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(54) **Title**: CURABLE COMPOSITIONS AND MEMBRANES

(57) **Abstract**: A curable composition comprising: (i) 2.5 to 50 wt% crosslinker comprising at least two acrylamide groups; (ii) 20 to 65 wt% curable ionic compound comprising an ethylenically unsaturated group and an anionic group; (iii)15 to 45 wt% solvent; and (iv) 0 to 10 wt% of free radical initiator; wherein the molar ratio of (i):(ii) is 0.1 to 1.5. The compositions are useful for preparing ion exchange membranes.

CURABLE COMPOSITIONS AND MEMBRANES

This invention relates to curable compositions, to their use in the preparation of membranes and to the use of such membranes in ion exchange processes.

Ion exchange membranes are useful in a number of applications, including electrodeionisation (EDI), continuous electrodeionisation (CEDI), electrodialysis (ED), electrodialysis reversal (EDR) and capacitive deionisation used in e.g. flow through capacitors (FTC) for the purification of water, Donnan or diffusion dialysis (DD) for e.g. fluoride removal or the recovery of acids, pervaporation for dehydration of organic solvents, fuel cells, electrolysis (EL) of water or for chlor-alkali production, and reverse electrodialysis (RED) where electricity is generated from two streams differing in salt concentration separated by an ion-permeable membrane.

Electrodeionization (EDI) is a water treatment process wherein ions are removed from aqueous liquids using a membrane and an electrical potential to effect ion transport. It differs from other water purification technologies, such as conventional ion exchange, in that it is does not require the use of chemicals such as acids or caustic soda. EDI can be used to produce ultra pure water.

Electrodialysis (ED) and Electrodialysis Reversal (EDR) are electrochemical separation processes that remove ions and other charged species from water and other fluids. ED and EDR use small quantities of electricity to transport these species through membranes composed of ion exchange material to create separate purified and concentrated streams. Ions are transferred through the membranes by means of direct current (DC) voltage and are removed from the feed fluid as the current drives the ions through the membranes to desalinate the process stream. ED and EDR are suitable techniques for producing drinking water. Ion exchange membranes are also used in Zero Discharge Desalination (ZDD).

A membrane electrode assembly (MEA) appears suitable for a variety of applications such as electrolysis, sensors and especially fuel cells.

A flow through capacitor (FTC) is an efficient means of chemical-free Total Dissolved Solids (TDS) reduction using electrically charged carbon electrodes to remove ions.

One of the important problems in the production of ion exchange membranes is how to provide thin membranes with minimal defects. Desirably the membranes have good permselectivity and low electrical resistance. Additionally the membranes are desired to be strong, while at the same time being flexible. Flexibility is required for membranes which are to be wound into tight

circumferential structures. The membranes also need to retain their physical integrity over an extended period of time. Desirably the method used to prepare the membranes does not result in excessive curl. It is also desirable for the membranes to be resistant to the chemicals that they can come into contact with, e.g. resistant to hydrolysis.

Membrane users require the lowest prices available, which means production processes for the membranes are ideally inexpensive and the membranes should be easily capable of mass production.

US 2008/286627 describes the preparation of membranes for use in fuel cells. Example 6 comprises approximately 10 parts of crosslinker having two acrylamide groups, 40 parts curable ionic monomer and 50 parts water, together with a photoinitiator. However the compositions used in the Examples contain more than 45 wt% of solvent.

The present invention seeks to provide compositions suitable for use in the preparation of membranes, in addition to rapid processes for preparing the membranes, the membranes prepared by the processes and their uses.

According to a first aspect of the present invention there is provided a curable composition comprising:

(i) 2.5 to 50 wt% crosslinker comprising at least two acrylamide groups;

(ii) 20 to 65 wt% curable ionic compound comprising an ethylenically unsaturated group and an anionic group;

(iii) 15 to 45 wt% solvent; and

(iv) 0 to 10 wt% of free radical initiator;

wherein the molar ratio of (i):(ii) is 0.1 to 1.5.

Surprisingly when the molar ratio of (i):(ii) is from 0.1 to 1.5 membranes derived from the compositions have good combination of high permselectivity and low resistivity compared to when the molar ratio is outside of this range.

Preferably the composition has a pH of 0.8 to 12, more preferably 1 to 11.

The preferred pH of the composition depends to some extent on whether the curable ionic compound is in the free acid or salt form. When the curable ionic compound is in the free acid form the composition preferably has a pH of 1.1 to 5, more preferably 1.1 to 2.5, especially about 1.5. When the curable ionic compound is at least 95% in the salt form the composition preferably has a pH of 2 to 10, more preferably 3 to 8, especially 4 to 7 and more especially 4 to 5.

In one embodiment the composition is free from free radical initiators or further comprises 0.005 to 10 wt% of photoinitiator.

The crosslinker is preferably present in the composition in an amount of 4 to 45 wt%, more preferably 6 to 45 wt%, especially 8 to 40 wt% and more especially 9 to 25 wt%. A relatively high crosslinker content generally results in a

high permselectivity with a high electrical resistance while for a relatively low crosslinker content the formed membrane structure is more open resulting in a somewhat lower permselectivity. A relatively low crosslinker content allows for a higher content of curable ionic compounds and a higher degree of swelling, both of which can be useful for obtaining a membrane having low electrical resistance.

The ratio of crosslinker:curable ionic compound is selected depending on the desired properties for the resultant membrane, which in turn depend on the intended use of the membrane.

When a membrane having low electrical resistance is desired, the amount of curable ionic monomer used in the composition is preferably high, while the amount of crosslinker will be reduced in order to accommodate the higher amount of curable ionic monomer. Thus to prepare membranes having low electrical resistance the preferred crosslinker content is 4 to 20 wt% (e.g. 4 to 20 wt%), more preferably 6 to 15 wt% (e.g. 6 to 15 wt%), especially about 6 to about 12 wt%. With this amount of crosslinker, one can still obtain a reasonably strong membrane with good permselectivity and without excessive swelling. When a membrane having high permselectivity is desired, the amount of crosslinker present in the composition will generally be chosen higher, preferably in an amount of 14 to 48 wt%, more preferably from 22 to 43 wt%, especially 28 to 38 wt%.

The crosslinker preferably has two or three acrylamide groups, more preferably two acrylamide groups.

The molecular weight of the crosslinker preferably satisfies the equation:

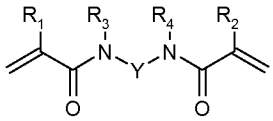
$$(Y \times m) > \text{molecular weight of the crosslinker}$$

wherein m is the number of acrylamide groups in the crosslinker; and

Y is 120, more preferably 105, especially 90, more especially 85 or 77.

The lower values of Y mentioned above are preferred because the resultant crosslinkers crosslink more efficiently than when Y is higher. Furthermore, crosslinkers having the lower values of Y mentioned above have lower molecular weights, leaving room for higher amounts of curable ionic compound and thereby achieving a lower electrical resistance for the same level of crosslinking and permselectivity.

The crosslinker is preferably of the Formula (1):



Formula (1)

wherein:

R_1 and R_2 are each independently H or methyl;

R_3 and R_4 are each independently H, alkyl, R_3 and R_4 together with the N groups to which they are attached and Y form an optionally substituted 6- or 7-membered ring; and

Y is an optionally substituted and optionally interrupted alkylene group.

When R_3 or R_4 is alkyl it is preferably C_{1-4}-alkyl.

When R_3 and R_4 together with the N groups to which they are attached and Y form an optionally substituted 6- or 7-membered ring they preferably form a piperazine, homopiperazine or triazine ring.

The optional interruptions which may be present in Y are preferably ether or, more preferably, amino groups. Y is preferably of the formula $-(C_nH_{2n})-$ wherein n is 1, 2 or 3.

Examples of suitable crosslinkers there may be mentioned N,N'- methylene bis(meth) acrylamide, N,N'-ethylenebis(meth)acrylamide, N,N'-propylenebis(meth)acrylamide, N,N'-butylenebis(meth)acrylamide, N,N′-(1,2-dihydroxyethylene) bis-(meth)acrylamide, 1,4-diacryoyl piperazine, 1,4-bis(acryloyl)homopiperazine, triacryloyl-tris(2-aminoethyl)amine, triacroyl diethylene triamine, tetra acryloyl triethylene tetramine, 1,3,5-triacryloylhexahydro-1,3,5-triazine and/or 1,3,5-trimethacryloylhexahydro-1,3,5-triazine. The term '(meth)' is an abbreviation meaning that the 'meth' is optional, e.g. N,N'-methylene bis(meth) acrylamide is an abbreviation for N,N'-methylene bis acrylamide and N,N'-methylene bis methacrylamide.

More preferably R_3 and R_4 are both H and Y is an optionally substituted C_{1-3}-alkylene group or an optionally substituted -(C_{1-3}-alkylene-NR_5- C_{1-3}-alkylene)-group wherein R_5 is H or C_{1-4} -alkyl. Especially preferred crosslinkers are N,N'-methylene bis(meth) acrylamide, N,N'-ethylenebis(meth)acrylamide, N,N'-propylenebis(meth)acrylamide, N,N′-(1,2-dihydroxyethylene) bis-(meth)acrylamide, triacryloyl-tris(2-aminoethyl)amine and triacroyl diethylene triamine. The curable ionic compound is preferably present in the composition in an amount of 25 to 65 wt%, more preferably 35 to 60 wt%, especially 40 to 57 wt% and more especially 45 to 55 wt%. In general, if one wishes to maximise the

electrical charge density in the membrane one will choose an amount of curable ionic compound which is at or towards the higher end of the aforementioned ranges.

Preferably the molar ratio of component (i) to (ii) is 0.1 to 1.0, more preferably 0.13 to 0.7.

Preferred curable ionic compounds comprise an acidic group, for example a sulpho, carboxy and/or phosphato group. In view of the pH of the composition these groups will be often be partially or wholly in salt form. The preferred salts are lithium, ammonium, sodium and potassium salts and mixtures comprising two or more thereof.

Examples of curable ionic compounds include acrylic acid, beta carboxy ethyl acrylate, maleic acid, maleic acid anhydride, vinyl sulphonic acid, phosphonomethylated acrylamide, (2-carboxyethyl)acrylamide and 2-(meth)acrylamido-2-methylpropanesulfonic acid.

The total wt% of components (i) + (ii) relative to the total weight of the composition is preferably 30 to 90 wt%, more preferably 30 to 85 wt%, especially 40 to 80 wt%, more especially 50 to 75 wt%, particularly 58 to 70 wt%, e.g. about 61 wt% or about 65 wt%. If one wishes to avoid swelling of the membrane and lower permselectivity the total wt% of components (i) + (ii) is preferably above 30 wt%.

The curable composition may comprise one or more than one crosslinker as component (i). In a particularly preferred embodiment component (i) consist of crosslinking agent(s) having two acrylamide groups and component (ii) consists of curable ionic compound(s) having one ethylenically unsaturated group and one or more anionic group(s). Preferably the ethylenically unsaturated group in component (ii) is a (meth)acrylamide group because this can result in membranes having particularly good resistance to hydrolysis. The most preferred curable ionic compound is 2-acrylamido-2-methylpropanesulfonic acid and salts thereof.

Generally component (i) provides strength to the membrane, while potentially reducing flexibility.

When component (ii) has only one acrylamide group (e.g. one H_2C=CHCON< group) it is unable to crosslink. However it is able to react with component (i). Component (ii) can provide the resultant membrane with a desirable degree of flexibility, which is particularly useful in applications requiring tightly wound membranes. Component (ii) also assists the membrane in distinguishing between ions of different charges by the presence of anionic groups.

In one embodiment the composition comprises less than 10wt%, more preferably less than 5wt%, of ethylenically unsaturated compounds other than

components (i) and (ii). In a preferred embodiment the composition is free from ethylenically unsaturated compounds other than components (i) and (ii).

The solvent content of the composition is preferably the minimum, or less than 5% more than the minimum, necessary to achieve the composition in the form of a homogeneous solution, while at the same time being at least 15 wt%.

Polar solvents, especially aqueous solvents, are preferred because these are particularly good at dissolving the curable ionic compound. Preferably at least half, more preferably at least 40 wt%, of the solvent is water, with the balance comprising organic solvent. The organic solvent can be useful for providing a homogenous solution of all the components of the composition. The inclusion of an organic solvent may also have advantages in the process for preparing the membrane because many organic solvents will usefully reduce the viscosity and/or surface tension of the composition, making the manufacturing process easier in some respects. Preferably the solvent comprises at least 40 wt% water, more preferably at least 60 wt% water. Preferably the composition comprises 15 to 45 wt%, more preferably 16 to 40 wt%, especially 20 to 40 wt% and more especially 22 to 35 wt% solvent.

The solvent is preferable water or a mixture comprising water and a water-miscible organic solvent. Due to the presence of a water-miscible organic solvent, water-immiscible solvents may also be tolerated in small amounts such that the overall solvent mixture is miscible.

When the solvent comprises water and an organic solvent the weight ratio of water:organic solvent is preferably higher than 2:3, more preferably between 10:1 and 1:1, more preferably between 10:1 and 1:2, especially between 4:1 and 1:1, and more especially between 3:1 and 2:1.

The organic solvent is optionally a single organic solvent or a combination of two or more organic solvents.

Preferred organic solvents include C_{1-4} -alcohols (e.g. methanol, ethanol and propan-2-ol, diols (e.g. ethylene glycol and propylene glycol), triols (e.g. glycerol), carbonates (e.g. ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, di-t-butyl dicarbonate and glycerin carbonate), dimethyl formamide, acetone, N-methyl-2-pyrrolidinone and mixtures comprising two or more thereof. A particularly preferred organic solvent is propan-2-ol.

In one embodiment the organic solvent has a low boiling point, e.g. a boiling point below 100°C. Solvents having a low boiling point can be easily removed by evaporation, avoiding the need for a washing step for removal of the solvent.

The optimum solvent content for the curable composition depends to some extent on the interaction between the solvent, the curable compound(s) and the

crosslinker, and can be determined for each combination by simple experimentation.

When the composition contains 0% free radical initiator it may be cured using electron beam radiation.

Preferably the composition comprises 0.01 to 10 wt%, more preferably 0.05 to 5 wt%, especially 0.1 to 2 wt% free radical initiator. The preferred free radical initiator is a photoinitiator.

The curable composition may comprise one or more than one free radical initiator as component (iv).

For acrylamides, diacrylamides, and higher-acrylamides, type I photoinitiators are preferred. Examples of type I photoinitiators are as described in WO 2007/018425, page 14, line 23 to page 15, line 26, which are incorporated herein by reference thereto. Especially preferred photoinitiators include alpha-hydroxyalkylphenones, e.g. 2-hydroxy-2-methyl-1-phenyl propan-1-one and 2-hydroxy-2-methyl-1-(4-tert-butyl-) phenylpropan-1-one, and acylphosphine oxides, e.g. 2,4,6-trimethylbenzoyl-diphenylphosphine oxide, and bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide.

The curable composition optionally contains (v) 0 to 20wt%, preferably 0 to 10wt%, of curable compound(s) having one ethylenically unsaturated group and no ionic groups.

When a radical initiator is present in the composition, preferably a polymerization inhibitor is also included (e.g. in an amount of below 2 wt%). This is useful to prevent premature curing of the composition during, for example, storage. Suitable inhibitors include hydroquinone, hydroquinone mono methyl ether, 2,6-di-t-butyl-4-methylphenol, 4-t-butyl-catechol, phenothiazine, 4-oxo-2,2,6,6-tetramethyl-1-piperidinoloxy, free radical, 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinoloxy, free radical, 2,6-dinitro-sec-butylphenol, tris(N-nitroso-N-phenylhydroxylamine) aluminum salt, Omnistab™ IN 510 and mixtures comprising two or more thereof.

The curable composition may contain other components, for example acids, pH controllers, preservatives, viscosity modifiers, stabilisers, dispersing agents, antifoam agents, organic/inorganic salts, anionic, cationic, non-ionic and/or amphoteric surfactants, buffers and the like.

The curable composition may of course contain further components not specifically mentioned or excluded above.

Curing rates may be increased by including an amine synergist in the curable composition. Suitable amine synergists are, for example, free alkyl amines, e.g. triethylamine or triethanol amine; aromatic amines, e.g. 2-ethylhexyl-

4-dimethylaminobenzoate, ethyl-4-dimethylaminobenzoate and also polymeric amines as polyallylamine and its derivatives.

Curable amine synergists such as ethylenically unsaturated amines (*e.g.* acrylated amines) are preferable since their use will give less odour due to their ability to be incorporated into the membrane by curing and also because they may contain a basic group which can be useful in the final (anion permeable) membrane.

The amount of amine synergists, when used, is preferably from 0.1 to 10 wt.% based on the total weight of polymerisable components in the composition, more preferably from 0.3 to 3 wt%.

In view of the foregoing a particularly preferred composition comprises a curable composition comprising:

(i) 8 to 16 wt% crosslinker comprising at least two acrylamide groups;

(ii) 40 to 60 wt% curable ionic compound comprising an ethylenically unsaturated group and an anionic group;

(iii) 22 to 40 wt% solvent; and

(iv) 0.01 to 2 wt% of photoinitiator;

wherein the molar ratio of (i):(ii) is 0.1 to 1.5, preferably 0.1 to 1.0.

In another embodiment a particularly preferred composition comprises:

(i) 4 to 30 wt% crosslinker comprising at least two acrylamide groups;

(ii) 35 to 60 wt% curable ionic compound comprising an ethylenically unsaturated group and an anionic group;

(iii) 26 to 45 wt% solvent; and

(iv) 0.01 to 2 wt% of photoinitiator;

wherein the molar ratio of (i):(ii) is 0.1 to 1.0, preferably 0.13 to 0.7.

Preferably the ethylenically unsaturated group is a (meth)acrylamide group.

Preferably the number of parts of (i), (ii), (iii) and (iv) (when present) in the aforementioned curable compositions add up to 100. This does not rule out the presence of further, different components, but merely sets the ratio of the mentioned components relative to each other.

Preferably the curable composition is free from, or substantially free from, methacrylic compounds (e.g. methacrylate and methacrylamide compounds), i.e. the composition comprises at most 10 wt% of compounds which are free from acrylic groups and comprise one or more methacrylic groups.

Preferably the curable composition is free from, or substantially free from, divinyl benzene.

Preferably the curable composition is free from, or substantially free from, styrene.

Preferably the curable composition is free from, or substantially free from, dyes and pigments. This is because there is no need to include dyes or pigments in the composition.

Thus the preferred curable composition is free from, or substantially free from, divinyl benzene, dyes, pigments, styrene, methacrylic compounds and compounds having tetralkyl-substituted quaternary ammonium groups.

According to a second aspect of the present invention there is provided a process for preparing a membrane comprising the following steps:

(i) applying a curable composition to a support; and

(ii) curing the composition to form a membrane;

wherein the curable composition is as defined in the first aspect of the present invention.

Hitherto such membranes have often been made in slow and energy intensive processes, often having many stages. The present invention enables the manufacture of membranes in a simple process that may be run continuously for long periods of time to mass produce membranes relatively cheaply.

Optionally the process comprises the further step of separating the cured composition and support. However if desired this further step may be omitted and thereby a composite membrane is produced comprising the cured composition and a porous support.

The membrane is preferably a cation exchange membrane.

The thickness of the membrane, including the support, when present, is preferably less than 250 μm, more preferably between 10 and 200 μm, most preferably between 20 and 150 μm.

Preferably the membrane has an ion exchange capacity of at least 0.1meq/g, more preferably of at least 0.3meq/g, especially more than 0.6meq/g, more especially more than 1.0meq/g, based on the total dry weight of the membrane and any porous support and any porous strengthening material which remains in contact with the resultant membrane. Ion exchange capacity may be measured by titration as described by Djugolecki et al, J. of Membrane Science, 319 (2008) on page 217.

Preferably the membrane has a permselectivity for small cations (e.g. Na^+) of more than 85%, more preferably more than 90% and especially more than 95%.

Preferably the membrane has an electrical resistance less than 15ohm.cm^2, more preferably less than 5ohm.cm^2, most preferably less than 3ohm.cm^2. For certain applications a high electrical resistance may be acceptable especially when the permselectivity is very high, e.g. higher than 95%. The electrical resistance may be determined by the method described below in the examples section.

Preferably the membrane exhibits a swelling in water of less than 100%, more preferably less than 75%, most preferably less than 60%. The degree of swelling can be controlled by the amount of crosslinker, the amount of non-curable compounds and by selecting appropriate parameters in the curing step and further by the properties of the porous support.

Electrical resistance, permselectivity and % swelling in water may be measured by the methods described by Djugolecki et al, J. of Membrane Science, 319 (2008) on pages 217-218.

Typically the ion exchange membrane is substantially non-porous e.g. the pores are smaller than the detection limit of a standard Scanning Electron Microscope (SEM). Thus using a Jeol JSM-6335F Field Emission SEM (applying an accelerating voltage of 2kV, working distance 4 mm, aperture 4, sample coated with Pt with a thickness of 1.5nm, magnification 100,000x, 3° tilted view) the average pore size is generally smaller than 5nm, preferably smaller than 2 nm.

The resultant membrane preferably has a low water permeability so that ions may pass through the membrane and water molecules do not pas through the membrane. Preferably the membrane's water permeability is lower than 1.10^{-7} $m^3/m^2.s.kPa$, more preferably lower than 1.10^{-8} $m^3/m^2.s.kPa$, most preferably lower than 5.10^{-9} $m^3/m^2.s.kPa$, especially lower than 1.10^{-9} $m^3/m^2.s.kPa$. The requirements for water permeability depend on the intended use of the membrane.

Where desired, a surfactant or combination of surfactants may be included in the composition as a wetting agent or to adjust surface tension. Commercially available surfactants may be utilized, including radiation-curable surfactants. Surfactants suitable for use in the composition include non-ionic surfactants, ionic surfactants, amphoteric surfactants and combinations thereof.

Preferably the components of the curable composition are selected such that no phase separation occurs during the curing step. In this way, the likelihood of a porous structure in the resultant membrane is reduced.

The network structure of the membrane is determined to a large extent by the identity of the crosslinking agent(s) and the curable compound and their functionality, e.g. the number of crosslinkable groups they contain per molecule.

During the curing process, the curable composition may form a layer on top of the support, or it may permeate wholly or partially into the pores of the support thereby forming an impregnated composite membrane. The curable composition may also be applied to both sides of the support to achieve a symmetrical composite membrane. In a preferred embodiment the support is saturated with the composition and the saturated support is cured by EB or UV irradiation.

The process of the present invention may contain further steps if desired, for example washing and/or drying the resultant membrane.

Before applying the curable composition to the surface of the support, the support may be subjected to a corona discharge treatment, plasma glow discharge treatment, flame treatment, ultraviolet light irradiation treatment, chemical treatment or the like, e.g. for the purpose of improving its wettability and the adhesiveness.

The support may also be treated to modify its surface energy, e.g. to values above 70 mN/m.

While it is possible to prepare the membrane on a batch basis using a stationary support, to gain full advantage of the invention it is much preferred to prepare the membrane on a continuous basis using a moving support. The support may be in the form of a roll which is unwound continuously or the support may rest on a continuously driven belt (or a combination of these methods). Using such techniques the curable composition can be applied to the support on a continuous basis or it can be applied on a large batch basis.

The curable composition may be applied to the support by any suitable method, for example by curtain coating, blade coating, air-knife coating, knife-over-roll coating, slide coating, nip roll coating, forward roll coating, reverse roll coating, micro-roll coating, dip coating, foulard coating, kiss coating, rod bar coating or spray coating. The coating of multiple layers can be done simultaneously or consecutively. When coating multiple layers the curable compositions may be the same of different. For simultaneous coating of multiple layers, curtain coating, slide coating and slot die coating are preferred. The curable composition(s) may be applied to one side of the support or to both sides of the support.

In one embodiment at least two of the curable compositions, which may be the same of different, are applied to the support, e.g. simultaneously or consecutively. The curable compositions may be applied to the same side of the support or to different sides. Thus the application step may be performed more than once, either with or without curing being performed between each application. When applied to different sides the resultant composite membrane may be symmetrical or asymmetrical and the layers of curable composition may have the same or different thicknesses. When applied to the same side a composite membrane may be formed comprising at least one top layer and at least one bottom layer that is closer to the support than the top layer. In this embodiment the top layer and bottom layer, together with any intervening layers, constitute the membrane and the porous support provides strength to the resultant composite membrane.

Thus in a preferred process, the curable composition is applied continuously to a moving support, more preferably by means of a manufacturing unit comprising one or more curable composition application station(s), one or more irradiation source(s) for curing the composition, a membrane collecting station and a means for moving the support from the curable composition application station(s) to the irradiation source(s) and to the membrane collecting station.

The curable composition application station(s) may be located at an upstream position relative to the irradiation source(s) and the irradiation source(s) is/are located at an upstream position relative to the membrane collecting station.

In order to produce a sufficiently flowable curable composition for application by a high speed coating machine, it is preferred that the curable composition has a viscosity below 5000mPa.s when measured at 35°C, more preferably from 1 to 1500mPa.s when measured at 35°C. Most preferably the viscosity of the curable composition is from 2 to 500mPa.s when measured at 35°C. For coating methods such as slide bead coating the preferred viscosity is from 2 to 150mPa.s when measured at 35°C.

With suitable coating techniques, the curable composition may be applied to a support moving at a speed of over 5m/min, preferably over 10m/min, more preferably over 15m/min, e.g. more than 20m/min, or even higher speeds, such as 60m/min, 120m/min or up to 400m/min can be reached.

Curing is preferably performed by radical polymerisation, preferably using electromagnetic radiation. The source of radiation may be any source which provides the wavelength and intensity of radiation necessary to cure the composition. A typical example of a UV light source for curing is an D-bulb with an output of 600 Watts/inch (240 W/cm) as supplied by Fusion UV Systems. Alternatives are the V-bulb and the H-bulb from the same supplier.

When no photo-initiator is included in the curable composition, the composition can be cured by electron-beam exposure, e.g. using an exposure of 50 to 300 keV. Curing can also be achieved by plasma or corona exposure

During curing the components (i) and (ii) polymerise to form a polymeric membrane. The curing may be brought about by any suitable means, e.g. by irradiation and/or heating. Preferably curing occurs sufficiently rapidly to form a membrane within 30 seconds. If desired further curing may be applied subsequently to finish off, although generally this is not necessary.

The curing is preferably achieved thermally (e.g. by irradiating with infrared light) or, more preferably, by irradiating the composition with ultraviolet light or an electron beam.

For thermal curing the curable composition preferably comprises one or more thermally reactive free radical initiators, preferably being present in an amount of 0.01 to 5 parts per 100 parts of curable composition, wherein all parts are by weight.

Examples of thermally reactive free radical initiators include organic peroxides, e.g. ethyl peroxide and/or benzyl peroxide; hydroperoxides, e.g. methyl hydroperoxide, acyloins, e.g. benzoin; certain azo compounds, e.g. α,α'-azobisisobutyronitrile and/or γ,γ'-azobis(γ-cyanovaleric acid); persulfates; peracetates, e.g. methyl peracetate and/or tert-butyl peracetate; peroxalates, e.g. dimethyl peroxalate and/or di(tert-butyl) peroxalate; disulfides, e.g. dimethyl thiuram disulfide and ketone peroxides, e.g. methyl ethyl ketone peroxide. Temperatures in the range of from about 30°C to about 150°C are generally employed for infrared curing. More often, temperatures in the range of from about 40°C to about 110°C are used.

Preferably curing of the curable composition begins within 3 minutes, more preferably within 60 seconds, after the composition has been applied to the support.

Preferably the curing is achieved by irradiating the curable composition for less than 30 seconds, more preferably less than 10 seconds, especially less than 3 seconds, more especially less than 2 seconds. In a continuous process the irradiation occurs continuously and the speed at which the curable composition moves through the beam of irradiation is mainly what determines the time period of curing.

Preferably the curing uses ultraviolet light. Suitable wavelengths are for instance UV-A (390 to 320nm), UV-B (320 to 280nm), UV-C (280 to 200nm) and UV-V (445 to 395nm), provided the wavelength matches with the absorbing wavelength of any photo-initiator included in the curable composition.

Suitable sources of ultraviolet light are mercury arc lamps, carbon arc lamps, low pressure mercury lamps, medium pressure mercury lamps, high pressure mercury lamps, swirlflow plasma arc lamps, metal halide lamps, xenon lamps, tungsten lamps, halogen lamps, lasers and ultraviolet light emitting diodes. Particularly preferred are ultraviolet light emitting lamps of the medium or high pressure mercury vapour type. In most cases lamps with emission maxima between 200 and 450nm are particularly suitable.

The energy output of the irradiation source is preferably from 20 to 1000 W/cm, preferably from 40 to 500 W/cm but may be higher or lower as long as the desired exposure dose can be realized. The exposure intensity is one of the parameters that can be used to control the extent of curing which influences the final structure of the membrane. Preferably the exposure dose is at least

40mJ/cm^2, more preferably between 40 and 1500mJ/cm^2, most preferably between 70 and 900mJ/cm^2 as measured by an High Energy UV Radiometer (UV PowerMap™ from EIT, Inc) in the UV-A and UV-B range indicated by the apparatus. Exposure times can be chosen freely but preferably are short and are typically less than 10 seconds, more preferably less than 5 seconds, especially less than 3 seconds, more especially less than 2 seconds, e.g. between 0.1 and 1 second.

To reach the desired exposure dose at high coating speeds, more than one UV lamp may be used, so that the curable composition is irradiated more than once. When two or more lamps are used, all lamps may give an equal dose or each lamp may have an individual setting. For instance the first lamp may give a higher dose than the second and following lamps or the exposure intensity of the first lamp may be lower. Varying the exposure dose of each lamp may influence the polymer matrix structure and the final crosslink density. In a preferred embodiment the composition is cured by simultaneous irradiation from opposite sides using two or more irradiation sources, e.g. two lamps (one at each side). The two or more irradiation sources preferably irradiate the composition with the same intensity as each other. By using this symmetric configuration, a higher crosslinking efficiency can be achieved and curling of the membrane can be reduced or prevented.

Photoinitiators may be included in the curable composition, as mentioned above, and are usually required when curing uses UV or visible light radiation. Suitable photoinitiators are those known in the art.

Curing by irradiation with UV or electron beam is preferably performed at between 20 and 60°C. While higher temperatures may be used, these are not preferred because they can lead to higher manufacturing costs.

Preferred supports are porous, e.g. they may be a woven or non-woven synthetic fabric, e.g. polyethylene, polypropylene, polyacrylonitrile, polyvinyl chloride, polyester, polyamide, and copolymers thereof, or porous membranes based on e.g. polysulfone, polyethersulfone, polyphenylenesulfone, polyphenylenesulfide, polyimide, polyethermide, polyamide, polyamideimide, polyacrylonitrile, polycarbonate, polyacrylate, cellulose acetate, polypropylene, poly(4-methyl 1-pentene), polyinylidene fluoride, polytetrafluoroethylene, polyhexafluoropropylene, polychlorotrifluoroethylene, and copolymers thereof.

Various porous supports are available commercially, e.g. from Freudenberg Filtration Technologies (Novatexx materials) and Sefar AG.

Surprisingly, ion exchange membranes with anionic groups (e.g. sulpho, carboxyl and phosphato groups) can exhibit good properties in terms of their

permselectivity and conductivity while at the same time being not overly expensive to manufacture by the present process.

The present process allows the preparation of membranes having a desirable degree of flexibility, without being overly flexible or too rigid. The presence of the solvent improves coatability for the curable composition and can provide thin membranes with low numbers of defects, low tendency to curl while retaining good durability in use.

According to a third aspect of the present invention there is provided a membrane obtained by a process according to the second aspect of the present invention.

The membranes according to the third aspect of the present invention may also be put to other uses requiring membranes having anionic groups.

The membranes according to the third aspect of the present invention preferably have the properties described above in relation to the second aspect of the present invention.

The membranes of the invention are particularly useful for ED, (C)EDI, EDR, FTC, ZDD and RED, although they may also be used for other purposes.

According to a fourth aspect of the present invention there is provided use of a membrane according to the third aspect of the present invention for water purification or for the generation of electricity.

According to a fourth aspect of the present invention there is provided an electrodialysis or reverse electrodialysis unit, an electrodeionization module or a flow through capacitor comprising one or more membranes according to the third aspect of the present invention. The electrodeionization module is preferably a continuous electrodeionization module.

Preferably the electrodialysis or reverse electrodialysis unit or the electrodeionization module or the flow through capacitor comprises at least one anode, at least one cathode and one or more membrane according to the third aspect of the present invention. Further the unit preferably comprises an inlet for providing a flow of relatively salty water along a first side of a membrane according to the present invention and an inlet for providing a less salty flow water along a second side of the membrane such that ions pass from the first side to the second side of the membrane. Preferably the one or more membranes of the unit comprise a membrane according to the third aspect of the present invention having anionic groups and a further membrane having cationic groups.

In a preferred embodiment the unit comprises at least 3, more preferably at least 5, e.g. 36, 64 or up to 500, membranes according to the third aspect of the present invention, the number of membranes being dependent on the application. The membrane may for instance be used in a plate-and-frame or stacked-disk

configuration or in a spiral-wound design. Alternatively, a continuous first membrane according to the present invention having anionic groups may be folded in a concertina (or zigzag) manner and a second membrane having cationic groups (i.e. of opposite charge to the first membrane) may be inserted between the folds to form a plurality of channels along which fluid may pass and having alternate anionic and cationic membranes as side walls.

The invention will now be illustrated with non-limiting examples where all parts and percentages are by weight unless specified otherwise.

In the examples the following properties were measured by the methods described below.

General Test Methods

Permselectivity was measured by using a static membrane potential measurement. Two cells are separated by the membrane under investigation. Prior to the measurement the membrane was equilibrated in a 0.1 M NaCl solution for at least 12 hours. Two streams having different NaCl concentrations were passed through cells on opposite sides of the membranes under investigation. One stream had a concentration of 0.1M NaCl (from Sigma Aldrich, min. 99.5% purity) and the other stream was 0.5 M NaCl. The flow rate of both streams was 0.90dm^3/min. Two Calomel reference electrodes (from Metrohm AG, Switzerland) were connected to Haber-Luggin capillary tubes that were inserted in each cell and were used to measure the potential difference over the membrane. The effective membrane area was 3.14 cm^2 and the temperature was 21°C.

When a steady state was reached, the membrane potential was measured (ΔV_{meas})

The permselectivity (α (%))of the membrane was calculated according the formula:

$$\alpha\ (\%) = \Delta V_{meas} / \Delta V_{theor} * 100\%.$$

The theoretical membrane potential (ΔV_{theor}) is the potential for a 100% permselective membrane as calculated using the Nernst equation.

To compensate for day-to-day measurement fluctuations in all α (%) measurements an internal standard was included which was used to normalize the results. The internal standard used was CMX membrane from Tokuyama Soda; its α (%) value was determined to be 98%.

Electrical resistance ER (ohm.cm^2) was measured by the method described by Djugolecki et al, J. of Membrane Science, 319 (2008) on page 217-218 with the following modifications:

- the auxiliary membranes were CMX and AMX from Tokuyama Soda, Japan;

- a Cole Parmer masterflex console drive (77521-47) with easy load II model 77200-62 gear pumps was used for all compartments;
- the flowrate of each stream was 475 ml/min controlled by Porter Instrument flowmeters (type 150AV-B250-4RVS) and Cole Parmer flowmeters (type G-30217-90);
- the effective area of the membrane was 3.14 cm^2.

Ingredients

MBA is N,N'-methylene bisacrylamide from Sigma Aldrich.

BAHP is 1,4-bis(acryloyl) homopiperazine, synthesized as described in WO 2010/106356

AMPS is 2-Acryloylamido-2-methylpropanesulfonic acid from Hang-Zhou (China).

HDMAP is 2-hydroxy-2-methyl-1-phenyl-propan-1-one, a photoinitiator from Cytec.

LiOH is lithium hydroxide monohydrate from Chemetall.

MeHQ is hydroquinone monomethyl ether, a polymerisation inhibitor from Merck.

IPA is 2-propanol from Shell.

Viledon® Novatexx™ 2597 is a nonwoven polyamide material and Viledon® Novatexx™ 2226-14E is a nonwoven polyolefine material from Freudenberg Filtration Technologies.

Examples 1 to 12 and Comparative Examples 1 to 3

Curable compositions CC1 to CC12 and comparative curable compositions CE1 to CE3 were prepared by mixing at a temperature of 65°C the ingredients expressed as wt% shown in Table 1.

The resultant curable compositions (described in Table 1) were applied to an aluminium underground carrier using a 150 µm wire wound bar, at a speed of approximately 5 m/min, by hand, followed by application to a non-woven support (Viledon® Novatexx™ 2597 for CC1 to CC9 and CE1 to CE3, Viledon® Novatexx™ 2226-14E for CC10 to CC12) levelled using a 4 micrometer wire wound rod coater. The temperature of the curable compositions was about 50°C during coating and somewhat lower just before curing.

A membrane was prepared by curing the coated support using a Light Hammer LH6 from Fusion UV Systems fitted with a D-bulb working at 100% intensity with a speed of 30 m/min (single pass). The exposure time was 0.47 seconds.

After curing, the membrane was stored in a 0.1 M NaCl solution for at least 12 hours. Membranes of the invention obtained from compositions having a pH of 0.8 to 12 did not need a washing step in pH 6 buffer. Instead they were washed with an NaCl solution. Membranes made from AMPS without neutralization were washed with a pH 6 buffer.

In the calculation of the solvent content the solvents present as part of an ingredient is included and crystal water of ingredients is treated as solvent.

Table 1

Ingredient	**CE1**	**CC1**	**CC2**	**CC3**	**CC4**	**CC5**	**CC6**	**CC7**
AMPS (ii)	59.28	57.11	52.21	55.12	50.19	49.24	42.61	40.53
MBA (i)	2.19	4.25	5.18	6.15	7.47	11.73	16.01	0
BAHP (i)	0	0	0	0	0	0	0	27.16
HDMAP	0.5	0.5	0.91	0.5	0.9	0.5	0.92	0.5
Water + 1000 ppm MeHQ	24.74	23.86	22.38	23.04	22.48	20.64	22.86	17.08
IPA	1.52	2.94	8.95	4.25	8.99	8.11	9.14	6.68
$LiOH.H_2O$	11.77	11.34	10.37	10.94	9.97	9.78	8.46	8.05
Molar ratio (i):(ii)	0.05	0.1	0.13	0.15	0.2	0.32	0.5	0.67
Solvent content (wt%)	35.6	35.8	40	35.9	39.8	36.9	39.1	30
α (%)	66	87.8	91.8	91.3	94.1	94.1	96.3	95.8
ER ($ohm.cm^2$)	1.1	1.1	3.5	1.4	2.9	3	5.6	4.5

Table 1 (continued)

Ingredient	CE2	CC8	CC9	CC10	CC11	CC12	CE3
AMPS (ii)	34.64	34.63	28.75	55.12	49.24	40.53	24.58
MBA (i)	8.25	0	0	6.15	11.73	0	0
BAHP (i)	0	34.79	43.33	0	0	27.16	49.38
HDMAP	0.50	0.5	0.5	0.50	0.5	0.5	0.5
Water + 1000 ppm MeHQ	44.03	14.66	12.25	23.04	20.64	17.08	10.55
IPA	5.71	8.55	9.46	4.25	8.11	6.68	10.11
$LiOH.H_2O$	6.88	6.87	5.71	10.94	9.78	8.05	4.88
Molar ratio (i):(ii)	0.32	1	1.5	0.15	0.32	0.67	2
Solvent content (wt%)	55.5	28.4	26	35.9	36.9	30	24.2
α (%)	84.2	96.7	97.2	91.7	93.9	95.7	92.9
ER ($ohm.cm^2$)	1.7	8.3	14.9	1.0	3.2	5.6	13.3

CLAIMS

1. A curable composition comprising:
(i) 2.5 to 50 wt% crosslinker comprising at least two acrylamide groups;
(ii) 20 to 65 wt% curable ionic compound comprising an ethylenically unsaturated group and an anionic group;
(iii) 15 to 45 wt% solvent; and
(iv) 0 to 10 wt% of free radical initiator;
wherein the molar ratio of (i):(ii) is 0.1 to 1.5.

2. A composition according to claim 1 wherein the molar ratio of (i):(ii) is 0.1 to 1.0.

3. A composition according to claim 1 wherein the molar ratio of (i):(ii) is 0.13 to 0.7.

4. A composition according to any one of the preceding claims which comprises 20 to 40 wt% solvent.

5. A composition according to any one of the preceding claims wherein the total wt% of components (i) + (ii) relative to the total weight of the composition is 30 to 85 wt%.

6. A composition according to any one of the preceding claims wherein the solvent comprises at least 40 wt% water.

7. A composition according to any one of the preceding claims wherein the solvent comprises water and a water-miscible organic solvent.

8. A composition according to any one of the preceding claims wherein the solvent comprises a water-miscible organic solvent having a boiling point below 100°C.

9. A composition according to any one of the preceding claims which comprises 0.005 to 10 wt% photoinitiator.

10. A composition according to any one of the preceding claims which is free from ethylenically unsaturated compounds other than components (i) and (ii).

11. A composition according to any one of the preceding claims wherein the ethylenically unsaturated group is an acrylamide or a methacrylamide group.

12. A composition according claim 1 or any one of claims 4 to 11 comprising:
(i) 8 to 16 wt% crosslinker comprising at least two acrylamide groups;
(ii) 40 to 60 wt% curable ionic compound comprising an ethylenically unsaturated group and an anionic group;
(iii) 22 to 40 wt% solvent; and
(iv) 0.01 to 2 wt% of photoinitiator;
wherein the molar ratio of (i):(ii) is 0.1 to 1.5.

13. A composition according claim 1 or 2 or any one of claims 4 to 11 comprising:
(i) 4 to 30 wt% crosslinker comprising at least two acrylamide groups;
(ii) 35 to 60 wt% curable ionic compound comprising an ethylenically unsaturated group and an anionic group;
(iii) 26 to 45 wt% solvent; and
(iv) 0.01 to 2 wt% of photoinitiator;
wherein the molar ratio of (i):(ii) is 0.1 to 1.0.

14. A process for preparing a membrane comprising the following steps:
(i) applying a curable composition to a support; and
(ii) curing the composition to form a membrane;
wherein the curable composition is as defined in any one of claims 1 to 13.

15. A process according to claim 14 wherein the curing is performed using electron beam or UV radiation.

16. A process according to claim 15 wherein the composition is cured by irradiation with an electron beam or UV light for a period of less than 30 seconds.

17. A process according to any one of claims 14 to 16 wherein the curable composition is applied continuously to a moving support by means of a manufacturing unit comprising a curable composition application station, an irradiation source for curing the composition, a membrane collecting station and a means for moving the support from the curable composition application station to the irradiation source and to the membrane collecting station.

18. A process according to any one of claims 14 to 17 wherein the membrane has a ion exchange capacity of at least 0.1 meq/g based on the dry weight of the membrane.

19. A process according to any one of claims 14 to 18 wherein the curable composition is applied to the support moving at a speed of over 5 m/min.

20. A membrane obtained or obtainable by a process according to any one of claims 14 to 19.

21. A membrane comprising a porous support and a polymeric material obtainable by curing a composition according to claim 1.

22. Use of a membrane according to claim 20 or 21 as an ion exchange membrane in ion separation processes, for water purification, desalination, waste water treatment, electrolysis, pervaporation or for the generation of electricity.

23. An electrodialysis or reverse electrodialysis unit comprising one or more membranes according to claim 20 or 21.

24. A flow through capacitor device comprising one or more membranes according to claim 20 or 21.

25. An electrodeionization module comprising one or more membranes according to claim 20 or 21.

26. A fuel cell comprising one or more membranes according to claim 20 or 21.

27. A diffusion dialysis apparatus comprising one or more membranes according to claim 20 or 21.

28. A membrane electrode assembly comprising one or more membranes according to claim 20 or 21.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/052060

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F220/58 B01J39/20 C02F1/42 H01M8/10 H01M8/22
ADD.

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)
C08F B01J C02F H01M

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 practical, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 786 054 A1 (TOAGOSEI CO LTD [JP]) 16 May 2007 (2007-05-16) cited in the application paragraphs [0001], [0009], [0051]; example 1	1-28
A	WO 2008/122777 A1 (ITM POWER RES LTD [GB]; HIGHGATE DONALD JAMES [GB]) 16 October 2008 (2008-10-16) page 1 page 2, lines 20-24 example 1	1-28
A	US 2008/264867 A1 (MIKA ALICJA M [CA] ET AL) 30 October 2008 (2008-10-30) paragraphs [0016], [0 74], [0 75], [0 93], [104]; example 5	1-28

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[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 document 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
26 January 2011	01/02/2011

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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/052060

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2009/131294 A1 (KOREA ENERGY RESEARCH INST [KR]; CHOI YOUNG WOO [KR]; PARK JIN SOO [KR) 29 October 2009 (2009-10-29) paragraphs [0002], [00 9], [0 13]; example 1	1-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2010/052060

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