Method for preparing porous membranes from waste poly(vinyl chloride) plastics

Technical Field

[0001] The disclosure relates to a method for preparing porous membranes from waste poly(vinyl chloride) (PVC) plastics comprising unknown fixed quantities of plasticizer.

Background

[0002] The discussion of the background to the disclosure is intended to facilitate an understanding of the disclosure. However, it should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was published, known or part of the common general knowledge as at the priority date of the application.

[0003] Utilization of waste materials in various industries has gained considerable attention in recent years due to the potential to mitigate environmental impact, particularly in regard to landfill, and promote sustainable practices. Among these materials, waste PVC particles have emerged as a potential resource for membrane fabrication, offering an eco-friendly alternative to conventional materials.

[0004] Unlike other plastics such as polyethylene or polypropylene, PVC is generally combined with a plasticizer to achieve desired mechanical properties such as malleability and flexibility. The presence of plasticizers within the PVC matrix affects both the free volume and pore structure (see Polymer, Volume 44, Issue 6, 2003, 1921-1926) of the polymeric material. With the addition of plasticizer to PVC, positron annihilation lifetime spectroscopy has been used to show that the free volume increases with the generation of sub-nanometer pores. To achieve the aims of plasticization (i.e., imparting flexibility and mechanical strength in the polymer material), the plasticizer concentration must typically be at least 15 parts per hundred resin (Applied Plastics Engineering Handbook, 2011, Chapter 5 – Poly(vinyl chloride)) although typical plasticizer concentration in cabling can be as high as 50 parts per

hundred resin depending on the exact cabling application and plasticizer that is used (Polymer Degradation and Stability, 101, 2014, 24-31).

[0005] Membranes play a crucial role in various industrial applications, including water filtration, separation, and purification processes. Given that waste PVC initially has a high level of additives, such as plasticizers, stabilisers, binders, colourants and so forth, conventional membrane fabrication with waste PVC in comparison to pure virgin PVC is complicated significantly by the presence of these additives in unknown fixed concentrations.

[0006] For example, the presence of pre-existing plasticizers in waste PVC increases the viscosity of a casting solution making dissolution of the waste PVC much more challenging. Separately, dissolving the waste PVC and the porogen is advantageous as the porogen itself can act as an anti-solvent and impede the dissolution of the waste PVC. Additionally, while it is not expected that plasticizers will significantly contribute to the transport characteristics of a membrane formed from waste PVC since the pores formed by plasticizer in PVC are sub-nanometer, the presence of the plasticizer has an unpredictable and complex effect on the behaviour of the porogen within the PVC matrix as the solvent evaporates during membrane fabrication, which in turn influences the size and formation of pores and their connectivity in the membrane.

[0007] The present disclosure seeks to provide a process to facilitate use of waste PVC particles in membrane fabrication and contribute to a circular economy model by repurposing waste materials.

Summary

[0008] The disclosure relates to a method of preparing porous membranes from waste PVC plastics comprising unknown fixed quantities of plasticizer.

[0009] In accordance with one aspect of the disclosure there is provided a method of preparing porous membranes from waste PVC plastics comprising unknown fixed quantities of plasticizer, the method comprising the steps of:

providing a first solution comprising waste PVC particles and said plasticizer in a

first aprotic solvent;

providing a second solution comprising a porogen in a second aprotic solvent;

mixing the first and second solutions to provide a dope solution comprising solubilised waste PVC particles, said plasticizer and the porogen in the first and second aprotic solvents;

casting the dope solution in a layer on a surface of a substrate to form a membrane precursor; and

immersing the membrane precursor in a non-solvent for a period of time sufficient for the membrane precursor to undergo phase inversion and produce the porous membrane.

[0010] In one embodiment, the waste PVC particles may comprise comminuted PVC sheath from electrical cables. The waste PVC particles may have a particle size of about 1 mm to about 2 mm. The inventors have found that a particle size of about 1 mm to 2 mm leads to efficient dissolution of the waste PVC particles in the first aprotic solvent. A larger particle size will hinder the dissolution process as there is insufficient surface area for a solvent/particle interaction. A smaller particle size is also undesirable as the waste PVC particles tend to coalesce during the dissolution process and can easily form a gelatinous/partially dissolved layer that severely hinders dissolution.

[0011] Apart from comminution and classification, the waste PVC particles have not undergone any other pretreatment processes, in particular chemical processes. Accordingly, it will be appreciated that the waste PVC particles may also comprise unknown additives such as plasticisers, stabilisers, binders, colourants and utilised in the fabrication of PVC sheath that are present in unknown and fixed concentrations in the waste PVC.

[0012] In one embodiment, the dope solution may consist essentially of solubilised waste PVC particles, said plasticizer and the porogen in the first and second aprotic solvents.

[0013] In another embodiment, the dope solution may consist of solubilised waste PVC particles, said plasticizer and the porogen in the first and second aprotic solvents.

[0014] In one embodiment, the dope solution comprises from about 12.5 wt% to about 25 wt% waste PVC particles and about 2 wt% to about 5 wt% porogen.

[0015] In one embodiment, the porogen comprises polyvinyl pyrrolidone (PVP), polyethylene glycol (PEG), polyvinyl alcohol (PVA) or polyethylene oxide (PEO).

[0016] In one embodiment, the first aprotic solvent and the second aprotic solvent may be the same or different.

[0017] In one embodiment the aprotic solvent may comprise N-N-dimethylacetamide, (DMAc), N, N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), or tetrahydrofuran (THF).

[0018] In one embodiment, the step of casting the dope solution may be performed at a casting speed of about 0.5 cm/s to about 1.5 cm/s.

[0019] In one embodiment, the layer of the cast dope solution has a predetermined thickness of from about 50 micron to about 400 micron.

[0020] In one embodiment, the substrate on which the dope solution is cast may be glass, stainless steel, or aluminium plate.

[0021] In one embodiment, the dope solution may be cast at a temperature of about 25 ºC to 60 ºC.

[0022] In one embodiment, the layer of cast dope solution is retained on the surface of the substrate for a period of about 50 seconds to about 60 seconds before immersing the membrane precursor in the non-solvent.

[0023] In one embodiment the membrane precursor is immersed in the non-solvent for a period of about 40 seconds to about 300 seconds.

[0024] In one embodiment, the non-solvent comprises water, optionally with isopropranol in an amount of up to about 45 vol%.

Brief Description of Drawings

[0025] Notwithstanding any other forms which may fall within the scope of the process and system as set forth in the Summary, specific embodiments will now be described with reference to the accompanying figures below:

[0026] Figures 1A-1C are scanning electron microscopy (SEM) images at varying degrees of magnification of one embodiment of a porous membrane prepared from waste PVC particles as disclosed herein;

[0027] Figure 2 is a schematic representation of a dead-end filtration arrangement used for performance evaluation testing of embodiments of the porous membrane prepared from waste PVC particles as disclosed herein;

[0028] Figure 3 is a graphical representation of membrane flux measured with the dead-end filtration arrangement shown in Figure 2 with bovine serum albumin (BSA) 0.5 wt% at constant pressure of 1 bar;

[0029] Figure 4 is a Standard Lowry Curve for absorbance and concentration of each control kit;

[0030] Figure 5 is a graphical representation of the amount of absorbed protein calculated using the Lowry method for each membrane;

[0031] Figure 6 is a schematic representation of a humic acid absorption test procedure;

[0032] Figure 7 is a graphical representation of Total Organic Carbon (TOC) analysis for remaining humic acid absorbed by one embodiment of the porous membrane prepared in accordance with the present disclosure;

[0033] Figure 8 is a graphical representation of maximum load (N) at breaking point of membranes prepared in accordance with embodiments of the disclosure;

[0034] Figure 9 is a graphical representation of elongation (%) at breaking point of membranes prepared in accordance with embodiments of the disclosure; and

[0035] Figures 10a, 10b and 10c are respective SEM images of membranes D, E and B, as prepared with reference to Example 8.

Description of Embodiments

[0036] The disclosure relates to a method for preparing porous membranes from waste PVC plastics.

GENERAL TERMS

[0037] Throughout this specification, unless specifically stated otherwise or the context requires otherwise, reference to a single step, composition of matter, group of steps or group of compositions of matter shall be taken to encompass one and a plurality (i.e. one or more) of those steps, compositions of matter, groups of steps or groups of compositions of matter. Thus, as used herein, the singular forms "a", "an" and "the" include plural aspects unless the context clearly dictates otherwise. For example, reference to "a" includes a single as well as two or more; reference to "an" includes a single as well as two or more; reference to "the" includes a single as well as two or more and so forth.

[0038] Each example of the present disclosure described herein is to be applied *mutatis mutandis* to each and every other example unless specifically stated otherwise. The present disclosure is not to be limited in scope by the specific examples described herein, which are intended for the purpose of exemplification only. Functionally-equivalent products, compositions and processes are clearly within the scope of the disclosure as described herein.

[0039] The term "and/or", e.g., "X and/or Y" shall be understood to mean either "X and Y" or "X or Y" and shall be taken to provide explicit support for both meanings or for either meaning.

[0040] Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

[0041] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although processes and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable processes and materials are described below. In case of conflict, the present specification, including definitions, will control. In addition, the materials, processes, and examples are illustrative only and not intended to be limiting.

[0042] The term “about” as used herein means within 5%, and more preferably within 1%, of a given value or range. For example, “about 3.7%” means from 3.5 to 3.9%, preferably from 3.66 to 3.74%. When the term “about” is associated with a range of values, e.g., “about X% to Y%”, the term “about” is intended to modify both the lower (X) and upper (Y) values of the recited range. For example, “about 20% to 40%” is equivalent to “about 20% to about 40%”.

SPECIFIC TERMS

[0043] The term “dope solution” as used herein refers to a homogeneous thermodynamically stable polymer solution formed by dissolving a polymer or a copolymer in a solvent or a solvent mixture, optionally with one or more additives.

[0044] The term “aprotic solvent” as used herein refers to a solvent that is capable of dissolving a wide range of solutes, including polar and nonpolar compounds. An aprotic solvent is polar but lacks an acidic proton (i.e. the aprotic solvent has no O-H or N-H bonds).

[0045] The term “non-solvent” as used herein refers to a liquid that is miscible with the aprotic solvent but is not capable of dissolving PVC polymer. The non-solvent may comprise one or more miscible liquids. The non-solvent will be used to dissolve the porogen following membrane casting.

[0046] The term “phase inversion” as used herein refers to chemical process in which solvent molecules present in a polymer membrane precursor exchange with non-solvent molecules when the polymer membrane precursor is immersed in a coagulation bath containing non-solvent, thereby facilitating dissolution of a porogen in the non-solvent and precipitation of a porous polymer membrane. The exchange of solvent molecules and porogens with non-solvent molecules is a combination of mass transfer and phase separation.

PREPARING POROUS MEMBRANES FROM WASTE PVC PLASTICS

[0047] Porous membranes may be prepared from waste PVC plastics comprising unknown fixed quantities of plasticizer. The waste PVC plastics may be derived from PVC sheath from wires and cables. The waste PVC plastics may be comminuted by any suitable comminution techniques such as shredding, granulating, milling and so forth.

[0048] The comminuted PVC plastics may be classified into particles having a particle size of about 1 mm to about 2 mm. While it is possible to reduce the particle size of waste PVC plastic to below 1 mm, the inventors have found that the additional energy required to decrease the particle size increases the thermal energy transferred to the PVC particles, causing them to soften and agglomerate, thereby deleteriously affecting their flow characteristics and handling properties.

[0049] It will be appreciated that the waste PVC particles may be separated from metal contaminants, such as copper, brass, aluminium and steel by physical separation techniques such as gravity separation, centrifugation, air, vibration bed, vacuum, hydraulic or magnetic separation techniques prior to use of the waste PVC particles in the process to prepare porous membranes.

[0050] Apart from comminution and classification, the waste PVC particles do not undergo any other pretreatment processes, in particular chemical processes. Accordingly, the waste PVC particles also comprise plasticisers, stabilisers, binders, colourants and other additives utilised in the fabrication of PVC sheath. It will be appreciated that several different plasticisers, stabilisers, binders, colourants and other additives may be used in the fabrication of PVC sheath and therefore the nature of the

specific additives and their concentration in the PVC sheath are unknown. Furthermore, the concentration of the plasticisers, stabilisers, binders, colourants and other additives is fixed. Additionally, the waste PVC particles may also comprise small volumes of other waste polymeric materials such as nylon, polyethylene, teflon, paper and polyurethane. Such additives influence the solubility of PVC in aprotic solvents and the viscosity of the resulting solution.

[0051] The method of preparing porous membranes from waste PVC plastics comprising unknown fixed quantities of plasticizer comprises the steps of:

providing a first solution comprising waste PVC particles and said plasticizer in a first aprotic solvent;

providing a second solution comprising a porogen in a second aprotic solvent;

mixing the first and second solutions to provide a dope solution comprising solubilised waste PVC particles, said plasticizer and the porogen in the first and second aprotic solvents;

casting the dope solution in a layer on a surface of a substrate to form a membrane precursor; and

immersing the membrane precursor in a non-solvent for a period of time sufficient for the membrane precursor to undergo phase inversion and produce the porous membrane.

[0052] The first solution may be prepared by mixing the waste PVC particles and said plasticiser with the first aprotic solvent. Suitable examples of the first aprotic solvent include, but are not limited to, N-N-dimethylacetamide, (DMAc), N, N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), or mixtures of thereof. The first solution may have a concentration up to 40 wt% of waste PVC. Preferably, the first solution may have a viscosity less than 100 cP.

[0053] The mixture of waste PVC particles, said plasticiser and the first aprotic solvent may be heated and mechanically stirred for about 24 h at 60 ºC to solubilise the waste PVC particles in the dope solution. It will be appreciated, however, that even after heating and stirring for 24 h, the first solution may contain solid deposits and suspended solids comprising non-soluble materials present in the waste PVC

particles. Moreover, dissolved impurities such as plasticizers, stabilizers and colourants may contribute to the colour and transparency of the first solution.

[0054] It will be appreciated that the first solution may be filtered to remove any insoluble solids that may be present in the PVC waste that were not previously removed. For example, the dope solution may undergo micro-filtration with filters having a pore size of less than 120 micron.

[0055] The second solution may be prepared by mixing the porogen with a second aprotic solvent. The first and second aprotic solvents may be the same or different. Suitable examples of the second aprotic solvent include, but are not limited to, N-N-dimethylacetamide, (DMAc), N, N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), or mixtures thereof. The second solution may have a concentration up to 20 wt% of porogen. Preferably, the second solution may have a viscosity less than 1000 cP.

[0056] High porosity, suitable pore size, and pore size distribution are desirable attributes of porous membranes. The porogens may be hydrophilic polymers which are miscible with the non-solvent. When the membrane precursor is immersed in the non-solvent, the porogens are solubilised by the non-solvent in a process referred to as diffusion induced phase separation, thereby favouring the formation of pores in the membrane. Suitable porogens include, but are not limited to, polyvinyl pyrrolidone (PVP), polyethylene glycol (PEG), polyvinyl alcohol (PVA) or polyethylene oxide (PEO).

[0057] It is important that the first and second solutions are prepared separately. The inventors have noted that plasticizer that is already present in the waste PVC will increase viscosity of the first solution, in comparison to a solution of PVC alone, thus hindering the dissolution of PVC. The presence of plasticiser in the resulting dope solution also increases its viscosity, making processing much more challenging. The porogen is not miscible with PVC and will also hinder the dissolution of waste PVC in the first aprotic solvent. Consequently, the first and second solutions should be prepared separately.

[0058] The first solution and the second solution may be combined with stirring to provide the dope solution. Preferably, the second solution is gradually added to the first solution with stirring so as to prevent the PVC and plasticiser from falling out of solution. The resulting dope solution may be maintained at a temperature up to 60 °C so as to maintain the PVC, plasticiser and porogen in solution.

[0059] The dope solution may comprise from about 12.5 wt% to about 25 wt% of waste PVC particles as described above. The dope solution may comprise about 12.5 wt%, 13 wt%, 14 wt%, 15 wt%, 16 wt%, 17 wt%, 18 wt%, 19 wt%, 20 wt%, 21 wt%, 22 wt%, 23 wt%, 24 wt% or up to 25 wt% waste PVC particles.

[0060] The dope solution may comprise from about 2 wt% to about 5 wt% porogen. The dope solution may comprise about 2 wt%, 2.5 wt%, 3 wt%, 3.5 wt%, 4 wt%, 4.5 wt % or 5 wt% waste porogen.

[0061] The dope solution may have a viscosity less than 50 cP.

[0062] The dope solution may then be cast in a layer on a surface of a substrate to form a membrane precursor. The substrate may be glass, stainless steel, aluminium plate or any other suitable substrate that provides a smooth, continuous surface.

[0063] The dope solution may be cast at a temperature of about 25 ºC to 60 ºC. For example, the dope solution may be at a temperature of about 25 ºC to 60 ºC and the temperature of the substrate on which the dope solution is cast may be at a temperature of about 25 ºC to 60 ºC.

[0064] The casting step may be performed with a ductor blade configured to provide a layer of the cast dope solution with a desired predetermined thickness. The predetermined thickness of the layer of cast dope solution may be from about 50 micron to about 400 micron, in particular about 200 micron. For example, the predetermined thickness of the layer of cast dope solution may be 50 micron, 60 micron, 75 micron, 100 micron, 150 micron, 200 micron, 250 micron, 300 micron, 350 micron or 400 micron.

[0065] The casting step may be performed at a casting speed of about 0.5 cm/s to about 1.5 cm/s. For example, the casting speed may be 0.5 cm/s, 0.6 cm/s, 0.7 cm/s, 0.8 cm/s, 0.9 cm/s, 1.0 cm/s, 1.1 cm/s, 1.2 cm/s, 1.3 cm/s, 1.4 cm/s and 1.5 cm/s.

[0066] The layer of cast dope solution is retained on the surface of the substrate for a period of about 50 seconds to about 60 seconds in which time the layer of cast dope solution gels and forms a sheet-like membrane precursor. The membrane precursor is then detached from the surface of the substrate and then immersed in the non-solvent to facilitate phase inversion by a diffusion induced phase separation as discussed above.

[0067] In the immersing step, the membrane precursor may be immersed in the non-solvent for a period of about 40 seconds to about 300 seconds. For example, the membrane precursor may be immersed in the non-solvent for a period of 40 seconds, 50 seconds, 75 seconds, 100 seconds, 150 seconds, 200 seconds, 250 seconds or 300 seconds.

[0068] The non-solvent may be selected, at least in part, according to its capability to dissolve the porogen. The non-solvent comprises water, optionally with isopropranol in an amount of up to about 45 vol%. Alternatively, the non-solvent may comprise ethanol.

[0069] The complex phase separation process that occurs during membrane casting will affect the surface roughness and porosity which in turn will have a significant impact on surface wettability (see Science, 2003, 299, 1377). Despite the fact that the amount of plasticizer in the waste PVC is fixed, the inventors have been able to successfully prepare porous membranes from waste PVC with advantageous properties. Mixing a second solution of an appropriate porogen (that has a degree of immiscibility with the plasticizer and PVC and is fully miscibile water) at an appropriate concentration to a first solution of waste PVC can lead to the development of membranes for a wide variety of potential applications. This is likely possible in part because porogens generate pores with a much large size of approximately 5 to 100 nm. Furthermore, DMF is strategically first added to the waste PVC (a mixture of PVC and plasticizer) and then the second solution comprising porogen is added; this is done to aid in the dissolution of waste PVC and plasticiser as the addition of the

porogen from the outset will impede the PVC dissolution - the porogen will necessarily act as a non-solvent for PVC. Furthermore, the mixing of the first solution with the second solution as disclosed herein to produce a dope solution avoids the solution viscosity challenges that negatively impact the practical ability to dissolve the waste PVC.

[0070] Indeed, the fact that the inventors were able to produce porous membranes from waste PVC comprising plasticiser was surprising, given that the PVC/porogen/plasticizer system is complex and the solubility of the plasticiser in the porogen and/or the non-solvent may be unpredictable.

[0071] Embodiments of the porous membranes as prepared as described herein have a pore size in a range of 0.005 micron to 5 micron, in particular 5 to 500 nanometers.

[0072] Embodiments of the porous membranes as prepared as described herein have a porosity of 30% to 70 %.

[0073] Embodiments of the porous membranes as prepared as described herein have a density of 0.3 g/cm^3 to 1.2 g/cm^3.

[0074] Embodiments of the porous membranes as prepared as described herein have a maximum load of 1.5 N to 3.5 N.

[0075] Embodiments of the porous membranes as prepared as described herein have a reversible elongation of 25% to 70%.

[0076] The porous membranes as described herein may be suitable for in various applications including water treatment, desalination, mineral recovery, dewatering, gas and liquid purification.

EXAMPLES

[0077] Various embodiments may be illustrated by the following examples. The examples are provided for illustrative purposes only and are not to be construed as limiting the scope or content of the disclosure in any way.

Example 1. Preparation of dope solutions

[0078] Respective dope solutions of different of waste PVC particles batches (Batch 1 – moderate impurities, Batch 2 – maximum impurity allowance of 15 wt% and Batch 3 – minimum impurity allowance of 5 wt% were prepared by stirring a respective first solution comprising solubilised waste PVC particles (of varying purity) (5 g PVC in 10 g of DMF) and gradually introducing a second solution comprising polyvinylpyrrolidone (PVP) (0.8 g PVP in 4.2 g DMF) to produce respective dope solutions comprising 25 wt% waste PVC particles (1-2 mm), 4 wt% polyvinylpyrrolidone (PVP) and dimethylformamide (DMF). The dope solutions were stirred for 24 h at 60 °C. Each dope solution contained a significant amount of insoluble material which either settled or remained suspended, giving the dope solutions a turbid appearance. The dope solutions were carefully decanted to reduce the amount of insoluble solids present in the resulting porous membranes. It will be appreciated that the nature of the plasticiser and the amount of the plasticiser in the waste PVC are not known.

[0079] A dope solution was similarly prepared from a sample of Batch 1 that had undergone a physical purification process based on its density relative to water to remove metal contaminants present in the PVC cables (Purified Batch 1). In this case, the impurities were removed by solid-liquid separation techniques.

[0080] For comparison purposes, respective dope solutions of pure PVC and polyethersulfone (PES) were also prepared by stirring a mixture of pure PVC (25 wt%) or PES (25 wt%), with PVP (4 wt%) and DMF for 24 h at 60 °C.

Example 2. Casting and Phase Inversion

[0081] The dope solutions as prepared above were cast on a glass plate (12 cm x 20 cm) with a ductor blade adjusted to provide a 200 micron thick layer of dope solution.

The layer was allowed to rest for about 60 seconds post-casting before it was detached from the glass plate. The resulting membrane precursor was then immersed in deionised water for about 10 h to undergo phase inversion.

[0082] Figures 1a, 1b, 1c are scanning electron microscopy images of the porous membranes prepared from Batch 3.

Example 3. Membrane Performance – Dead-End Filtration

[0083] Figure 2 is a representation of a dead-end cell set up (Sterlitech HP4750 high-pressure stirred cell kit) used to evaluate membrane performance. Argon or air is used to exert pressure on a 0.5 wt% BSA solution at room temperature within the dead-end cell, enabling its filtration and passage through the porous membrane. The membrane is sealed with an O-ring and a spacer at the base of the cylindrical dead-end cell.

[0084] Water flux and flux recovery were assessed using the dead-end cell filtration. Pure water flux measurements were conducted at room temperature and a pressure of 1 bar, utilizing an effective membrane area of 0.0019 m^2. The flux gradually decreased due to compaction until reaching a constant flux for the clamped membrane, typically after approximately 30 minutes. Prior to experimentation, the membranes were wetted by soaking in ethanol for 10 minutes.

[0085] Clean water fluxes were measured under a constant pressure of 1 bar, while filter membrane fouling occurred with a 0.5 wt% BSA solution after 2 hours. Subsequently, the fouled membranes underwent both hydraulic and chemical cleaning. Hydraulic cleaning involved rinsing the membranes twice, followed by stirring with 60 ml of Milli-Q water for 5 minutes, and then rinsing twice more. For chemical cleaning, 100 ml of sodium hydroxide solution (2 g/L, pH 12) was added to the cell, stirred for 20 minutes, and then rinsed twice.

[0086] To calculate the flux of BSA (0.5 wt%), Equation 1 should be used:

$$\text{Flux(LMH)} = \frac{V(Litre)}{A(m^2).h(Hours)} \quad (1)$$

[0087] Figure 3 illustrates the flux of three primary membranes.

[0088] To assess membrane fouling performance, flux recovery (FR) and membrane resistance were calculated using the following equations:

$$FR\% = \frac{J_{AF}}{J_{BF}} \times 100 \quad (2)$$

[0089] where J_{BF} and J_{AF} represent the pure water flux of the membrane before fouling and after both physical and chemical cleaning, respectively.

[0090] Fouling behaviour can be determined by assessing the membrane's resistance (Rm):

$$R_m = \frac{TMP}{\mu \times J_{BF}} \quad (3)$$

[0091] where TMP is trasmembrane pressure (1 Bar = 100 Kpa), and μ is the permeate viscosity (10-3 μ.s).

[0092] Irreversible resistance (Rir) is calculated according to Equation 4:

$$R_{ir} = \frac{TMP}{\mu \times J_{AF}} - R_m \quad (4)$$

[0093] The J_{AF} is measured at 100 kPa.

[0094] Reversible resistance (Rr) is calculated according to Equation 5:

$$R_r = \frac{TMP}{\mu \times J_{AF}} - R_m - R_{ir} \quad (5)$$

[0095] where J_F is the BSA (0.5 wt%) filtration flux.

[0096] The total resistance is calculated according to Equation 6:

$$R_{Total}=R_m+R_r-R_{ir} \quad (6)$$

[0097] The measured flux for the membranes are provided in Table 1.

Membrane	FR (%)	R_m	R_{ir}	R_r	R_{Total}
	X 10^{11} m^{-1}				
Purified Batch 1	43	15.6	17.1	57.3	55.8
Batch 3	70	11.25	4.4	35.8	42.55

Table 1

[0098] The flux recovery of the membrane fabricated from Batch 3 demonstrates a substantial improvement, reaching 70%, compared to the purified Batch 1 membrane, which achieves a flux recovery of 43%. Additionally, the irreversible resistance of the Batch 3 membrane is markedly lower than that of the purified Batch 1 membrane, indicating reduced fouling. This suggests that the Batch 3 membrane can be effectively rejuvenated through washing after fouling by BSA, enhancing its utility compared to the purified Batch 1 membrane.

Example 4. Calculating membrane rejection with absorption spectroscopy

[0099] Light absorption spectroscopy was employed to assess the BSA solution (0.5 wt%) before and after filtration to evaluate the membrane ability to reject BSA. The initial solution is the feed solution (0.5 wt% BSA) and the permeate concentration represents the solution filtered through the membrane. Absorption spectroscopy may be used to determine the percentage rejection of BSA by the membrane.

[0100] The rejection of the membrane is calculated using Equation 7, where C_P is the concentration of the permeate solution and C_F is the concentration of the feed solution.

$$\text{Rejection}\% = \left(1 - \frac{C_p}{C_p}\right) \times 100 \qquad (7)$$

[0101] The respective concentration of the permeate and feed solutions for various membranes, are represented by absorption in Table 2 below. The increase in rejection rate after purification of the membranes demonstrates the effectiveness of the purification process in achieving rejection levels within the desired range. Various embodiments of the membrane have a rejection of about 50-60%.

Membrane	**Absorption of Feed solution**	**Absorption of permeate solution**	**Rejection (%)**
Batch 1	0.1	0.05	50
Purified Batch 1	0.2	0.094	55
Batch 3	2.5	1.05	58

Table 2

Example 5. Static protein absorption test

[0102] The Lowry assay analysis method was employed to assess the protein resistance characteristics of the porous membranes prepared according to the method disclosed herein. For the Lowry assay, a series of ten standard solutions with varying concentrations were prepared as specified in the kit manual. One of these solutions contained the BSA released from the membrane. Following the preparation, the standards were allowed to react for 30 minutes. During this time, each solution's colour changed from light blue to dark blue, depending on the BSA concentration. The samples were then evaluated using spectrophotometry, analyzing the absorbance at specific wavelengths. This analysis enabled the assessment of the membrane's performance and its BSA adsorption capacity.

[0103] The membranes were immersed in a 0.5 wt% bovine serum albumin (BSA) solution for 4 hours. Figure 4 shows a Lowry Standard Curve for absorbance and concentration, and Figure 5 illustrates the differences between membranes made with pure PVC and porous membranes made from waste PVC particles (Batch 2 and Batch 3). The results show that the performance of the membranes fabricated from waste PVC in accordance with the disclosure exhibit properties similar to the membrane derived from pure PVC (which does not contain any plasticizer).

Example 6. Static humic acid absorption test

[0104] The static humic acid (HA) absorption test evaluates the efficiency and effectiveness of membranes in dealing with organic contaminants like humic acid, providing insights into their anti-fouling properties and performance.

[0105] Six 50 ml bottles were filled with a soluble 0.1 wt % HA solution and porous membranes of identical size (2 cm x 2 cm) were then immersed into each bottle for six consecutive days. After each day, one membrane was removed from its respective bottle and immersed in 50 ml of Milli-Q water. The membrane was stirred for two hours to release the absorbed HA. At the end of the six-day period, a total of twelve samples were obtained: six bottles containing HA solution without membranes and six bottles containing MilliQ water with membranes. The experimental procedure is illustrated in Figure 6.

[0106] Total organic carbon (TOC) concentrations of each sample were measured with a combustion oxidation analysis using a TOC-L Series (Shimadzu Corporation).

[0107] The absorption curve shown in Figure 7 indicates that there is continuous absorption of humic acid.

Example 7. Tensile strength and elongation

[0108] The mechanical properties, in particular tensile strength and elongation at break, of the porous membranes as prepared in accordance with the disclosure were assessed using a uniaxial tensile test machine (Instron 5868). The test was conducted at a crosshead speed of 50 mm/min, with a static load cell of 10N.

Measurements were carried out at room temperature (25 °C) using film specimens having dimensions 30 mm in width and 100 mm in length.

[0109] The tensile strength test quantifies mechanical properties such as elastic properties and membrane maximum strength. Figures 8 and 9 show the maximum load force at breaking point and membrane elongation at breaking point, respectively, of porous membranes fabricated from pure PVC, pure polyethersulfone (PES), three (3) porous membranes prepared from different batches of waste PVC particles (Batches 1, 2 and 3) and a porous membrane prepared from a purified sample of Batch 1 of waste PVC particles.

[0110] The breaking point and the elongation at breaking point for all membranes prepared from waste PVC particles exceed those of the pure PVC membrane.

Example 8

[0111] For the membranes tested in the previous examples, waste PVC and PVP loadings of 25 and 4 wt.%, respectively, were used regardless of the source or purity of the PVC. This corresponds to a nominal mass ratio of 0.16:1 for the PVP to PVC/plasticizer waste mixture. In this example, a mass ratio of 0.2:1 for the PVP to PVC/plasticizer (70:30 PVC/plasticizer) mixture is used. This example is included to show that it is important to control the porogen to plasticizer loading. In a previous study examining the effect of plasticizer on membrane parameters such as strength, water flux and salt rejection, a range of porogen to PVC/plasticizer mass ratio from 0.28:1 to 0.625:1 were studied (i.e., by keeping the porogen content constant in the dope solution and varying the PVC to DOP plasticizer ratio from 16:0 to 16:20). In this example, DMF is first added to the PVC/plasticizer mixture and then the porogen is added; this is done to aid in the dissolution as the addition of the porogen from the outset will impede the PVC dissolution.

[0112] A 30 to 35 wt.% loading of plasticizer (i.e., a plasticizer to PVC ratio of 1:1.85 to 1:2.33) in PVC sheaths for electrical cables seems to be typical (Environ. Sci. Technol. 2022, 56, 14507−14516 and J. Appl. Polym. Sci., 128: 1948-1961). Furthermore, dioctyl adipate, dioctyl maleate and di(2-ethylhexyl)phthalate are broadly representative of plasticizers that could be found in waste PVC. As such, these

plasticizers are used in this example at a 1:2.33 ratio with a PVP:PVC/plasticizer loading of 0.2;1 and 0.1:1 for membrane F. These are much lower values than previously used and is a desirable trait as it also limits the amount of non-waste material used in the membrane formulation.

[0113] The membrane formulations are set out in Table 3 below.

Membrane	PVC (g)	PVP (g), porogen	DMF g), solvent	Plasticizer (g)
Pure PVC (as control) – Membrane B	2.5	0.5	20	0
PVC/dioctyl adipate (DOA) – Membrane C	1.75	0.5	20	0.75
PVC/bis(2-ethylhexyl)phthalate (DOP) – Membrane D	1.75	0.5	20	0.75
PVC/dioctyl maleate (DOM) – Membrane E	1.75	0.5	20	0.75
PVC/di(octyl adipate) – Membrane F	1.75	0.25	20	0.75

Table 3

[0114] The water flux was determined using the protocols in Example 3. The BSA rejection was determined using the protocols in Example 4. A static protein absorption test was conducted on these membranes using the protocols in Example 5. A static humic acid absorption test was conducted on these membranes using the protocols in

Example 6. The tensile strength for these membranes was determined using the protocols in Example 7.

[0115] The results of the above tests are summarised in Table 4.

	Water flux ($L/m^2 \cdot h$)	BSA rejection	Static protein absorption test (µg/mL)	Static humic acid adsorption test (after 144 hours)	Tensile strength (N)	Contact angle (°)
Membrane B	90	31.2 %	100	5.2	1.5	70-80
Membrane D	95	34.4 %	82	6.3	4.1	70-85
Membrane E	99	35.2 %	61	3.6	4.7	70-85
Membrane F	18					85-95

Table 4

[0116] For membranes D and E with DOP and DOM, respectively, the water flux is not changed greatly compared to membrane B (which has no plasticizer). However, the tensile strength is significantly increased for membranes D and E which is consistent with the presence of a plasticiser. Interestingly, membrane F with DOA as a plasticizer shows noticeably lower water flux. Based on the Hansen solubility parameters, it is evident that the miscibility of DOA with both PVC and PVP is relatively poor in comparison to the miscibility of DOP and DOM with PVC. When comparing membrane B with membranes D/E, the BSA rejection is not strongly

affected. The pore size differences between membranes B, D and E likely explains the differences in the humic acid adsorption as humic acid is a class of relatively large molecules. Notably, there is a correlation between contact angle and water flux; membranes B, D and E have a higher water flux and lower contact angle than membrane F which has a markedly lower water flux and a higher contact angle. This is consistent with the more hydrophobic membrane F having a lower water flux.

[0117] It is evident from SEM images in Figure 10 that membranes D and E have a smooth surface with a fairly well-defined surface pore structure. Membrane B (PVC without any plasticizer) has a distinctly different and less well-defined surface pore structure. While membrane B has good water flux, its mechanical strength is problematic suggesting that the presence of a plasticizer (which is present in waste PVC) is advantageous. DOA is less miscible with both PVC and PVP which negatively impacts pore formation while plasticisers which are miscible with PVC but not PVP, such as DOM and DOP, assist with the pore formation.

[0118] It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the above-described embodiments, without departing from the broad general scope of the present disclosure. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

[0119] In the claims which follow and in the preceding description except where the context requires otherwise due to express language or necessary implication, the word “comprise” or variations such as “comprises” or “comprising” is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

CLAIMS:

1. A method of preparing porous membranes from waste PVC plastics comprising unknown fixed quantities of plasticizer, the method comprising the steps of:

providing a first solution comprising waste PVC particles and said plasticizer in a first aprotic solvent;

providing a second solution comprising a porogen in a second aprotic solvent;

mixing the first and second solutions to provide a dope solution comprising solubilised waste PVC particles, said plasticizer and the porogen in the first and second aprotic solvents;

casting the dope solution in a layer having a predetermined thickness on a surface of a substrate to form a membrane precursor; and

immersing the membrane precursor in a non-solvent for a period of time sufficient for the membrane precursor to undergo phase inversion and produce the porous membrane.

2. The method according to claim 1, wherein the waste PVC particles comprise comminuted PVC sheath from electrical cables.

3. The method according to claim 1 or claim 2, wherein the waste PVC particles have a particle size of about 1 mm to about 2 mm.

4. The method according to any one of claims 1 to 3, wherein the dope solution consists essentially of solubilised waste PVC particles, said plasticizer and the porogen in the first and second aprotic solvents.

5. The method according to any one of claims 1 to 3, wherein the dope solution consists of solubilised waste PVC particles, said plasticizer and the porogen in the first and second aprotic solvents.

6. The method according to any one of claims 1 to 5, wherein the dope solution comprises from about 12.5 wt% to about 25 wt% waste PVC particles and about 2 wt% to about 5 wt% porogen.

7. The method according to any one of claims 1 to 6, wherein the porogen comprises polyvinyl pyrrolidone (PVP), polyethylene glycol (PEG), polyvinyl alcohol (PVA) or polyethylene oxide (PEO).

8. The method according to any one of claims 1 to 7, wherein the first and second aprotic solvents may be the same or different.

9. The method according to any one of claims 1 to 8, wherein the aprotic solvent comprises N-N-dimethylacetamide, (DMAc), N, N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), or tetrahydrofuran (THF).

10. The method according to any one of claims 1 to 9, wherein the step of casting the dope solution is performed at a casting speed of about 0.5 cm/s to about 1.5 cm/s.

11. The method according to any one of claims 1 to 10, wherein the predetermined thickness of the layer of the cast dope solution is from about 50 micron to about 400 micron.

12. The method according to any one of claims 1 to 11, wherein the substrate on which the dope solution is cast is glass, stainless steel, aluminium plate.

13. The method according to any one of claims 1 to 12, wherein the dope solution is cast at a temperature of about 25 ºC to 60 ºC.

14. The method according to any one of claims 1 to 13, wherein the layer of cast dope solution is retained on the surface of the substrate for a period of about 50 seconds to about 60 seconds before immersing the membrane precursor in the non-solvent.

15. The method according to any one of claims 1 to 14, wherein the membrane precursor is immersed in the non-solvent for a period of about 40 seconds to about 300 seconds.

16. The method according to any one of claims 1 to 15, wherein the non-solvent comprises water, optionally with isopropranol in an amount of up to about 45 vol%.