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(54) **Titre :** MEMBRANES HYDROPHILIQUES
(54) **Title:** HYDROPHILIC MEMBRANES

(57) **Abrégé/Abstract:**

A method of coating a polymer comprising the step of treating said polymer with an activating agent to produce a reactive polymer, for example treating a polymer bearing at least one X (halogen) group and at least one H with base to eliminate HX. The reactive polymer is then with a reactive coating, for example PVP, preferably in the presence of an initiator like persulfate anions, to produce a coated polymer, which maybe hydrophilic in nature.

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HYDROPHILIC MEMBRANES

TECHNICAL FIELD

The invention relates to polymeric membranes having a hydrophilic layer grafted to the surface thereof and to methods for the preparation of such membranes. The invention particularly relates to the field of ultrafiltration and microfiltration.

BACKGROUND ART

The following discussion is not to be construed as an admission with regard to the state of the common general knowledge.

Synthetic polymeric membranes are well known in the field of ultrafiltration and microfiltration for a variety of applications including desalination, gas separation, filtration and dialysis. The properties of the membranes vary depending on the morphology of the membrane i.e. properties such as symmetry, pore shape, pore size and the chemical nature of the polymeric material used to form the membrane.

Different membranes can be used for specific separation processes, including microfiltration, ultrafiltration and reverse osmosis. Microfiltration and ultrafiltration are pressure driven processes and are distinguished by the size of the particle or molecule that the membrane is capable of retaining or passing. Microfiltration can remove very fine colloidal particles in the micrometer and submicrometer range. As a general rule, microfiltration can filter particles down to 0.05µm, whereas ultrafiltration can retain particles as small as 0.01µm and smaller. Reverse Osmosis operates on an even smaller scale.

Microporous phase inversion membranes are particularly well suited to the application of removal of viruses and bacteria.

A large surface area is needed when a large filtrate flow is required. A commonly used technique to minimize the size of the apparatus used is to form a membrane in the shape of a hollow porous fibre. A large number of these hollow fibres (up to several thousand) are bundled together and housed in modules. The fibres act in parallel to filter a solution for purification, generally water, which flows in contact with the outer surface of all the fibres in the module. By applying pressure, the water is forced into the central channel, or lumen, of each of the fibres while the microcontaminants remain trapped outside the fibres. The filtered water collects inside the fibres and is drawn off through the ends.

The fibre module configuration is a highly desirable one as it enables the modules to achieve a very high surface area per unit volume.

In addition to the arrangement of fibres in a module, it is also necessary for the polymeric fibres themselves to possess the appropriate microstructure to allow microfiltration to occur.

Desirably, the microstructure of ultrafiltration and microfiltration membranes is asymmetric, that is, the pore size gradient across the membrane is not homogeneous, but rather varies in relation to the cross-sectional distance within the membrane. Hollow fibre membranes are preferably asymmetric membranes possessing tightly bunched small pores on one or both outer surfaces and larger more open pores towards the inside edge of the membrane wall.

This microstructure has been found to be advantageous as it provides a good balance between mechanical strength and filtration efficiency.

As well as the microstructure, the chemical properties of the membrane are also important. The hydrophilic or hydrophobic nature of a membrane is one such important property.

Hydrophobic surfaces are defined as “water hating” and hydrophilic surfaces as “water loving”. Many of the polymers used to cast porous membranes are hydrophobic polymers. Water can be forced through a hydrophobic membrane by use of sufficient pressure, but the pressure needed is very high (150-300 psi), and a membrane may be damaged at such pressures and generally does not become wetted evenly.

Hydrophobic microporous membranes are typically characterised by their excellent chemical resistance, biocompatibility, low swelling and good separation performance. Thus, when used in water filtration applications, hydrophobic membranes need to be hydrophilised or “wet out” to allow water permeation.

It is also important that membranes have a high resistance to aggressive chemical species typically found in water requiring filtration, in particular, to oxidising agents and conditions of high pH (i.e. caustic solutions). In particular with water filtration membranes, chlorine resistance is highly desirable. Chlorine is used to kill bacteria and is invariably present in town water supplies. Even at low concentrations, a high throughput of chlorinated water can expose membranes to large amounts of chlorine over the working life of a membrane can lead to yellowing or brittleness which are signs of degradation of the membrane.

Currently, poly(tetrafluoroethylene) (PTFE), polyethylene (PE), polypropylene (PP) and poly(vinylidene fluoride) (PVDF) are the most popular and available hydrophobic membrane materials. However, the search for membrane materials which will provide better chemical stability and performance while retaining the desired physical properties required to allow the membranes to be formed and worked in an appropriate manner has suggested that halogentated polymers may be suitable. In particular, Halar ultrafiltration (UF) membranes have been found to be superior in nearly every way to any unsupported hollow-fibre UF membrane on the market.

Microporous synthetic membranes are particularly suitable for use in hollow fibres and are produced by phase inversion. In this process, at least one polymer is dissolved in an appropriate solvent and a suitable viscosity of the solution is achieved. The polymer solution can be cast as a film or hollow fibre, and then immersed in precipitation bath such as water. This causes separation of the homogeneous polymer solution into a solid polymer and liquid solvent phase. The precipitated polymer forms a porous structure containing a network of uniform pores. Production parameters that affect the membrane structure and properties include the polymer concentration, the precipitation media and temperature and the amount of solvent and non-solvent in the polymer solution. These factors can be varied to produce microporous membranes with a large range of pore sizes (from less than 0.1 to 20μm), and possess a variety of chemical, thermal and mechanical properties.

Hollow fibre ultrafiltration and microfiltration membranes are generally produced by either diffusion induced phase separation (the DIPS process) or by thermally induced phase separation (the TIPS process).

The TIPS process is described in more detail in PCT AU94/00198 (WO 94/17204) AU 653528, the contents of which are incorporated herein by reference.

The quickest procedure for forming a microporous system is thermal precipitation of a two component mixture, in which the solution is formed by dissolving a thermoplastic polymer in a solvent which will dissolve the polymer at an elevated temperature but will not do so at lower temperatures. Such a solvent is often called a latent solvent for the polymer. The solution is cooled and, at a specific temperature which depends upon the rate of cooling, phase separation occurs and the polymer rich phase separates from the solvent.

The term "solvent" as used herein will be understood by those in the art to encompass: single component mixtures and multiple component mixtures. Multiple component mixtures may include, in addition to solvent components, one or more non-solvents.

In the present case the inventors have sought to find a way to modify polymers and polymeric membranes made from halogenated polymers to enhance the range of applications in which they may be used, while at the same time, retaining the good intrinsic resistance of the material to chemical, physical and mechanical degradation. One such polymer is halar.

Halar, or poly (ethylene chlorotrifluoroethylene), is a 1:1 alternating copolymer of ethylene and chlorotrifluoroethylene with the following structure:

$$-(-CH_2-CH_2-CFCl-CF_2-)_n-$$

Halar and related membranes have extremely good chemical resistance to species such as chlorine, peroxide and ozone, and are stable over a wide range of pHs (0-14)

Processes used to produce flat sheet Halar membranes are disclosed for example in US 4702836. The properties of Halar make it highly desirable in the field of ultrafiltration and microfiltration. In particular, Halar has extremely good properties in relation to its resistance both to chlorine and to caustic solutions, but also to ozone and other strong oxidising agents.

Halar membranes also have good mechanical and structural properties. Halar produces membranes of near-perfect sub-structure, with little or no defects or macrovoids. Good permeabilities, in the range of 300-1000 lmh/bar can be achieved. Halar membranes, particularly hollow fibre membranes, have a good break extension, of greater than100%, a break force in excess of 2N and exhibit high flexibility with little or no brittleness.

As a result of this good integrity, Halar membranes have been able to achieve log virus retentions (LRV) of ≥ 4, ie better than 1 in 10,000 viral particles removed.

However, Halar and related membranes are not without some drawbacks. They have a tendency to exhibit reasonable performance initially, but after a relatively short time in use, can suffer from irreversible fouling, pore-compaction or both.

In the present case the inventors have sought to find a way to modify polymers and polymeric membranes made from halogenated polymer such as Halar to enhance the range of applications in which they may be used, while at the same time, retaining the good intrinsic resistance of the material to chemical, physical and mechanical degradation. The most desirable modification is to render the material hydrophilic.

Hydrophilisation of membranes with agents such as PVP has been attempted previously. US 5,376,274 and US 5,629,084 both disclose coating a polysulfone membrane with a PVP/initiator (persulfate) solution and then heating the soaked membrane to crosslink the PVP. This was successful in converting the hydrophobic membrane into a hydrophilic one to improve the wettability of the membrane for filtering aqueous solutions. However, the treatment is of a very short term nature and only a minor increase in the time to irreversible fouling is realised.

Halar, because of its very inertness, is not readily amendable to functionalisation or chemical modification, and for this reason, has not been used as widely as some other membrane forming polymers which are less resistant to environmental degradation. Attempts to hydrophilise Halar in the past have proved difficult for this very reason.

One approach to hydrophilising halar membranes carried out by the present applicant has been to remove HCl from the polymer by exposure to aqueous solutions of alkali earth hydroxides or alkoxides, such as caustic soda or sodium methoxide to produce an activated form of halar possessing double bonds at the surface of the polymer. The activated halar is then treated with an oxidising agent, such Fenton's reagent, which acts as a source of hydroxyl radicals. The hydroxyl radicals react with the double bonds to produce a hydroxylated form of halar which is more hydrophilic than unmodified halar. This is disclosed in AU 2004903680, the contents of which is incorporated by reference in its entirety in the present application. This hydroxylated form of halar is also more amenable to reaction with other chemical species. However, alternative approaches for the long term hydrophilisation of hydrophobic membranes are still desirable.

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative, particularly in terms of methods of production.

Unless the context clearly requires otherwise, throughout the description and the claims, the words ‘comprise’, ‘comprising’, and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of “including, but not limited to”.

DESCRIPTION OF THE INVENTION

According to a first aspect, the invention provides a method of coating a polymer comprising the step of treating said polymer with an activating agent to produce a reactive polymer, and reacting said reactive polymer with a reactive coating to produce a coated polymer.

Preferably, the polymer bears at least one X group, where X is F or Cl, and at least one H.

The polymer which bears at least one X group may be a wholly or partially halogenated homopolymer, copolymer or terpolymer, one or more wholly or partially halogenated homopolymers, copolymers or terpolymers, or a blend of one or more wholly or partially halogenated homopolymers, copolymers or terpolymers with any miscible non-halogenated polymer, polymer blend or polymer mixture.

Preferably, the polymer has at least one X (halogen) bonded to a carbon in a position α to a hydrogen, that is, it is preferred if the X and the H are on adjacent carbon atoms.

Specific examples of halogenated polymers suitable for use in the present invention are PVdF (poly vinylidene fluoride) homopolymer, for example Kynar ® or Solef ®, Ethylene-chlorotrifluoroethylene copolymer (Halar) or Ethylene-chlorotrifluoroethylene terpolymer with n-butyl acrylate; terpolymers of Vinyl Fluoride/Chloride; Vinylidene Fluoride/Chloride; Hexafluoropropylene, Chlorotrifluoroethlyene, Tetrafluoroethylene.

Most preferably, the polymer is halar, or poly (ethylene chlorotrifluoroethylene), a 1:1 alternating copolymer of ethylene and chlorotrifluoroethylene, and having the following structure:

$$-(-CH_2-CH_2-CFCl-CF_2-)_n-$$

Alternatively, any polymer resistant to base attack containing or formed from and miscible with one or more of the following monomers may be used: chlorotrifluoroethylene vinyl fluoride, vinyl chloride; vinylidene fluoride/ vinylidene chloride; hexafluoropropylene, chlorotrifluoroethlyene, tetrafluoroethylene.

Preferably, the activating agent acts to removes HX from the polymer to produce a reactive polymer. Preferably, the activating agent is a base.

Preferably the base is an alkali earth hydroxide, more particularly sodium, potassium, lithium or calcium hydroxide. Alternatively, the base may be an alkali metal alkoxide, such as sodium methoxide, sodium ethoxide, sodium propoxide, potassium methoxide, potassium ethoxide, potassium propoxide and the like. As a further alternative, a strong amine base maybe used, such as tetraethylene pentamine.

Preferably, once in its reactive form, the polymer bears a double bond.

Preferably the reactive coating is a hydrophilic polymer. Most preferably, the reactive coating is PVP.

Preferably, the reactive coating is reacted to the reactive polymer in the presence of an initiator. One preferred initiator is persulfate, ($S_2O_8^{2-}$). Preferably the persulfate is in the form of potassium persulfate, ammonium persulfate, sodium di-persulfate or sodium mono-persulfate.

According to a second aspect, the invention provides a method of hydrophilising a polymer comprising the step of, where applicable modifying the polymer to incorporate a cross linkable functionality and treating said polymer containing a cross linkable functionality with a cross linkable hydrophilising agent, and applying cross linking conditions.

Alternatively, a reactive coating in can be applied to a polymer naturally bearing a cross linkable functionality in the presence of an initiator to hydrophilise the polymer.

Preferably the crosslinkable functionality is a double bond

Preferably the crosslinkable hydrophilising agent is PVP.

Preferably the cross linking conditions involve the use of an initiator and/or cross linking radiation. A preferred initiator is persulfate.

According to a third aspect, the invention provides a method of hydrophilising a halar microfiltration or ultrafiltration membrane comprising the steps of:

i) treating said halar microfiltration or ultrafiltration membrane with a base to eliminate HCl and produce a base treated polymer; and

ii) treating said base treated polymer with PVP in the presence of a cross linking initiator to produce a halar microfiltration or ultrafiltration membrane with a crosslinked surface coating of PVP.

Preferably the initiator is a persulfate anion.

According to a fourth aspect the invention provides a halar microfiltration or ultrafiltration membrane with a crosslinked surface coating of PVP.

Preferably, the membranes of the present invention are asymmetric membranes, which have a large pore face and a small pore face, and a pore size gradient which runs across the membrane cross section. The membranes may be flat sheet, or more preferably, hollow fibre membranes.

According to a fifth aspect, the invention provides a functionalised membrane prepared according to the present invention for use in the microfiltration and ultrafiltration of water and wastewater.

According to a sixth aspect, the invention provides a functionalised membrane prepared according to the present invention for use as an affinity membrane.

According to a seventh aspect, the invention provides a functionalised membrane prepared according to the present invention for use as protein adsorption.

According to an eighth aspect, the invention provides a functionalised membrane prepared according to the present invention for use in processes requiring bio-compatible functionalised membranes.

BEST METHOD OF PERFORMING THE INVENTION

The present invention is disclosed herein with respect to polymeric ultrafiltration membranes or microfiltration membranes. However, it will be appreciated by those skilled in the art that the method can be applied to any appropriate polymeric material where modifications of the kind described are desirable. Any article prepared from a suitable polymer may be hydrophilised in accordance with the present invention.

As mentioned above, the present invention can be carried out upon any polymeric microfiltration or ultrafiltration membrane which bears at least one X group; and may be a wholly or partially halogenated homopolymer, copolymer or terpolymer, one or more wholly or partially halogenated homopolymers, copolymers or terpolymers, or a blend of one or more wholly or partially halogenated homopolymers, copolymers or terpolymers with any miscible non-halogenated polymer, polymer blend or polymer mixture.

Specific examples of halogenated polymers suitable for use in the present invention are PVdF (poly vinylidene fluoride) homopolymer, for example Kynar ®, Solef ®, Ethylene-chlorotrifluoroethylene copolymer (Halar) or Ethylene-chlorotrifluoroethylene terpolymer with n-butyl acrylate (Halar XPM2); terpolymers of Vinyl Fluoride/Chloride; Vinylidene Fluoride/Chloride; Hexafluoropropylene, Chlorotrifluoroethlyene, Tetrafluoroethylene.

The present invention will be described with particular reference to halar, the most preferred compound of the present invention. Halar is a 1:1 alternating copolymer of ethylene-chlorotrifluoroethylene copolymer.

$-(CH_2-CH_2-CCl_2-CClF)_n-$

Halar membranes in the form of hollow fibres were prepared according to the method disclosed in PCT AU94/00198 (WO 94/17204) and AU 653528, the contents of which are incorporated herein by reference. Halar membranes used in the experiment were either microfiltration (MF) membranes (nominal pore size = 0.1μm) or ultrafiltration (UF) membranes (nominal pore size = 0.01μm). The polymer, halar, used for both membrane types was identical.

A halar membrane with PVP bound to the surface was prepared. In order to do this, opportunities for a reaction between PVP and otherwise inert halar polymer first needed to be created. The first step in the process was carried out by treatment of halar with a concentrated solution of sodium hydroxide to generate double bonds (via dehydrohalogenation) on the membrane surface that can react with radicals.

The elimination of HX, which in the case of halar is HCl, was more specifically carried out by treating a preformed polymeric ultrafiltration or microfiltration membrane with a 20 wt% caustic solution at 80-120°C for a period of between 30 minutes and 4 hours. The membrane was then removed from the caustic solution and rinsed with water for 1-2 hours, until the pH of the solution was neutral. The fibres underwent a colour change from white to dark beige/brown during the caustic treatment, known from experience to be evidence that double bonds are forming.

The effect of the length of exposure to caustic solution was investigated and it was established that fibres treated for two hours or longer in caustic were wetting in water after post treatment.

The conditions for successful modification of the halar membrane were found to be unexpectedly mild. Halar UF membranes could be successfully made hydrophilic by initial treatment of the membrane with 30wt% caustic at 40°C for 168hrs (7 days), followed by a treatment of the membrane with PVP at 40°C for 2 hours. The reaction was accelerated by using higher temperatures, but the permeability was detrimentally affected in the case of UF membranes.

Once the caustic treatment was performed, the membrane is then allowed to react with PVP and free radicals arising from an initiator such as persulfate.

Modified membranes prepared according to the present invention suffer minimal loss of properties. Hydraulic/mechanical properties and chemical resistance appear largely unaffected. Initial non-optimised samples tested for Virus rejection gave LRV > 3.5.

In use, halar membranes are likely to be exposed to high concentrations of oxidisers like chlorine and ozone. These oxidising agents can provide satisfactory cleaning of the membrane well but are also known to degrade PVP, and can eliminate any advantage in those prior art systems where the PVP is not bound to the membrane.

Binding the coating to the membrane surface in accordance with the present invention improves the resistance of the hydrophilic layer to oxidation. Even when the coating is partially oxidised, it appears that fragments of hydrophilising polymer remain bound to the surface, beneficially affecting the anti-fouling characteristic of the membrane.

Experimental, Results & Discussion

All of the experiments had the same general procedure of caustic treatment with subsequent surface modification as set out below. All percentages are by weight.

1. Wetting with ethanol (if fibres are not already stored in water) (0.5hr)
2. Water wash (0.5hr)
3. Soak in concentrated NaOH solution (0.5hr)
4. NaOH treatment at elevated temperature for various lengths of time
5. Water wash (2-3hrs)
6. Soak in PVP/Persulfate solution (1-2hr)
7. Treatment at elevated temperature (1-2hr) in 100% humid atmosphere
8. Water wash (>2hrs)
9. Soak in 20% Glycerol

MF Fibres

The reactions were initially carried out on microfiltration membranes with a pore size of 0.1μm. Samples were exposed to a 20% caustic solution at a temperature of 90°C for 21hrs (overnight). The treatment was otherwise as above with the exception that all fibres were washed in ethanol for 3hrs immediately after treatment with persulfate.

Control #1 was a completely untreated sample. Control #2 was a sample exposed only to the persulfate treatment only. Control #3 had no PVP included; the persulfate treatment consisted of initiator alone.

Membrane samples were initially white and turned brown on caustic treatment. Treatment with persulfate/PVP treatment caused a colour change from brown to light beige.

TABLE 1 MF Experiments

	Control #1	**Control #2**	**Control #3**	**a**	**b**	**c**	**d**
OD	650	650	650	650	650	650	650
ID	310	310	310	310	310	310	310
NaOH %			20	20	20	20	20
Oven temp (°C)			90	90	90	90	90
Time in Caustic (hr)			18	18	18	18	18
Persulfate (%)		5	5	5	5	5	5
H2SO4 (%)		0.1	0.1	0.1	0.1	0.1	0.1
PVP (%)		0.5		1	0.5	0.35	0.1
PVP-VA (%)		0.5		1	0.5	0.35	0.1
Total Modifier (%)		1	0	2	1	0.7	0.2
Time in Persulfate (hr)		18	18	18	18	18	18
Oven temp (°C)		90	90	90	90	90	90
Time in Oven (hr)		2	2	2	2	2	2
Time Washing (hr)		4	4	4	4	4	4
Hydrophilic (Y/N)?	N	N	N	Y	Y	Y	Y
Permeability (lmh/bar)	1487	0	0	517	1565	1473	1932

The permeability of the samples was evaluated as-is. Apart from control 1, which was wet with ethanol, the samples were wet only with water.

All samples treated with both caustic and PVP/Persulfate became clearly hydrophilic, as a permeability for treated samples could be obtained.

Given that the permeability of the samples with a PVP or PVP/VA concentration of ≤1% (b – d) have a permeability at least equal to the untreated sample (Control #1), the MF membrane porosity is affected by concentrations greater than this. The permeability of the membrane with the lowest concentration of PVP (d) is also similar to the control. This indicates that concentrations as low as 0.2% PVP are sufficient to impart hydrophilicity to the membrane.

It is clear from Control #3 that the absence of PVP prevents the membrane from becoming hydrophilic, despite receiving an otherwise identical treatment. Thus it can be concluded that the PVP is required to generate hydrophilicity.

Surprisingly however, Control #2 was *not* hydrophilic. This suggests that at least for Halar membranes, it is necessary to graft the PVP to the membrane for any permanency of the treatment. Even if the treatment had caused a hydrophilic coating of the membrane, washing the membranes with ethanol may be the reason for the apparent lack of hydrophilicity in the test. Any unbound PVP would wash away in ethanol, particularly in these low concentrations (0.5%).

These experiments were repeated successfully with various different types of PVP. A number of types of PVP, including K15, K30, K90, K120 and PVP-VA (S630) successfully produced a hydrophilic fibre, a with similar results.

However PVP K15 produced the best results in terms of minimal gel formation and evenness of coverage. K15 can be dissolved into water relatively easily without clumping, and does not greatly affect the viscosity of the solution.

UF Fibres

Once it was established from MF fibres that the treatment was successful, it was applied to UF fibres which typically have even smaller pores. A number of attempts were made using identical parameters and the membranes repeatedly became hydrophilic under identical conditions to the MF fibres.

However, using the same conditions as used to successfully coat MF membranes, it was found that UF membranes lost a significant amount, up to 70 to 80%, of their inherent permeability. Without wishing to be bound by theory, it is believed that this was due to the double bond density achieved at the membrane surface being not sufficiently high. In order to increase double bond density, a variety of temperatures, times and concentrations were investigated. It was found possible, and most desirable, to increase double bond density by increasing the concentration of caustic and the contact times, rather than increasing temperature.

The shortest exposure time possible is the most economic but lower concentrations are better for mass transfer as caustic solutions become more viscous with increasing concentration. There are also safety concerns involved. Around 20% to 30% caustic at 40°C for varying lengths of time was found to be suitable.

The remainder of the treatment was unchanged, except that the temperature at which the persulfate treatment was performed was decreased to 40°C in line with the temperature of the caustic treatment. The details of the experiments performed are set out in table 2.

TABLE 2 - UF Results

	Control	**1b**	**1c**	**1e**	**2a**	**2a**
		2	**3**	**5**	**7**	**7**
OD	1050	1050	1050	1050	1050	1050
ID	622	622	622	622	622	622
NaOH (%)		20	20	20	30	30
Oven Temp (°C)		40	40	40	40	40
Time in Caustic (hr)		95	120	168	72	72
Persulfate (%)		5	5	5	5	5
H_2SO_4 (%)		0.1	0.1	0.1	0.1	0.1
PVP K15 (%)		0.5	0.5	0.5	0.5	0.5
Total Modifier (%)		0.5	0.5	0.5	0.5	0.5
Time in Persulfate (hr)		1	1	2	1	1
Time in oven (hr)		1.5	1.5	1.5	1.5	1.5
Oven temp (°C)		40	40	40	40	40
Time (hr) Washing		17	0.5	2	17	17
Time (hr) in 20% glycerol		2	2	17	2	2
Hydrophilic (Y/N)?	N	N	N	N	Y	EtOH
Permeability (lmh/bar)	147	82	123	69	33	68
% Of Ethanol permeability					**49%**	

TABLE 2 - UF Results (cont.)

	Control	**2b**	**2b**	**2c**	**2c**	**2d**	**2d**
		8	**8**	**9**	**9**	**10**	**10**
OD	1050	1050	1050	1050	1050	1050	1050
ID	622	622	622	622	622	622	622
NaOH (%)		30	30	30	30	30	30
Oven Temp (°C)		40	40	40	40	40	40
Time in Caustic (hr)		96	96	144	144	168	168
Persulfate (%)		5	5	5	5	5	5
H_2SO_4 (%)		0.1	0.1	0.1	0.1	0.1	0.1
PVP K15 (%)		0.5	0.5	0.5	0.5	0.5	0.5
Total Modifier (%)		0.5	0.5	0.5	0.5	0.5	0.5
Time in Persulfate (hr)		1	1	2	2	2	2
Time in oven (hr)		1.5	1.5	1.5	1.5	1.5	1.5
Oven temp (°C)		40	40	40	40	40	40
Time (hr) Washing		0.5	0.5	2	2	2	2
Time (hr)in 20% glycerol		2	2	2	2	2	2
Hydrophilic (Y/N)?	N	Y	EtOH	Y	EtOH	Y	EtOH
Permeability (lmh/bar)	147	52	82	98	121	71	80
% Of Ethanol permeability		**64%**		**81%**		**88%**	

The samples that were treated with 20% caustic showed a significantly lighter colour than those treated with 30% caustic for the same period of time. This is a clear indication that the surface double bond density has increased by increasing caustic concentration.

This is also supported by the results for hydrophilicity. Samples 1a – 1e received the same treatment times as 2a – 2e, but the results are dramatically different. None of the series 1a – 1e were hydrophilic, while the series 2a – 2e had varying degrees of hydrophilicity.

The permeability of samples 2a – 2e was measured before and after wetting with ethanol to assess whether any deviation was due to pore collapse or non-wetting.

Presuming the membrane had neither collapsed nor suffered from plugged pores (which should be evident in all samples) the maximum available permeability of a specific fibre sample should be related (within the normal margins of error) to the permeability after wetting thoroughly with ethanol. Therefore a relationship should be observed by plotting the % of total permeability available (ethanol wet) that was obtained by wetting with water, versus the time exposed to caustic, and in fact a very clear relationship exists between the length of time in 30% caustic and the water-wet permeability (hydrophilicity) as a proportion of the total permeability (ethanol-wet).

The longer a sample was exposed to 30% caustic at 40°C before PVP treatment, the more hydrophilic the final membranes were. This supports the theory for increasing surface double bond density of the membrane.

Even more importantly, the permeability of sample 2e is approximately 90% of the available permeability, close enough to the available permeability of the sample (within experimental error) to be considered fully hydrophilic.

While the invention has been described with reference to particular embodiments, it will be understood by those skilled in the art that the inventive concept disclosed herein is not limited only to those specific embodiments disclosed.

CLAIMS

1. A method of coating a polymer bearing at least one X (halogen) group and at least one H; comprising the step of treating said polymer with an activating agent to remove HX from the polymer to produce a reactive polymer, and reacting said reactive polymer with a reactive coating to produce a coated polymer.

2. A method according to claim 1 wherein X is F or Cl and at least one H.

3. A method according to claim 1 or 2 wherein the polymer has at least one X (halogen) bonded to a carbon in a position α to a hydrogen.

4. A method according to any one of the preceding claims wherein the polymer which bears at least one X group is a wholly or partially halogenated homopolymer, copolymer or terpolymer or a blend thereof.

5. A method according to claim 4 wherein the wholly or partially halogenated homopolymer, copolymer or terpolymer or a blend thereof further comprises a miscible non-halogenated polymer, polymer blend or polymer mixture.

6. A method according to any one of the preceding claim wherein the polymer is pvdf (poly vinylidene fluoride) homopolymer, ethylene-chlorotrifluoroethylene copolymer (halar) or ethylene-chlorotrifluoroethylene terpolymer with n-butyl acrylate, terpolymers of vinyl fluoride/chloride; vinylidene fluoride/chloride, hexafluoropropylene, chlorotrifluoroethlyene, tetrafluoroethylene.

7. A method according to any one of the preceding claims wherein the polymer is a polymer resistant to base attack containing and produced from one or more of the following monomers: chlorotrifluoroethylene vinyl fluoride, vinyl chloride; vinylidene fluoride/ vinylidene chloride; hexafluoropropylene, chlorotrifluoroethlyene, tetrafluoroethylene.

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8. A method according to claim 7 wherein the polymer is or poly (ethylene chlorotrifluoroethylene), halar, a 1:1 alternating copolymer of ethylene and chlorotrifluoroethylene, and having the following structure:

$$-(-CH_2-CH_2-CFCl-CF_2-)_n-$$

9. A method according to any one of the preceding claims wherein the activating agent is a base.

10. A method according to claim 9 wherein the base is an alkali earth hydroxide.

11. A method according to claim 10 wherein the alkali earth hydroxide is sodium, potassium, lithium or calcium hydroxide.

12. A method according to claim 9 wherein the base is an alkali metal alkoxide.

13. A method according to claim 12 wherein the alkali metal alkoxide is sodium methoxide, sodium ethoxide, sodium propoxide, potassium methoxide, potassium ethoxide, potassium propoxide.

14. A method according to claim 9 wherein the base is a strong amine base.

15. A method according to claim 14 wherein the strong amine base is tetraethylene pentamine.

16. A method according to any one of the preceding claims wherein the reactive polymer bears a double bond.

17. A method according to any one of the preceding claims wherein the reactive coating is a hydrophilic polymer.

18. A method according to any one of the preceding claims wherein the reactive coating is a hydrophilic polymer.

19. A method according to any one of the preceding claims wherein the reactive coating is PVP.

20. A method according to any one of the preceding claims wherein the reactive coating is reacted to the reactive polymer in the presence of an initiator.

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21. A method according to claim 20 wherein the initiator is persulfate ($S_2O_8^{2-}$).

22. A method according to claim 20 where the persulfate is in the form of potassium persulfate, ammonium persulfate, sodium di-persulfate or sodium mono-persulfate.

23. A method of hydrophilising a polymer comprising the step of, where applicable modifying the polymer to incorporate a cross linkable group and treating said polymer containing a cross linkable group with a cross linkable hydrophilising agent, and applying cross linking conditions.

24. A method according to claim 23 wherein the crosslinkable group is a double bond.

25. A method according to claim 23 or 24 wherein the crosslinkable hydrophilising agent is PVP.

26. A method according to any one of claim 23 to 25 wherein the cross linking conditions involve the use of an initiator and/or cross linking radiation.

27. A method of hydrophilising a halar microfiltration or ultrafiltration membrane comprising the steps of:

i) treating said halar microfiltration or ultrafiltration membrane with a base to eliminate HX and produce a base treated polymer; and

ii) treating said base treated polymer with PVP in the presence of a cross linking initiator to produce a halar microfiltration or ultrafiltration membrane with a crosslinked surface coating of PVP.

28. A halar microfiltration or ultrafiltration membrane with a crosslinked surface coating of PVP.

29. A membrane according to claim 28 in the form of an asymmetric membranes.

30. A membrane according to claim 29 in the form of a flat sheet.

31. A membrane according to claim 29 in the form of a hollow fibre.

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32. A functionalised membrane prepared according to any one of claims 1-27 for use in the microfiltration and ultrafiltration of water and wastewater.

33. A functionalised membrane prepared according to any one of claims 1-27 for use as an affinity membrane.

34. A functionalised membrane prepared according to any one of claims 1-27 for use as protein adsorption.

35. A functionalised membrane prepared according to any one of claims 1-27 for use in processes requiring bio-compatible functionalised membranes.