with a crosslinking agent (such as divinyl benzene) coated on a film of cross-linked poly(ether ether ketone) adhered to a sheet of the grafted microporous poly(ethylene). The improvement is in the selectivity of the asymmetric composite membrane obtained.

It is an object of the present invention to provide an asymmetric composite membrane with improved levels of protein rejection while maintaining an acceptable flux. It is an object of the present invention to provide a method to preparing the asymmetric composite membrane. It is an object of the present invention to provide a hydrophilicitized sheet of microporous polyolefin particularly suited for use in the method of preparing the asymmetric composite membrane. It is an object of the present invention to provide asymmetric composite membranes and hydrophilicitized sheets of microporous polyolefin adaptable for use in extracting or recovering water from feed streams in the beverage and food processing industries, including dairy. These objects are to be read in the alternative with the object at least to provide a useful choice in the selection of such methods, membranes and sheets.

STATEMENT OF INVENTION

In a **first** aspect the invention provides a hydrophilicitized microporous sheet of polyolefin where the microporous polyolefin has been grafted with a preformed poly(4-ethenyl benzene sulfonic acid).

Preferably, the polyolefin is selected from the group consisting of: poly(ethylene), poly(propylene), poly(butylene) and poly(methylpentene). More preferably, the polyolefin is poly(ethylene) or poly(propylene). Most preferably, the polyolefin is poly(ethylene).

Preferably, the preformed poly(4-ethenyl benzene sulfonic acid) is equivalent to that provided in the working solution prepared according to Example 1.

In a **second** aspect the invention provides an asymmetric composite membrane comprising a film of partially crosslinked poly(ethenol) adhered to a hydrophilicitized microporous sheet of polyolefin where the polyolefin has been grafted with a preformed poly(4-ethenyl benzene sulfonic acid) before adherence of the film of partially crosslinked poly(ethenol).

Preferably, the partially crosslinked poly(ethenol) is crosslinked to a degree in the range equivalent to that of the partially crosslinked poly(ethenol) provided in Vial 2 of Example 8 to that of the partially crosslinked poly(ethenol) provided in Vial 4 of Example 8. More preferably, the partially crosslinked poly(ethenol) is crosslinked to a degree substantially equivalent to that of the partially crosslinked poly(ethenol) provided in Vial 3 of Example 8.

Preferably, the polyolefin is selected from the group consisting of: poly(ethylene), poly(propylene), poly(butylene) and poly(methylpentene). More preferably, the polyolefin is poly(ethylene) or poly(propylene). Most preferably, the polyolefin is poly(ethylene).

In a preferred embodiment of the second aspect, the invention provides an asymmetric composite membrane consisting essentially of a film of partially crosslinked poly(ethenol) adhered to a hydrophilicitized microporous sheet of poly(ethylene) where the polyolefin has been grafted with a preformed poly(4-ethenyl benzene sulfonic acid) before adherence of the film of partially crosslinked poly(ethenol).

In a most preferred embodiment of the second aspect, the invention provides an asymmetric composite membrane consisting essentially of a film of partially crosslinked poly(ethenol) adhered to a hydrophilicitized microporous sheet of poly(ethylene) where the polyolefin has been grafted with a preformed poly(4-ethenyl benzene sulfonic acid) equivalent to that provided in the working solution prepared according to Example 1 before adherence of the film of partially crosslinked poly(ethenol) and the partially crosslinked poly(ethenol) is crosslinked to a degree substantially equivalent to that of the partially crosslinked poly(ethenol) provided in Vial 3 of Example 8.

An asymmetric composite membrane capable of providing at least 99.9% total protein rejection at a flux of 5 LMH with milk as a feed stream is provided.

In a **third** aspect the invention provides a method of preparing the hydrophilicitized microporous sheet of polyolefin of the first aspect of the invention comprising the steps of:

1. Contacting a microporous sheet of polyolefin with a dispersion comprising a preformed poly(4-ethenylbenzenesulfonic acid) in an aqueous solvent to provide a contacted microporous sheet;
2. Curing the contacted microporous sheet at a temperature and for a time sufficient for at least a portion of the poly(4-ethenylbenzenesulfonic acid) to be grafted onto the polyolefin substrate to provide a cured microporous sheet; and then
3. Washing the cured microporous sheet to provide the hydrophilicitized microporous sheet of polyolefin.

Preferably, the polyolefin is selected from the group consisting of: poly(ethylene), poly(propylene), poly(butylene) and poly(methylpentene). More preferably, the polyolefin is poly(ethylene) or poly(propylene). Most preferably, the polyolefin is poly(ethylene).

Preferably, the aqueous solvent is acetone-water.

Preferably, the curing the contacted microporous sheet is by irradiating with ultraviolet light at an intensity and at a temperature for a period of time sufficient for at least a portion of the poly(4-ethenylbenzenesulfonic acid) to be grafted onto the polyolefin.

Preferably, the irradiating is in the presence of a photoinitiator. More preferably, the irradiating is in the presence of a photoinitiator selected from the group consisting of: aceto-phenone, anthraquinone, benzoin, benzoin ether, benzoin ethyl ether, benzil, benzil ketal, benzophenone, benzoyl peroxide, n-butyl phenyl ketone, iso-butyl phenyl ketone, fluorenone, propiophenone, n-propyl phenyl ketone and iso-propyl phenyl ketone. Most preferably, the irradiating is in the presence of the photoinitiator benzophenone.

Preferably, the ultraviolet light has a broad spectrum centred on 250 nm and bandwidth limits of approximately 250 nm and 400 nm.

Preferably, the washing is with water.

In a preferred embodiment of the third aspect, the invention provides a method of preparing a hydrophilicitized microporous sheet of poly(ethylene) comprising the steps of:

1. Polymerising 4-ethenylbenzenesulfonic acid in the presence of a radical initiator to provide a first dispersion in a first solvent of a poly(4-ethenylbenzenesulfonic acid);
2. Contacting a microporous sheet of poly(ethylene) with a second dispersion in a second solvent of the poly(4-ethenylbenzenesulfonic acid) to provide a contacted microporous sheet of poly(ethylene);
3. Curing the contacted microporous sheet at a temperature and for a time sufficient for at least a portion of the poly(4-ethenylbenzenesulfonic acid) to be grafted onto the polyolefin substrate; and then
4. Washing the cured microporous sheet to provide the hydrophilicitized microporous sheet of poly(ethylene),

where the first solvent is water and the second solvent is acetone-water.

The 4-ethenylbenzenesulfonic acid may be provided in the form of a salt, e.g. as its sodium salt (SSS).

Preferably, the radical initiator is selected from the group consisting of: ammonium persulfate and sodium persulfate. More preferably, the radical initiator is sodium persulfate.

Preferably, the second solvent is 40 to 60% (v/v) acetone in water. Most preferably, the second solvent is 50% (v/v) acetone in water.

The second dispersion may be prepared by adding acetone to the first dispersion.

In a **fourth** aspect the invention provides a hydrophilicitized microporous sheet of polyolefin prepared according to the method of the third aspect of the invention.

In a **fifth** aspect the invention the invention provides a method of preparing the asymmetric composite membrane of the second aspect of the invention, comprising the steps of:

1. Contacting one side of the hydrophilicitized microporous sheet of the first or fourth aspect of the invention with a solution in a first solvent of partially cross-linked poly(ethenol) in the presence of a radical initiator to provide a contacted sheet;

2. Drying the contacted sheet at a temperature and for a time sufficient to allow the partially cross-linked poly(ethenol) to adhere to the one side of the hydrophilicitized microporous sheet of polyolefin and evaporate substantially all the solvent to provide a dried contacted sheet; and then

3. Washing the dried contacted sheet in a second solvent to provide the asymmetric composite membrane.

Preferably, the drying of the contacted sheet is by applying a positive thermal gradient across the thickness of the sheet from the contacted one side of the hydrophilicitized microporous sheet to the other side.

In the description and claims of this specification the following abbreviations, acronyms, terms and phrases have the meaning provided: "comprising" means "including", "containing" or "characterized by" and does not exclude any additional element, ingredient or step; "consisting of" means excluding any element, ingredient or step not specified except for impurities and other incidentals; "consisting essentially of" means excluding any element, ingredient or step that is a material limitation; "crosslinking agent" means a material that is incorporated into the crosslinking bridge of a cross-linked polymer network; "flux" means the rate (volume per unit of time) of permeate transported per unit of membrane area; "graft polymer" means a polymer in which the linear main chain has attached to it at various points side chains of a structure different from the main chain; "homopolymer" means a polymer formed by the polymerization of a single monomer; "hydrophilic" means having a tendency to mix with, dissolve in, or be wetted by water and "hydrophilicity", "hydrophilicitized" and "hydrophilicitizing" have a corresponding meaning; "microporous" means consisting of an essentially continuous matrix structure containing substantially uniform small pores or channels throughout the body of the substrate (such as may be manufactured using a cast (wet) process technology) and specifically excludes a discontinuous matrix of woven or non-woven fibres; "partially crosslinked" means that only a portion of the available sites for cross-linking are utilised and the cross-linking reaction has been limited by reagents, temperature or period of time; "photoinitiator" means a photolabile compound which upon irradiation forms a radical; "poly(ethanol)" and "polyvinyl alcohol" are used synonymously; "post-treated polymer" means a polymer that is modified, either partially or completely, after the basic polymer backbone has been formed; "preformed" means formed beforehand, i.e. prior to treatment; "PSSS" or "pSSS" denotes the product of the polymerization of SSS, i.e. poly(4-ethenylbenzenesulfonic acid); "PVA" denotes poly(ethenol) (or

polyvinyl alcohol); "SSS" denotes sodium styrene sulfonate, i.e. the sodium salt of 4-ethenylbenzenesulfonic acid; "UVA" means electromagnetic radiation having wavelengths between 320 and 400 nm; "UVB" means electromagnetic radiation having wavelengths between 290 and 320 nm; "UVC" means electromagnetic radiation having wavelengths between 200 and 290 nm, and "xPVA" denotes PVA that is at least partially crosslinked.

The terms "first", "second", "third", etc. used with reference to elements, features or integers of the subject matter defined in the Statement of Invention and Claims, or when used with reference to alternative embodiments of the invention are not intended to imply an order of preference. The numbering of the Examples and the Comparative Examples (if any) is not intended to mean any pair of Example and Comparative Example is directly comparable. Where values are expressed to one or more decimal places standard rounding applies. For example, 1.7 encompasses the range 1.650 recurring to 1.749 recurring. Where concentrations or ratios of reagents or solvents are specified, the concentration or ratio specified is the initial concentration or ratio of the reagents or solvents. References to the use of 4-ethenylbenzenesulfonic acid encompass references to the use of salts of the acid, including SSS. In the absence of further limitation the use of plain bonds in the representations (if used) of the structures of compounds encompasses the diastereoisomers, enantiomers and mixtures thereof of the compounds.

The invention will now be described with reference to embodiments or examples and the figures of the accompanying drawings pages.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1. FTIR spectra of the monomer 4-ethenylbenzenesulfonic acid (SSS) and poly(4-ethenylbenzenesulfonic acid) (PSSS) prepared according to the method described in Example 1 (water) and Example 2 (DMSO).

Figure 2. FTIR spectra recorded for poly(4-ethenylbenzenesulfonic acid)(PSSS), the photoinitiator benzophenone (BP), no washing protocol (1), washed with water at a temperature of 45 to 50°C before drying (2), washed with acetone (3) and washed with water at a temperature of 45 to 50°C, dried and then washed with acetone (4).

Figure 3. Photograph of vials containing partially crosslinked poly(ethenol) (xPVA) prepared according the Example 8. From left to right: Vial 1, Vial2, Vial 3 and Vial 4.

Figure 4. Flux (LMH)(♦, broken line), total solids (%)(▲, dotted line) and protein rejection (%)(■, solid line) of a sample of an asymmetric composite membrane (030918Sii) prepared according to Example 9 during repeated clean-in-place (C-i-P) protocols.

Figure 5. Pressure series testing (0 to 20 bar) of a sample (030918Siii) of an asymmetric composite membrane prepared according to Example 9. Flux and protein rejection with milk as the feed stream were measured.

Figure 6. Comparison of the FTIR spectra (full range) recorded for samples (240818Si and 240818Sii) of an asymmetric composite membrane prepared according to Example 9 and the poly(ethenol) (PVA) and cross-linked poly(ethenol) (xPVA) used in their preparation.

Figure 7. Comparison of the FTIR spectra (stretch mode region) recorded for samples (240818Si and 240818Sii) of an asymmetric composite membrane prepared according to Example 9 and the poly(ethenol) (PVA) and cross-linked poly(ethenol) (xPVA) used in their preparation.

Figure 8. Comparison of the FTIR spectra (finger print region) recorded for samples (240818Si and 240818Sii) of an asymmetric composite membrane prepared according to Example 9 and the poly(ethenol) (PVA) and cross-linked poly(ethenol) (xPVA) used in their preparation.

Figure 9. Scanning electronmicrographs of the surface of samples of asymmetric composite membrane prepared according to Example 9 before and after being subjected to repeated clean-in-place (CIP) protocols.

DETAILED DESCRIPTION

The invention resides in part in the selection of a preformed polymer of 4-ethenylbenzenesulfonic acid as the hydrophilicitizing agent used in the preparation of hydrophilicitized polyolefin substrates. This part of the invention is most advantageously applied to the hydrophilicitization of preformed sheets of microporous poly(ethylene). Use of poly(4-ethenylbenzenesulfonic acid) as the hydrophilicitizing agent has been found to provide greater and more consistent hydrophilicitization of the polyolefin substrate. This improvement is attributed at least in part to the reduced number of side reactions that may occur when compared with use of the monomer (*cf.* the method described in the publications of Exley (2016) and Craft *et al* (2017)). It is also anticipated that the use increases the likelihood of the preformed polymer grafting to the

polyolefin substrate at multiple sites. A structurally distinct form of grafted polyolefin substrate may therefore be being obtained.

The improved performance of a hydrophilicitized sheet of microporous poly(ethylene) prepared by the method of the present invention when compared with that prepared by the method disclosed in the publications of Exley (2016) and Craft *et al* (2017) is demonstrated by a higher flux with water as the feed stream whilst retaining the desired durability including tolerance to chlorine and other cleaning agents. The hydrophilicitized sheets of microporous poly(ethylene) prepared by the method of the present invention also "wet out" at pressures lower than those previously required. The method of preparing the hydrophilicitized sheets of microporous poly(ethylene) is also less wasteful of reagents, including the photoinitiator, and eliminates the need for the exclusion of oxygen during the preparation. The polymer of 4-ethenylbenzenesulfonic acid is advantageously prepared as a dispersion (the 'working solution') that can be used directly without the need to isolate the polymer. This advantage is illustrated in the methods of the following Examples.

The invention also resides in part in the use of the hydrophilicitized sheet of microporous polyolefin to prepare an asymmetric composite membrane. Providing a hydrophilicitized, i.e. wettable, sheet of microporous polyolefin facilitates the formation of the film of partially cross-linked poly(ethenol) (xPVA) on the surface and adherence to that surface. In contrast with the preparation of the asymmetric composite membranes disclosed in the publication of Craft *et al* (2017) persulfate is used as a cross-linking agent. The high levels of protein rejection demonstrated for the asymmetric composite membranes is attributed in part to the selection of this crosslinking agent. A porosity providing a size exclusion reduced to an estimated 30 kDa from an estimated 160 kDa is believed to be achieved (and is supported by the increased levels of total protein rejection of greater than 99.9%).

When drying the hydrophilicitized microporous sheet of polyolefin contacted with the dispersion in water of partially cross-linked poly(ethenol) (xPVA) applying a positive thermal gradient across the thickness of the sheet from the contacted side to the other side is also believed to assist in maintaining porosity of the hydrophilicitized microporous sheet of polyolefin and thereby provide an asymmetric composite membrane with higher flux rates than might otherwise be achievable. In Example 9 the application of a positive thermal gradient is a consequence of the sheet being supported on a glass plate during the drying steps. The positive thermal

gradient is believed to limit the extent to which the dispersion in water may permeate the pores of the hydrophilicitized microporous sheet.

The asymmetric composite membranes provided by the invention are therefore further distinguished from other membranes, e.g. those suggested in the publication of Linder *et al* (1988), where a superficial film of cross-linked PVA or PVA-copolymer is proposed to be coated on a hydrophobic, i.e. water repelling, sheet of microporous polyolefin.

MATERIALS AND METHODS

All microporous sheets used in the preparation of samples were prepared from virgin poly(ethylene), i.e. poly(ethylene) of high purity.

FTIR

Spectra of the samples were recorded using a Thermo Electron Nicolet 8700 FTIR spectrometer equipped with a single bounce ATR and diamond crystal. An average of 32 scans with a 4 cm^{-1} resolution was taken for all samples.

Flux

Permeability was determined using a filter assembly (Sterlitech Corp.) by measuring the flux with deionized water as the feed stream at various pressures. Flux J_V was then graphed against effective pressure difference across the membrane, p_{eff}, and the slope of the permeability L_p.

$$L_p = \frac{J_V}{\Delta p_{eff}}$$

The samples were mounted in the filter assembly. Deionized water was fed into the rig at 2.5 L min^{-1} and 4 to 8 °C. The time to collect a predetermined volume of permeate was noted. The flux rate (J) was calculated according to the following equation:

$$J = \frac{V}{t \times A}$$

where V is the permeate volume (L), t is the time (h) for the collection of V and A is area of the sample (m^2) which was determined to be 0.014 m^2.

Salt rejection

Rejection was measured using a 2 g/L solution in water of sodium chloride with a feed pressure of 16 bar. The conductivities from the feed and permeate were compared.

$$\%R_{NaCl} = \left(1 - \frac{\sigma_p}{\sigma_f}\right) \times 100$$

where σ_p is the conductivity of permeate and σ_f is the conductivity of the feed.

Total solids rejection

Rejection for whole milk samples was measured by pouring 20 mL of sample from the feed in a petri dish and measuring the dry weight after 2 hours in a 100 °C oven.

$$\%R_{TS} = \left(1 - \frac{m_{p,TS}}{m_{f,TS}}\right) \times 100$$

where $m_{p,TS}$ is total milk solids in the permeate and $m_{f,TS}$ is the mass of milk total solids in the feed.

Protein concentrations

Total protein and total whey protein concentrations in permeate were calculated on the basis of HPLC analysis with UV absorbance monitoring.

'Clean-in-Place' (CIP) protocol

To mimic commercial processing operations samples of the asymmetric composite membrane was subjected to repeated *in situ* washing protocols) as described in Craft *et al* (2017). The intermediate and subsequent flux rates were determined to assess the likely durability of the membrane in commercial processing operations. The *in situ* washing protocol was based on that employed in a commercial processing operation but modified in duration to compensate for the greater exposure of the membrane to the cleaning agents (caustic and acid) in the filter assembly. Prior to the washing steps the membrane was rinsed by circulating water at an initial temperature of 65°C through the filter assembly for a period of three minutes before draining the system.

The membrane was subjected to a first wash by circulating a 2% (w/v) sodium hydroxide solution ("caustic wash") through the filter assembly for a period of five minutes before draining and flushing the system by circulating water at an initial temperature of 65°C through the filter assembly system for a period of five minutes. The membrane was subjected to a second wash by circulating a 2% (w/w) nitric acid solution ("acid wash") through the filter assembly system for a period of ten minutes before draining and flushing the system of circulating water at an initial

temperature of 65°C for a period of ten minutes. The membrane was subjected to a third wash (a "caustic wash") before flushing the system by circulating water at an initial temperature of 65°C for a period of five minutes before circulating chilled water for a period of five minutes to cool the system. All rinsing and washing steps were performed with no pressure recorded on the pressure gauge of the filter assembly.

Preparation of poly(4-ethenylbenzenesulfonic acid)

EXAMPLE 1

A quantity of 50 g of the monomer 4-ethenylbenzenesulfonic acid as its sodium salt (SSS) was dissolved in a volume of 100 mL of distilled water to provide a solution. A quantity of 0.5 g of the initiator sodium persulfate (SPS) was then dissolved in the solution and the initiator-monomer mixture heated with stirring at a temperature of 80 to 90°C for a time of about 20 minutes. A viscous solution was obtained having a total volume of about 125 mL. The viscous solution was diluted with the same volume of distilled water to provide 250 mL of a working solution of poly(4-ethenylbenzenesulfonic acid).

The polymer could be precipitated from this working solution by the addition of an excess volume of acetone, followed by collection of the precipitate by filtration through a Buchner funnel and then washing with acetone to provide a light white solid that could be readily ground to a powder using a pestle and mortar.

EXAMPLE 2

A quantity of 5 g of the monomer 4-ethenylbenzenesulfonic acid as its sodium salt (SSS) was dissolved in a volume of 20 mL of dimethylsulfoxide (DMSO) to provide a solution.

A quantity of 0.05 g of the initiator ammonium persulfate (APS) was then dissolved in the solution and the initiator-monomer mixture heated with stirring at a temperature of 80 to 90°C for a time of about 20 minutes. The poly(4-ethenylbenzenesulfonic acid) was precipitated from the cooled solution by addition of an excess volume of acetone, collected by filtration through a Buchner funnel and washed with acetone to provide the same light white solid that could be readily ground to a powder obtainable in Example 1.

The Fourier transform infrared (FTIR) spectra of the powder obtained by the methods of preparation described in Example 1 (PSSS from water) and Example

2 (PSSS from DMSO) are compared with that of the FTIR spectrum of the monomer 4-ethenylbenzenesulfonic acid (SSS) in Figure 1. A comparison of the spectra was consistent with the polymerisation of the monomer in both methods of preparation. The polymer prepared by the method described in Example 1, i.e. the working solution, was used as the hydrophilicitizing agent in the preparation of hydrophilicitized sheets of microporous poly(ethylene) according to the following examples.

Preparation of hydrophilicitized sheets of microporous poly(ethylene)

EXAMPLE 3

A volume of 6 mL of the working solution obtained according to Example 1 was mixed with a volume of 5 mL of distilled water in a vial to provide a volume of initial solution containing 1.2 g of poly(4-ethenylbenzenesulfonic acid)(pSSS). A volume of 10 mL acetone was added to the volume of initial solution and allowed to become transparent before adding and dissolving in the solution a quantity of 0.2 g of the photoinitiator benzophenone to provide a hydrophilicitizing mixture. The surface of a sheet of microporous poly(ethylene)(TARGRAY™ wet process polyethylene separators, item no. SW320H (Targray, Kirkland QC, Canada)) dimensioned (13.5 cm x 18.5 cm) to fit the filter assembly (Sterlitech Corp.) was contacted with the hydrophilicitizing mixture and irradiated with ultraviolet (UV) light (broad spectrum centred on 320 nm) for a period of time of 2 minutes. The irradiated contacted sheets were then washed with cold tap water before being placed in a water bath maintained at a temperature of 45 to 50°C for a time of about 5 minutes. The washed sheets were then air dried before testing or use in the preparation of an asymmetric composite membrane.

EXAMPLE 4

The method of preparation described in Example 3 was repeated with the volume of initial solution containing 1.7 g of poly(4-ethenylbenzenesulfonic acid). This quantity of the polymer was close to the maximum that could be dissolved in the solvent system used.

EXAMPLE 5

A one step method of preparation including the monomer 4-ethenylbenzenesulfonic acid was evaluated.

A volume of 3 mL of the working solution obtained according to Example 1 was mixed with a volume of 8 mL of distilled water and a quantity of 0.6 g

of the monomer 4-ethenylbenzenesulfonic acid in a vial to provide a volume of initial solution containing 0.6 g of poly(4-ethenylbenzenesulfonic acid). A volume of 10 mL acetone was added to the volume of this initial solution and allowed to become transparent before adding a quantity of 0.4 g of the photoinitiator benzophenone to provide a hydrophilicitizing mixture.

The surface of a sheet of microporous poly(ethylene)(TARGRAY™ wet process polyethylene separators, item no. SW320H (Targray, Kirkland QC, Canada)) dimensioned (13.5 cm x 18.5 cm) to fit the filter assembly (Sterlitech Corp.) was contacted with the hydrophilicitizing mixture and irradiated with UV light (broad spectrum centred on 350 nm) for a period of time of 2 minutes before being washed with cold tap water and placed in a water bath maintained at a temperature of 45 to 50°C for about 5 minutes and then air dried.

EXAMPLE 6

A two-step method of preparation using only the monomer 4-ethenylbenzenesulfonic acid in the first of the two steps was evaluated.

In the first step a volume of 10 mL of distilled water followed by a volume of 10 mL of acetone was added to a foil wrapped vial containing a quantity of 2.4 g of the monomer and a quantity of 0.4 g of the photoinitiator benzophenone and the mixture shaken until all solids had dissolved. The surface of a sheet of microporous poly(ethylene)(TARGRAY™ wet process polyethylene separators, item no. SW320H (Targray, Kirkland QC, Canada)) dimensioned (13.5 cm x 18.5 cm) to fit the filter assembly of a test rig (Sterlitech Corp.) was contacted with the mixture and irradiated with ultraviolet (UV) light (broad spectrum centred on 350 nm) before washing with cold tap water and placing in a water bath maintained at a temperature of 45 to 50°C for a time of 5 minutes before being air dried.

In the second step a volume of 6 mL of the working solution obtained according to Example 1 was mixed with a volume of 5 mL of distilled water in a vial to provide a volume of initial solution containing 1.2 g of poly(4-ethenylbenzenesulfonic acid). A volume of 10 mL acetone was added to the volume of initial solution and allowed to become transparent before adding and dissolving in the solution a quantity of 0.2 of the photoinitiator benzophenone to provide a hydrophilicitizing mixture. The surface of the air dried sheet obtained according to the first step was contacted with the hydrophilicitizing mixture and irradiated with UV light (broad spectrum centered on 350 nm) for a period of time of 2 minutes

before washing with cold tap water and placing in a water bath maintained at a temperature of 45 to 50°C for a period of time of about 5 minutes and then air dried.

Observations

Grafting of the preformed poly(4-ethenylbenzenesulfonic acid) onto the sheet of microporous poly(ethylene) according to the methods of preparation described in Example 3, Example 4, Example 5 and Example 6 was confirmed by washing in acetone (solvent for the photoinitiator benzophenone) and water (solvent for poly(4-ethenylbenzenesulfonic acid)). Four washing protocols (1, 2, 3 and 4) were adopted and the FTIR spectra recorded for samples of hydrophilicitized sheets of microporous poly(ethylene) prepared according to the method described in Example 3 following application of these washing protocols are presented in Figure 2.

Preparation of asymmetric composite membrane

EXAMPLE 7

A series of preliminary experiments were performed to evaluate methods of preparing a film of cross-linked poly(ethenol) (xPVA) on a surface. A solution of the radical initiator sodium persulfate (SPS) was prepared by adding a quantity of 0.2 g of SPS to a volume consisting of 10 mL deionised water and 10 mL acetone. The solution of radical initiator was applied onto the surface of each of three glass plates (Plate 1, Plate 2 and Plate 3). Plate 2 and Plate 3 were transferred to an oven and dried at a temperature of 60°C until all solvent had evaporated to leave a thin layer of the initiator deposited on the surface. Solutions of poly(ethenol) (PVA) were prepared at a concentration of 1% (w/v) in either dimethyl sulfoxide (DMSO) or deionised water. The solution of poly(ethenol) (PVA) in DMSO was sprayed onto the wet surface of Plate 1 and the plate then transferred to an oven and dried at a temperature of 60°C. The solution of poly(ethenol)(PVA) in DMSO was also sprayed onto the dry surface of Plate 2 and the plate then transferred to an oven and dried at a temperature of 60°C. The solution of poly(ethenol) in deionised water was sprayed onto the dry surface of Plate 3 and the plate then transferred to an oven and dried at a temperature of 60°C. The desired film of cross-linked poly(ethenol) was not formed on Plate 1. The failure attributed to the presence of acetone causing the polymer to crash out of solution. The film formed on Plate 2 was too frangible to be useful as a rejection layer of an asymmetric composite membrane. A clear, peelable film formed on the surface of Plate 3. The film

was not brittle and this method of preparation was adopted for use in the preparation of the asymmetric composite membrane.

EXAMPLE 8

A series of preliminary experiments were performed to evaluate methods of preparing a film of partially cross-linked poly(ethenol) (xPVA) and thereby control the properties of the rejection layer of the asymmetric composite membrane. Volumes of 10 mL of a 1% (w/v) solution of poly(ethenol)(PVA) in deionised water containing a quantity of 0.1 g of SPS were dispensed into each four vials (Vial 1, Vial 2, Vial 3 and Vial 4). The solution in each vial was heated to a temperature of 75°C and maintained at this temperature with stirring until the following observations were made (and the vials then cooled):

- A yellow solid crashed out of solution (Vial 1; 3 to 4 minutes)
- A cloudy white solution with some precipitation formed (Vial 2, around 3 minutes)
- A cloudy white solution formed (Vial 3; 1.5 to 2 minutes)
- A cloudy solution started to form (Vial 4; 10 to 20 seconds)

The observations are also presented in Figure 3. The method of preparing partially cross-linked poly(ethenol) according to that formed in Vial 3 was adapted for use in the preparation of the membrane.

EXAMPLE 9

A volume of 20 mL of the solution of the radical initiator sodium persulfate (SPS) was prepared according to Example 7. A volume of the solution of partially cross-linked poly(ethenol) (xPVA) was prepared according to Example 8 (Vial 3).

The solution of the radical initiator was applied to one surface of a hydrophilicitized sheet of microporous poly(ethylene) prepared according to Example 3. The sheet was then placed on a glass plate and transferred to an oven and dried at a temperature of 60°C. The solution of partially cross-linked poly(ethenol) was applied to the same surface of the dried sheet and the sheet then returned to the oven and dried at 60°C. The dried membrane was then washed with cool water and air dried before evaluation for flux, total solids and salts rejection with different feed streams (water and milk).

Evaluation of samples of asymmetric composite membrane

Replicate samples (240818Si, 240818Sii, 240818Siii, 030918Si, 030918Sii, 030918Siii) of membrane prepared according to Example 9 were evaluated. The results of this evaluation are summarised in Table 1. Following an initial wetting with 20% (v/v) isopropanol in water, fluxes in the range 7.8 to 10.9 litres per square meter per hour (LMH) were obtainable for a feed stream of water at a pressure of 10 bar. Similar, if not slightly greater fluxes were obtained for a solution of salts with salt rejection in excess of 20%. For a feed stream of whole milk, fluxes were reduced but provided in excess of 50% total solids rejection and well in excess of greater than 99% protein rejection.

Sample	Initial flux (LMH)	Salt flux (LMH)	Salt rejection (%)	Milk flux (LMH)	Total solids rejection (%)	Protein rejection (%)
240818Si	10.9 at 10 bar	11.7 at 10 bar	20.3	-	-	
240818Sii	7.8 at 10 bar	10.7 at 10 bar	21.3	-	-	
240818Siii	8.9 at 10 bar	10.3 at 10 bar	28.4	4.5 at 10 bar	63.0	99.95
030918Si	2.1 at 5 bar	-	-	1.3 at 10 bar	-	99.83
030918Sii	-	-	-	0.7 at 5 bar	62.4	99.99
030918Siii	-	-	-	0.6 at 5 bar	55.7	100.00

Table 1. Evaluation of samples of asymmetric composite membrane prepared according to Example 9. The sample (240818Siii) demonstrating the highest salt rejection was also evaluated along with two other samples (030918Sii and 030918Siii) for total solids and protein rejection with milk as a feed stream.

One of the samples (030918Sii) was further evaluated for its tolerance to clean-in-place (CIP) protocols. One of the samples (030918Siii) was also further evaluated in a pressure series test to see how the flux and protein rejection were affected. The results of these further evaluations are summarised in Tables 2 and 3 and Figures 4 and 5.

Number of CIPs	Milk flux (LMH)	Total solids rejection (%)	Protein rejection (%)
0	0.7	62.4	99.99
1	2.3	55.9	99.94
2	2.0	-	99.94
3	4.7	50.7	99.93
4	5.0	46.3	99.88
5	5.7	42.0	99.84
10	5.7	49.0	99.87

Table 2. Flux, total solids and protein rejection of a sample of an asymmetric composite membrane (030918Sii) prepared according to Example 9 during repeated clean-in-place (CIP) protocols.

Pressure	Milk flux (LMH)	Protein rejection (%)
0	-	99.99
5	0.6	99.94
10	3.3	99.94
15	5.1	99.93
20	7.1	99.88

Table 3. Pressure series testing (0 to 20 bar) of a sample (030918Siii) of an asymmetric composite membrane prepared according to Example 9. Flux and protein rejection with milk as the feed stream were measured.

Although the invention has been described with reference to embodiments or examples it should be appreciated that variations and modifications may be made to these embodiments or examples without departing from the scope of the invention. Where known equivalents exist to specific elements, features or integers, such equivalents are incorporated as if specifically referred to in this specification. In particular, variations and modifications to the embodiments or examples that include elements, features or integers disclosed in and selected from the referenced publications are within the scope of the invention unless specifically disclaimed. The advantages provided by the invention and discussed in the description may be provided in the alternative or in combination in these different embodiments of the invention.

INDUSTRIAL APPLICABILITY

A durable asymmetric composite membrane with high levels of protein rejection whilst maintaining a high flux with feed streams such as whole milk is provided.

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CLAIMS

1) A **microporous sheet** of polyolefin grafted with a preformed poly(4-ethenyl benzene sulfonic acid).

2) The microporous sheet of claim 1 where the polyolefin is poly(ethylene).

3) An **asymmetric composite membrane** comprising a film of partially crosslinked poly(ethenol) adhered to one side of a microporous sheet of polyolefin grafted with poly(4-ethenyl benzene sulfonic acid).

4) The asymmetric composite membrane of claim 3 where the polyolefin is poly(ethylene).

5) A **method** of preparing a hydrophilicitized microporous sheet of polyolefin comprising the steps of:

   a) Contacting a microporous sheet of polyolefin with a dispersion comprising a preformed poly(4-ethenylbenzenesulfonic acid) in an aqueous solvent to provide a contacted microporous sheet;

   b) Curing the contacted microporous sheet at a temperature and for a time sufficient for at least a portion of the poly(4-ethenylbenzenesulfonic acid) to be grafted onto the polyolefin substrate to provide a cured microporous sheet; and then

   c) Washing the cured microporous sheet to provide the hydrophilicitized microporous sheet of polyolefin.

6) The method of claim 5 where the polyolefin is is poly(ethylene).

7) The method of claim 5 or 6 where the aqueous solvent is acetone-water.

8) The method of any one of claims 5 to 7 where the curing the contacted microporous sheet is by irradiating with ultraviolet light in the presence of a photoinitiator.

9) A **hydrophilicitized microporous sheet** of polyolefin prepared according to the method of any one of claims 5 to 8.

10) A **method** of preparing an asymmetric composite membrane comprising the steps of:

   a) Contacting one side of a hydrophilicitized microporous sheet of polyolefin with a solution in a first solvent of partially cross-

linked poly(ethenol) in the presence of a radical initiator to provide a contacted sheet;

b) Drying the contacted sheet at a temperature and for a time sufficient to allow the partially cross-linked poly(ethenol) to adhere to the one side of the hydrophilicitized microporous sheet of polyolefin and evaporate substantially all the solvent to provide a dried contacted sheet; and then

c) Washing the dried contacted sheet in a second solvent to provide the asymmetric composite membrane.

11) The method of claim 10 where the drying the contacted sheet is by applying a positive thermal gradient across the thickness of the sheet from the contacted one side of the hydrophilicitized microporous sheet to the other side.

12) An **asymmetric composite membrane** prepared according to the method of claim 10 or 11.

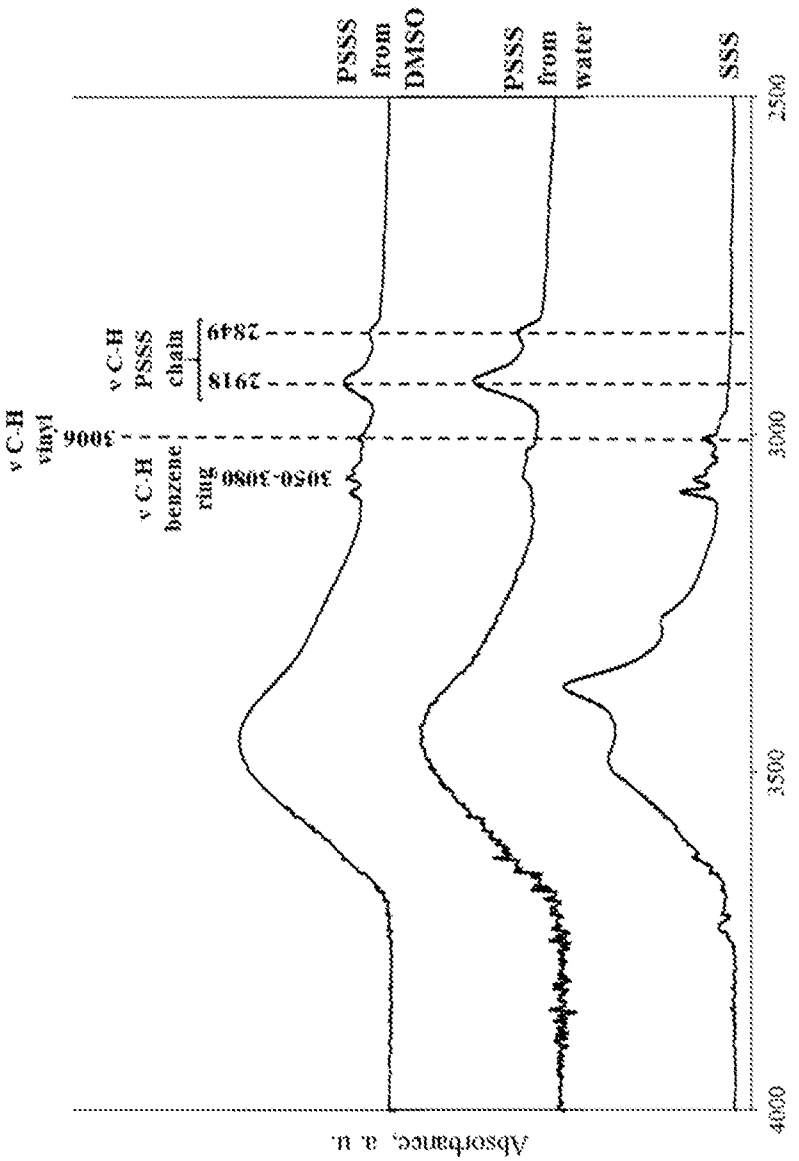

PSSS from DMSO
PSSS from water
SSS
ν C-H vinyl
3006
ν C-H benzene ring
3050-3080
ν C-H PSSS chain
2918
2849
Absorbance, a. u.
4000
3500
3000
2500
Wavenumber, cm-1

FIGURE 1

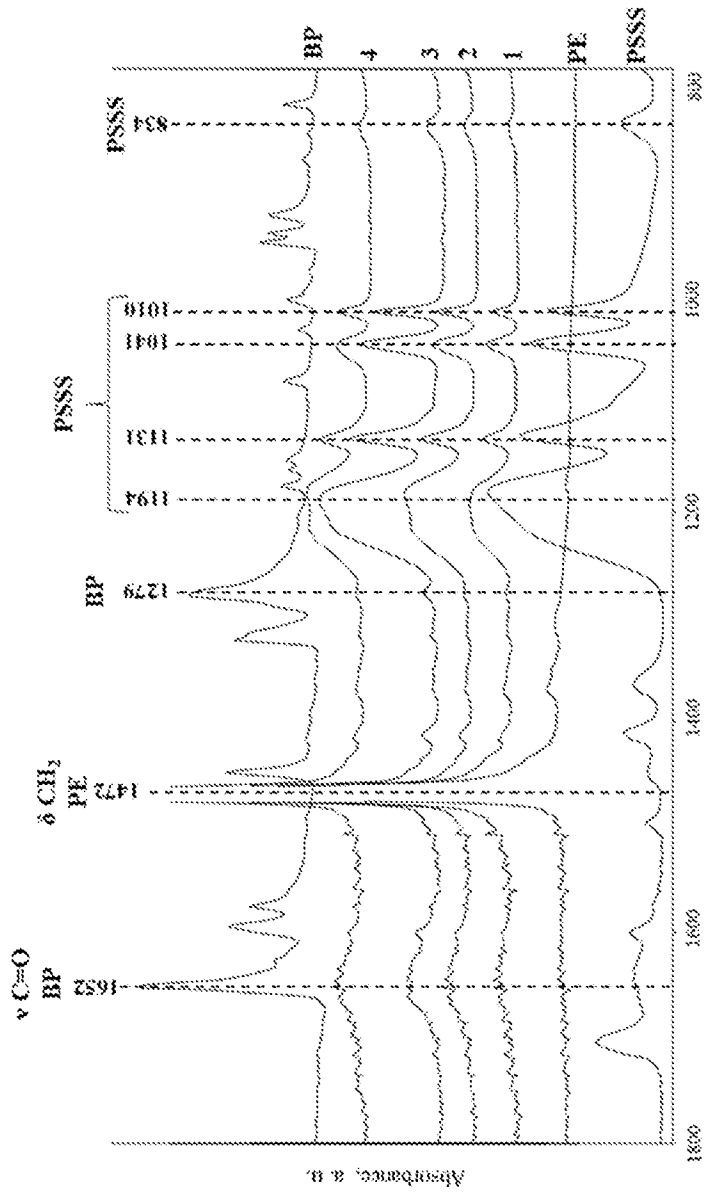

BP
4
3
2
1
PE
PSSS
834
1010
1041
1131
1194
PSSS
1279
BP
1472
δ CH2
PE
1652
ν C=O
BP
1800
1600
1400
1200
1000
800
Wavenumber, cm-1
Absorbance, a.u.

FIGURE 2

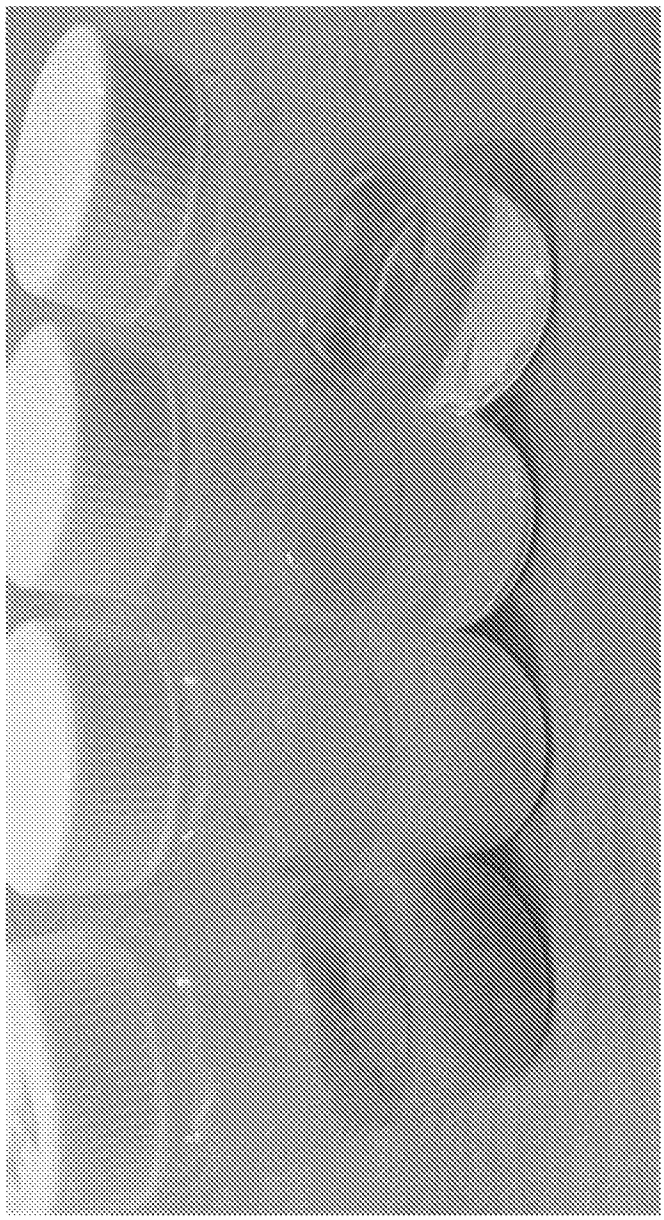


FIGURE 3

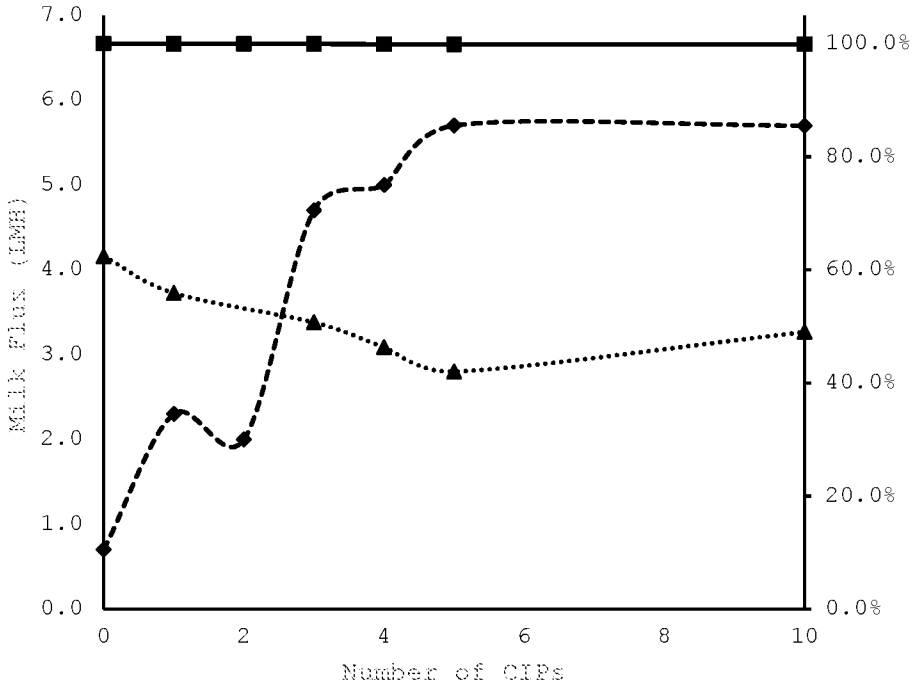


FIGURE 4

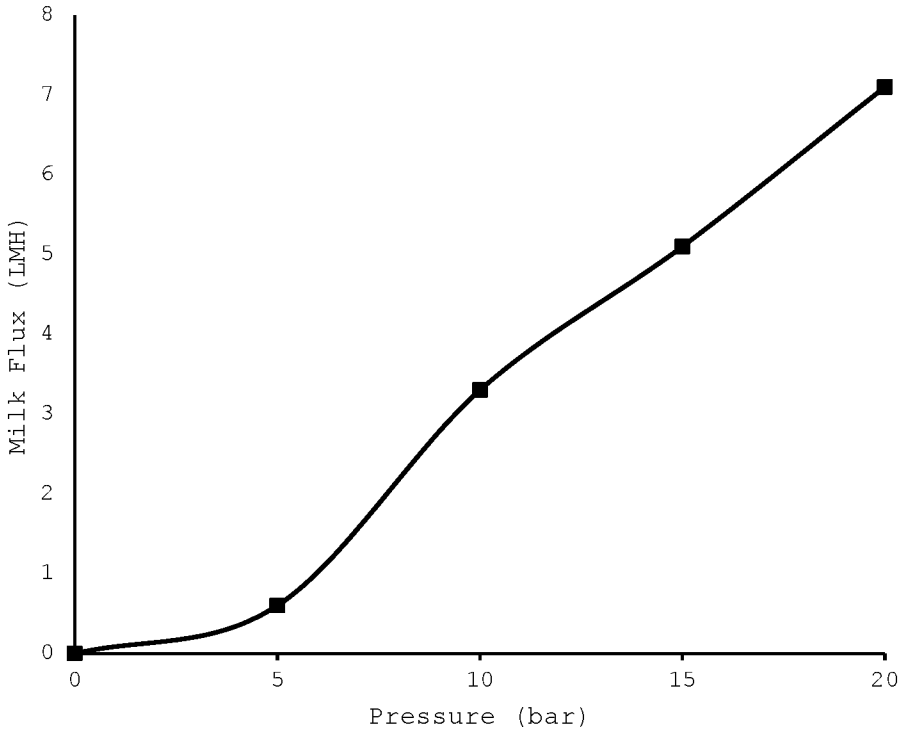


FIGURE 5

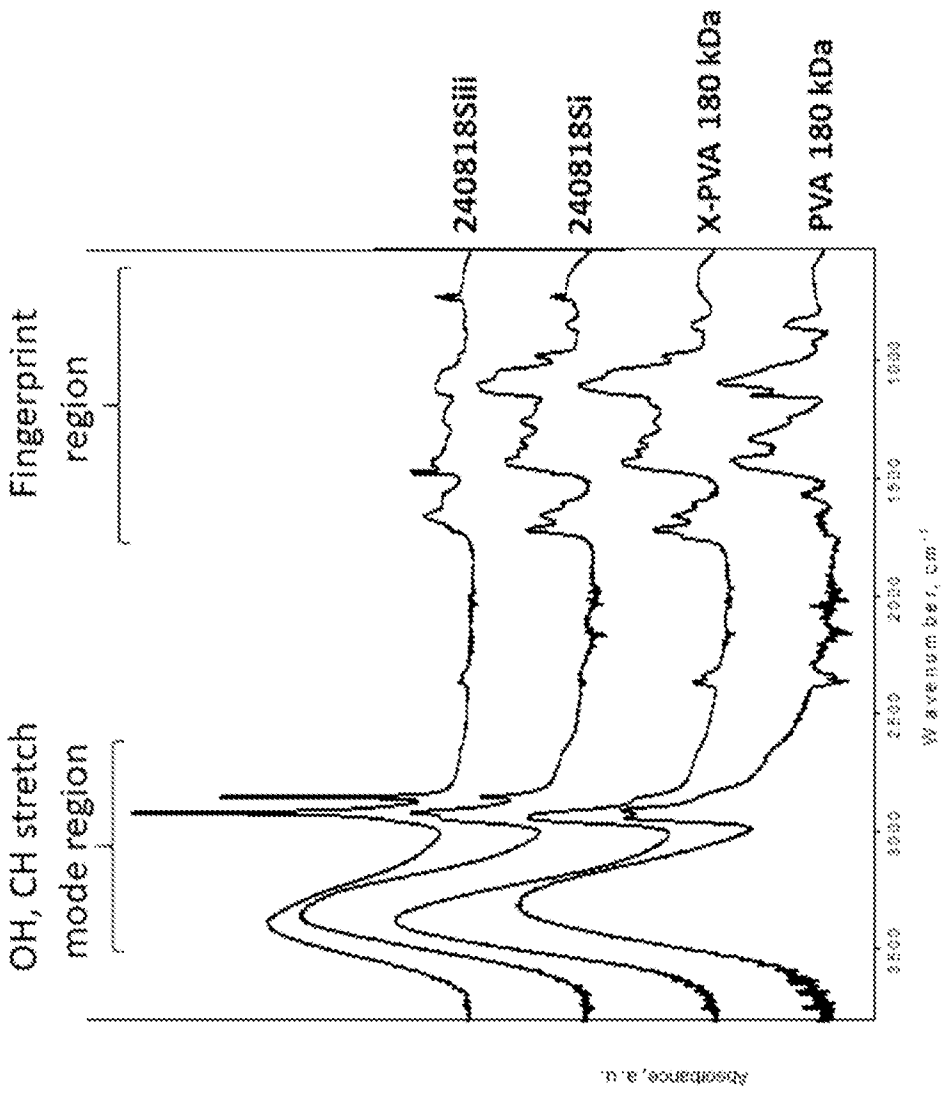

OH, CH stretch mode region
Fingerprint region
240818Siii
240818Si
X-PVA 180 kDa
PVA 180 kDa
Absorbance, a.u.
Wavenumber, cm-1
3800
3000
2500
2000
1500
1000

FIGURE 6

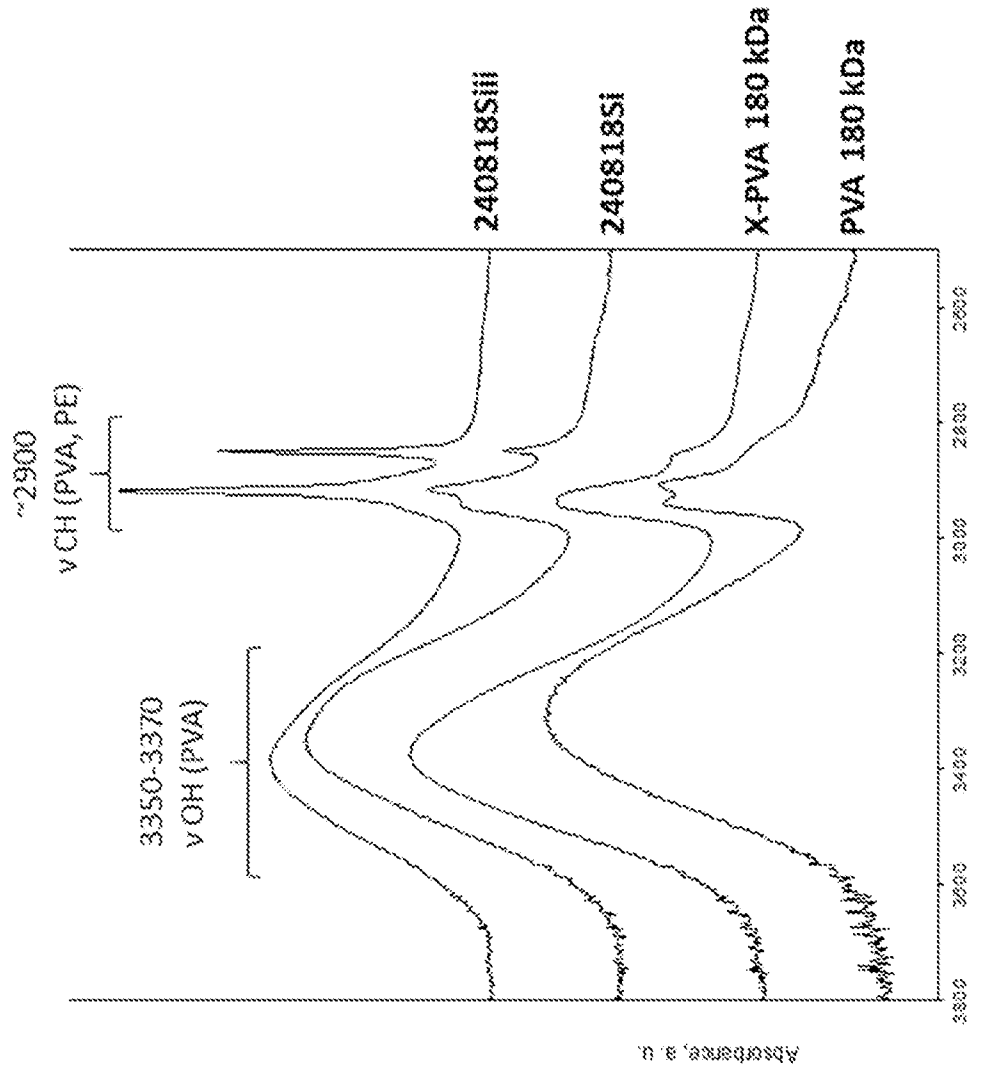

~2900
ν CH (PVA, PE)
3350-3370
ν OH (PVA)
240818Siii
240818Si
X-PVA 180 kDa
PVA 180 kDa
Absorbance, a.u.
Wavenumber, cm-1
3800
3600
3400
3200
3000
2800
2600

FIGURE 7

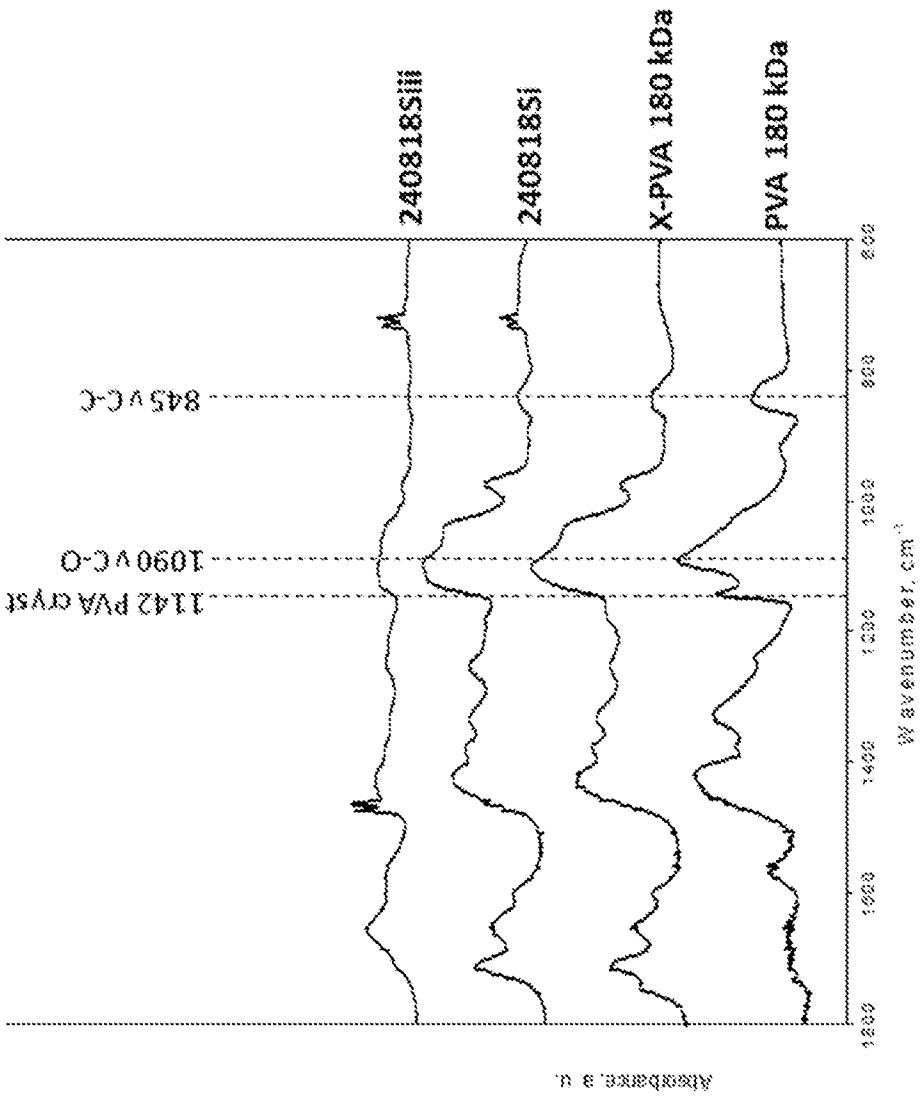
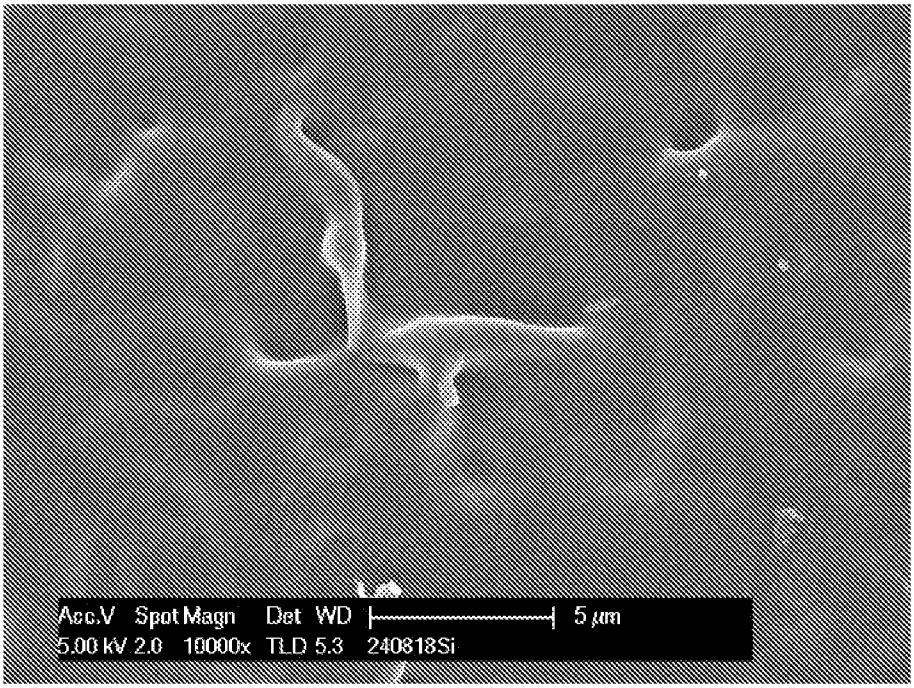
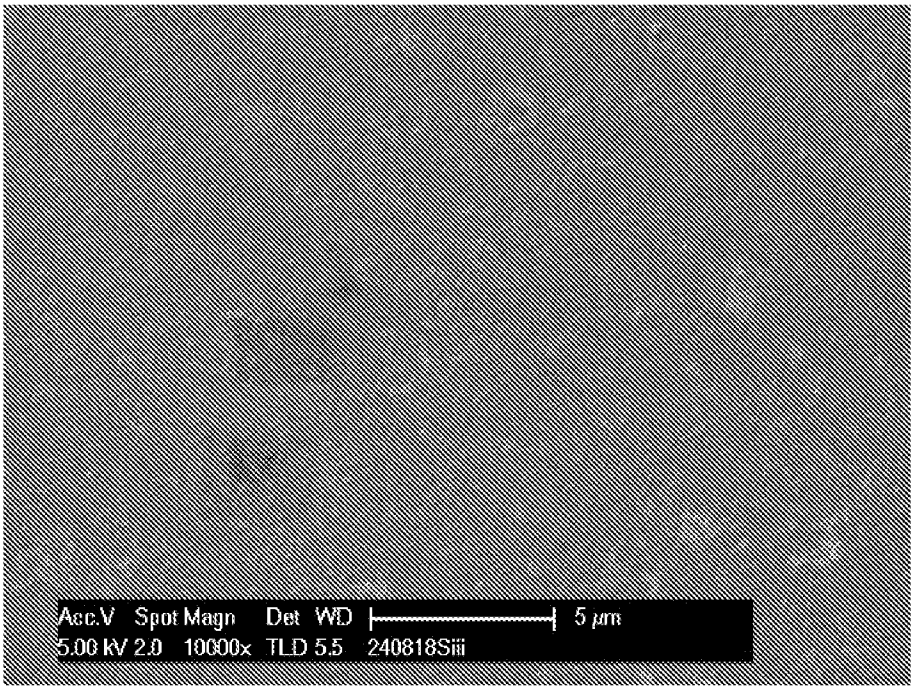

240818Siii
240818Si
X-PVA 180 kDa
PVA 180 kDa
845 νC-C
1090 νC-O
1142 PVA cryst
Absorbance, a.u.
Wavenumber, cm-1
1800
1600
1400
1200
1000
800
600

FIGURE 8


Acc.V Spot Magn Det WD 5 µm
5.00 kV 2.0 10000x TLD 5.3 240818Si

A


Acc.V Spot Magn Det WD 5 µm
5.00 kV 2.0 10000x TLD 5.5 240818Siii

B

FIGURE 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2019/052649

A. CLASSIFICATION OF SUBJECT MATTER

B01D 71/26 (2006.01) B01D 71/28 (2006.01) B01D 69/12 (2006.01)

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)

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

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

PATENW, CAPlus, Google Patents, Google Scholar: IPC/CPC (B01D71/78, B01D67/0093, B01D2325/022, B01D2323/02, B01D2323/38 and below, B01D71/26, B01D71/28, B01D69/125) and Keywords (copolymer, graft, asymmetric, composite, polystyrenesulfonic acid, polyvinyl alcohol, polyolefin and like terms)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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
2 July 2019	02 July 2019
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Deborah McDonnell AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262850724

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/IB2019/052649**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2016/081729 A1 (ENTEGRIS, INC) 26 May 2016 abstract; para 48-49, 51, 76	1-9
X	WO 2008/043507 A1 (DSM IP ASSETS BV) 17 April 2008 page 2, lines 16-35; page 3, lines 31-33; page 4, lines 4-27; page 5, lines 4-20	1-9
X	WO 2016/103239 A1 (EXLEY, M.) 30 June 2016 page 6, line 25-34; page 8, lines 4-22,	1-9
A	WO 2017/056074 A1 (CRAFT, L. et al.) 06 April 2017	
A	US 2013/0116589 A1 (ORIDION MEDICAL LTD) 09 May 2013	
A	BOLTO, B. et al., "Crosslinked poly(vinyl alcohol) membranes", Progress in Polymer Science, 2009, Vol 34, pages 969-981	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2019/052649

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box for Details

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-9

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Supplemental Box

Continuation of: **Box III**

This international application does not comply with the requirements for unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This authority has found there are different inventions based on the following features:

- Claims 1-9 are directed to a microporous sheet, an asymmetric composite membrane comprising a microporous sheet, and a method of preparing a microporous sheet. The feature of a microporous sheet of polyolefin grafted with poly(4-ethenyl benzene sulfonic acid) is specific to this group of claims.

- Claims 10-12 are directed to a method of preparing an asymmetric composite membrane. The feature of a microporous sheet of polyolefin having partially cross-linked poly(ethenol) adhered to one side is specific to this group of claims.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only feature common to all of the claimed inventions is *a microporous sheet of polyolefin*. However, microporous polyethylene sheets are generic in this particular art.

Therefore this common feature cannot be a special technical feature. Hence there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a priori*.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/IB2019/052649**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
WO 2016/081729 A1	26 May 2016	WO 2016081729 A1	26 May 2016
		CN 107106997 A	29 Aug 2017
		EP 3221035 A1	27 Sep 2017
		JP 2017536232 A	07 Dec 2017
		KR 20170084294 A	19 Jul 2017
		KR 101963063 B1	27 Mar 2019
		SG 11201704043V A	29 Jun 2017
		TW 201625357 A	16 Jul 2016
		US 2018290109 A1	11 Oct 2018
WO 2008/043507 A1	17 April 2008	WO 2008043507 A1	17 Apr 2008
		EP 1921702 A1	14 May 2008
		EP 2076932 A1	08 Jul 2009
		JP 2010506365 A	25 Feb 2010
		KR 20090091286 A	27 Aug 2009
		TW 200828655 A	01 Jul 2008
		US 2010203400 A1	12 Aug 2010
		US 8137436 B2	20 Mar 2012
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		AU 2015370441 A1	03 Aug 2017
		AU 2015370441 B2	07 Dec 2017
		AU 2017254972 A1	23 Nov 2017
		AU 2017254972 B2	06 Dec 2018
		AU 2018263979 A1	13 Dec 2018
		CN 107614093 A	19 Jan 2018
		EP 3237101 A1	01 Nov 2017
		GB 2549433 A	18 Oct 2017
		JP 2018505055 A	22 Feb 2018
		SG 11201705235U A	28 Jul 2017
		US 2018015424 A1	18 Jan 2018
WO 2017/056074 A1	06 April 2017	WO 2017056074 A1	06 Apr 2017
		AU 2016333025 A1	12 Apr 2018
US 2013/0116589 A1	09 May 2013	US 2013116589 A1	09 May 2013
		US 8540806 B2	24 Sep 2013
		CN 101822948 A	08 Sep 2010

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/IB2019/052649**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
		EP 2226116 A2	08 Sep 2010
		EP 2226116 B1	20 Apr 2016
		JP 2010209329 A	24 Sep 2010
		JP 5443213 B2	19 Mar 2014
		US 2010224066 A1	09 Sep 2010
		US 8366811 B2	05 Feb 2013
		US 2013338523 A1	19 Dec 2013
		US 8764888 B2	01 Jul 2014

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.