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[Continued on next page]

(54) Title: MICROPOROUS AND HYDROPHOBIC POLYMERIC HOLLOW FIBER MEMBRANES AND METHODS FOR PREPARATION THEREOF

(57) Abstract: There is provided a method for preparing microporous hollow fiber membranes comprising melt-extruding a polymer-salt blend followed by salt leaching. Microporous hollow fiber membranes are also disclosed.

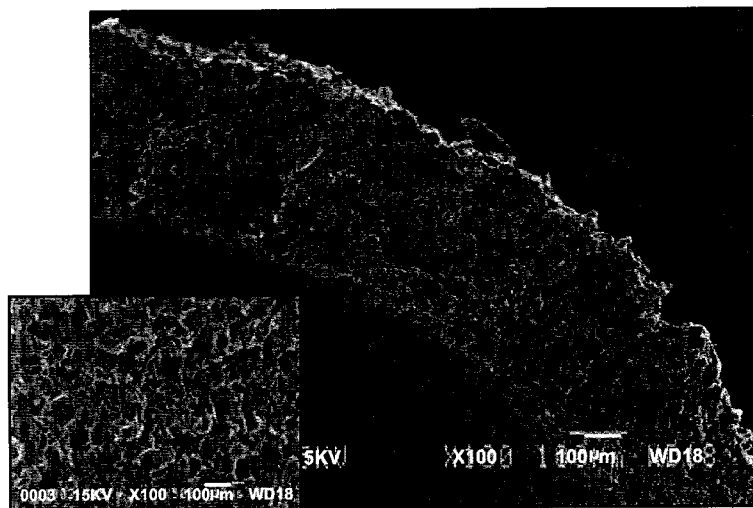


FIG. 14A

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MICROPOROUS AND HYDROPHOBIC POLYMERIC HOLLOW FIBER MEMBRANES AND METHODS FOR PREPARATION THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority on US 61/699,348 filed on September 11, 2012, that is hereby incorporated by reference in its entirety.

FIELD OF THE DISCLOSURE

[0002] The present disclosure generally relates to the field of polymeric microporous hollow fiber membranes. In particular, the present disclosure relates to methods for preparing microporous hollow fiber membranes, as well as the microporous hollow fiber membranes prepared by such methods.

BACKGROUND OF THE DISCLOSURE

[0003] Wetting of porous polymeric membranes by liquid absorbents has been considered to be the major problem in membrane gas/liquid contactors (MGLC). In the non-wetted condition, the membrane pores are only filled with the gas. However, partial wetting by the liquid absorbent can result in a significant increase in membrane resistance. 1

[0004] The wetting tendency of a membrane by a specific liquid is determined by membrane chemical and morphological properties and is directly proportional to its surface energy and pore size. The reported wettability of some examples of commonly used polymeric membranes with different solutions is summarized in Table 1. It can be seen that due to its lowest surface energy, polytetrafluoroethylene (PTFE) is the most resistant polymer to wetting and therefore it has been extensively used in MGLC systems. However, several serious drawbacks including i) complicated and high cost of fabrication, ii) environmentally malignant method of fabrication (PTFE is typically fabricated via solvent-employed methods), iii) small specific interfacial area leading to a reduction in absorption efficiency, iv) unavailability of small pore sizes, due to the complexity in porosity and pore size control and v) not being recyclable (PTFE is not considered in the category of recyclable polymers), practically limit the large scale utilization of PTFE materials.

Table 1

Membrane	Absorbent	Wettability	Reference
PTFE	MEA	-	Nishikawa et al. ²
	Amine solution (AMP, MEA, MDEA)	-	Falk Pedersen ³ Kim et al. ⁴
	NaOH solution, MEA solution	-	Matsumoto et al. ⁵
	MEA, AMP	-	deMontigny et al. ⁶
	Water, MEA	-	Khaisri et al. ⁷
PP	NaOH solution	+	Rangwala ⁸
		+	Falk Pedersen ³
	Alkanolamine solution	+	Kumar et al. ⁹
		+	Kumar et al. ⁹
		+	Matsumoto et al. ⁵
	Amino acid salts (Potassium taurate)	+	Dindore et al. ¹
	NaOH solution, MEA solution	+	Khaisri et al. ⁷
	Propylene carbonate	+	deMontigny et al. ⁶
	Water, MEA		Lu et al. ¹⁰
	MEA, AMP		
PE	Activated absorbent		
	NaOH solution, MEA solution	+	Matsumoto et al. ⁵
	MEA	+	Nishikawa et al. ²
PVDF			
	5% MEA + 5% TEA	-	Yeon et al. ¹¹
	Water, MEA	+	Khaisri et al. ⁷

[0005] The general characteristics of some kinds of commercial PTFE, polypropylene (PP) and polyvinylidene fluoride (PVDF) hollow fiber membranes are presented in Table 2. PP as an inexpensive and readily available alternative has been frequently considered in the literature. However, it has a large wettability and it has been reported to be wetted by alkanolamine solutions in short term operation.¹

Table 2

Description	PP	PVDF	PTFE	Reference
Max. available pore size (μm)	0.25	0.03	1.0	Lee et al. ¹²
Max. void fraction (%)	75.2	82.2	70.1	Khaisri et al. ⁷
	82.2	-	59.2	deMontigny et al. ⁶
Max. specific area (m^2/m^3)	2855	1488	1340	Lee et al. ¹²
	2752	-	429	deMontigny et al. ⁶
Cost (US \$/m)	0.01	-	23	deMontigny et al. ⁶
	0.01	0.36	11.5	Khaisri et al. ⁷

[0006] Polyethylene (PE), having the same wetting tendency as PP, can be another alternative which has been of little consideration in the literature. However, PE can be an interesting option due to its several advantages including recyclability, flexibility of operation, simplicity of transformation to flat and hollow fiber membranes through different methods, frequent availability and inexpensive price, chemical stability higher than that of PP (due to less side groups on its molecular chains)¹³ and the possibility of different hydrophobic modifications to diminish surface wettability. On the other hand, methods used for the hydrophobic treatment of polyolefins such as laser etching¹⁴, plasma treatment¹⁵ and solution casting¹⁶ are mostly uneconomic and unsafe, since they use specific installations, toxic solvents and complicated procedures. In addition, most of these methods cannot be applied on non-flat surfaces and thus are of no use for hollow fiber membranes.

[0007] It has been shown that effective roughening of a specific surface can significantly increase its hydrophobicity^{16,17,18,19}. For example, many natural plant leaves have super hydrophobic properties due to their rough surface structure²⁰. There have also been several attempts reported in the literature to produce artificial super hydrophobic surfaces via roughening low surface energy materials^{18,21}. However, despite its important role in the reduction of membrane wettability, increasing the hydrophobicity of porous polymeric membranes via creating rough structures remains untouched.

[0008] Currently, porous polymeric membranes are frequently fabricated via a conventional wet-phase inversion method through thermally induced phase

separation (TIPS)²² or non-solvent induced phase separation (NIPS)²³ processes. These processes mainly involve the dissolution of polymer in toxic organic solvents. The porous structure forms during phase separation that is induced either by thermally cooling the polymer solution or by adding a non-solvent. A serious drawback of these processes is the use of a large amount of expensive, harmful and partly flammable solvents which have to be removed after membrane formation via several intense washing procedures, making the process noneconomic and environmentally harmful. Besides the above mentioned disadvantages, these processes suffer from low production rates, due to the slow liquid-liquid phase separation phenomena²⁴.

[0009] Only a few solvent-free methods for fabrication of porous polymeric membranes have been reported in the literature.^{25,26,27} The most important solvent-free membrane manufacturing technique is the melt-spinning and stretching method. This technique is based on the melt extrusion of pure semi-crystalline polymers to form flat or hollow fiber precursors, followed by axial stretching of such precursors to form a porous structure. However, this technique is only applicable to semi-crystalline polymers and in addition to the mechanical stretching process, it requires several thermal post-treatments to promote the crystallinity and to avoid the membrane shrinkage²⁸.

[0010] There are few studies in the literature concerning the fabrication of open-cell foams containing polymer/filler composites. R.K.M. Chu et al.²⁹ fabricated open-cell PP foams for sound absorption applications, introducing NaCl of 106-850 μm . The foam products were then leached in water for at least 96 h to dissolve away the salts. Narkis and Joseph³⁰ studied the tensile properties of poly(methyl methacrylate) (PMMA), polysulfone (PSF) and polystyrene (PS) foams produced by salt extraction. Recently, Dangtungee and Supaphol³¹ investigated the rheological properties of low-density polyethylene (LDPE) and sodium chloride (NaCl) mixtures of varying particle size (i.e., 45, 75, and 125 μm) in the range of 5–25 wt.%. Verdolotti et al.³² studied the effect of the incorporation of several lithium salts (LiCl, LiClO₄ and LiCF₃SO₃) on the electrical and mechanical properties of polyurethane rigid (PUR) foams. However, despite the importance of porous polymeric products, there has been little concentration on the employment of open-cellular foams,

prepared via leaching the salts from a polymer/salt composite matrix, for membrane applications. Moreover, the leaching process, the most important part of this technique, still remains noticeably untouched. Long leaching durations (around 90 h) and a batch wise leaching process as a post treatment make the reported processes industrially inapplicable. Further, none of the abovementioned studies concentrated on the control of salt particle size, salt content and the final product shape (only film products were prepared). In addition, inhomogeneity and the large particle size of the salts used (45-850 μm) makes the reported foams inappropriate for membrane applications.

SUMMARY OF THE DISCLOSURE

[0011] It would thus be highly desirable to exploit a hybrid process which combines melt extrusion with a continuous template-leaching technique, as a novel solvent-free method for hydrophobic hollow fiber membrane fabrication.

[0012] Accordingly, there is provided a method for preparing a microporous hollow fiber membrane, which comprises:

mixing at least one polymer suitable for melt extrusion with at least one suitable water soluble salt so as to form a mixture;

extruding the mixture under conditions suitable to form a hollow fiber membrane comprising the mixture; and

leaching the hollow fiber comprising the mixture in water under conditions suitable for at least substantially removing the salt from the hollow fiber membrane.

[0013] According to another aspect, there is provided a method for preparing a microporous hollow fiber membrane, which comprises:

mixing at least one polymer suitable for melt extrusion with at least one suitable water soluble salt to form a mixture;

extruding the mixture under conditions suitable to form a hollow fiber membrane comprising the mixture; and

leaching the hollow fiber membrane comprising the mixture in water under conditions suitable for the removal of salt to proceed to a sufficient extent.

[0014] According to another aspect, the present application includes a hydrophobic microporous hollow fiber membrane comprising :

- a porosity of about 10 to about 80 %;
- a mean roughness (R_a) of about 100 nm to about 1000 nm;
- a water contact angle of about 110 to about 140°; and

microporous pores having a diameter of about 0.1 to about 1000 μm .

[0015] According to another aspect, the present application includes a hydrophobic microporous hollow fiber membrane comprising :

- a porosity of about 40 to about 60 %;
- a mean roughness (R_a) of about 600 to about 800 nm;
- a water contact angle of about 128 to about 140°; and

microporous pores having a diameter of about 1 to about 20 μm .

[0016] According to another aspect, the present application includes a hydrophobic microporous hollow fiber membrane comprising :

- a porosity of about 49 to about 51 %;
- a mean roughness (R_a) of about 650 to about 750 nm;
- a water contact angle of about 128 to about 140°; and

microporous pores having a diameter of about 2 to about 5 μm .

[0017] According to another aspect, the present application includes a hydrophobic microporous hollow fiber membrane comprising :

- a density of about 0.70 to about 0.72 g/cm³;
- a porosity of about 49 to about 51 %;
- a mean roughness (R_a) of about 650 to about 750 nm;
- a water contact angle of about 128 to about 140°; and

microporous pores having a diameter of about 2 to about 5 μm .

[0018] According to a further aspect, the application includes a microporous hollow fiber membrane prepared by a method for preparing a microporous hollow fiber membrane, which comprises:

mixing at least one polymer suitable for melt extrusion with at least one suitable water soluble salt under conditions suitable to form a polymer-salt blend;

extruding the polymer-salt blend under conditions suitable to form a hollow fiber comprising the polymer-salt blend; and

leaching the hollow fiber comprising the polymer-salt blend in water under conditions suitable for the removal of salt to proceed to a sufficient extent.

[0019] It was found that the methods and membranes disclosed in the present disclosure are capable to provide the effective roughness on a membrane surface which could, for example, significantly diminish the membrane wettability. For example, since no post-treatments are employed, these methods can be expected to be industrially applicable for various kinds of polymers.

[0020] For example, the present disclosure describes highly hydrophobic microporous LDPE hollow fiber membranes prepared using melt extrusion of LDPE/NaCl blends followed by a salt leaching process in water. Membrane porosity can be dependent on the amount of salt removed from the hollow fiber structure and, up to a certain limit dictated by operational constraints, can be increased with an increase in initial salt content. Surface roughness of the fabricated membranes due to the existence of micropapillas, resulted in a remarkable increase in hollow fiber membrane hydrophobicity compared to a blank hollow fiber with a smooth surface.

[0021] Other features and advantages of the present application will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples while indicating embodiments of the application are given by way of illustration only, since various changes and modifications within the spirit and scope of the application will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] The following drawings represent examples that are presented in a non-limitative manner.

[0023] Figure 1 is a schematic representation of a melt-extrusion, cooling and drawing system for hollow fiber precursor fabrication according to the present disclosure.

[0024] Figure 2 shows the percentage of salt removal from hollow fiber membranes with different initial salt contents.

[0025] Figure 3 shows thermogravimetric analysis (TGA) curves for LDPE hollow fiber membranes with initial salt content of 68 wt%, after leaching for 160 min.

[0026] Figure 4 shows TGA curves for LDPE hollow fiber membranes with initial salt content of 65 wt%, after leaching for 160 min.

[0027] Figure 5 shows TGA curves for LDPE hollow fiber membranes with initial salt content of 60 wt%, after leaching for 160 min.

[0028] Figure 6 shows TGA curves for LDPE hollow fiber membranes with initial salt content of 50 wt%, after leaching for 160 min.

[0029] Figure 7 shows TGA curves for LDPE hollow fiber membranes with initial salt content of 40 wt%, after leaching for 160 min.

[0030] Figure 8 shows TGA curves for LDPE hollow fiber membranes with initial salt content of 35 wt%, after leaching for 160 min.

[0031] Figures 9A-9C show exemplary scanning electron microscope (SEM) micrographs of blank LDPE hollow fiber: 9A) external surface, 9B) internal surface and 9C) cross sectional edge.

[0032] Figures 10A-10F show exemplary SEM micrographs of cross sectional (left side) and internal surfaces (right side) of LDPE hollow fiber membranes with 10A) 35 wt%, 10B) 40 wt%, 10C) 50 wt%, 10D) 60 wt%, 10E) 65 wt% and 10F) 68 wt % NaCl.

[0033] Figure 11 shows pore size distribution of LDPE hollow fiber membranes with different initial salt contents (35-68 wt%).

[0034] Figures 12A-12C show AFM analysis of 12A) blank LDPE hollow fibers, 12B) LDPE hollow fiber membrane with initial salt content of 40 wt% and 12C) LDPE hollow fiber membrane with initial salt content of 60 wt%.

[0035] Figure 13 shows stress-strain curves of LDPE hollow fiber membranes.

[0036] Figures 14A-E shows exemplary SEM images of (14A) examples fibers of the present application (5-10 μm salt-60 wt%): highly porous membranes (small pores); (14B-E) fibers fabricated using mixtures of polyethylene (LDPE) and sodium chloride (NaCl) as indicated in Dangtungee and Supaphol (2010)³¹: (14B) 125 μm salt-25 wt%; (14C) 125 μm salt-5 wt%; (14D) 45 μm salt-25 wt%; and (14E) 45 μm salt-5 wt%: non-porous fibers.

[0037] Figures 15A-15D shows exemplary backscattered electron detector (BSE) Images and energy dispersive x-ray spectroscopy (EDS) analysis of fibers prepared using the mixtures indicated in Dangtungee and Supaphol (2010)³¹: (15A) 125 μm salt-25 wt%; (15B) 125 μm salt-5 wt%; (15C) 45 μm salt-25 wt%; (15D) 45 μm salt-5 wt%. The contrast in the color shows the existence of impurities. White portions indicate salt crystals.

[0038] Figures 16A-16F shows TGA diagrams of (a-d) fibers prepared as indicated in Dangtungee and Supaphol (2010)³¹: (16A) 125 μm salt- 5 wt%; (16B) 125 μm salt-25 wt%; (16C) 45 μm salt-5 wt%; (16D) 45 μm salt-25 wt%— significant amount of salt remains in the fibers even after prolonged time of leaching (7 days); (16E) an example of membrane of the present application: 5-10 μm salt- 60 wt% – no salt remains in the fiber structure after leaching; (16F) pure salt and pure LDPE.

[0039] Figure 17 shows CO₂ absorption in amine solution corresponding to the hollow fiber membrane of the present application compared with the results reported in Lv et al.³³ Solution: aqueous monoethanolamine (MEA): 1 mol/l; Gas concentration: 20% CO₂; Liquid flow rate: 17 cc/min; Gas flow rate: 200 cc/min.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0040] Unless otherwise indicated, the definitions and embodiments described in this and other sections are intended to be applicable to all embodiments and aspects of the application herein described for which they are suitable as would be understood by a person skilled in the art.

[0041] As used in this application, the singular forms “a”, “an” and “the” include plural references unless the content clearly dictates otherwise. For example, an embodiment including “a polymer” should be understood to present certain aspects with one polymer, or two or more additional polymers.

[0042] In embodiments comprising an “additional” or “second” component, such as an additional or second polymer, the second component as used herein is chemically different from the other components or first component. A “third” component is different from the other, first, and second components, and further enumerated or “additional” components are similarly different.

[0043] The term “suitable” as used herein means that the selection of the particular compound or conditions would depend on the specific manipulation to be performed, but the selection would be well within the skill of a person trained in the art. All process/method steps described herein are to be conducted under conditions sufficient to provide the product shown. A person skilled in the art would understand that all reaction conditions, including, for example, reaction solvent, reaction time, reaction temperature, reaction pressure, reactant ratio and whether or not the reaction should be performed under an anhydrous or inert atmosphere, can be varied to optimize the yield of the desired product and it is within their skill to do so.

[0044] In understanding the scope of the present disclosure, the term “comprising” and its derivatives, as used herein, are intended to be open ended terms that specify the presence of the stated features, elements, components, groups, integers, and/or steps, but do not exclude the presence of other unstated features, elements, components, groups, integers and/or steps. The foregoing also applies to words having similar meanings such as the terms, “including”, “having” and their derivatives. The term “consisting” and its derivatives, as used herein, are intended to be closed terms that specify the presence of the stated features, elements, components, groups, integers, and/or steps, but exclude the presence of other unstated features, elements, components, groups, integers and/or steps. The term “consisting essentially of”, as used herein, is intended to specify the presence of the stated features, elements, components, groups, integers, and/or steps as well as those that do not materially affect the basic and novel characteristic(s) of features, elements, components, groups, integers, and/or steps.

[0045] Terms of degree such as “about” and “approximately” as used herein mean a reasonable amount of deviation of the modified term such that the end result is not significantly changed. These terms of degree should be construed as including a deviation of at least $\pm 5\%$ or at least $\pm 10\%$ of the modified term if this deviation would not negate the meaning of the word it modifies.

[0046] The expression “at least substantially removing the salt from the hollow fiber membrane” has used herein refers, for example, to removing at least 70, 75, 80, 85, 90, 95, 96, 97, 98 or 99 % by weight of the salt contained in the hollow fiber membrane.

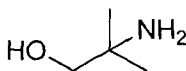
[0047] The expression “proceed to a sufficient extent” as used herein with reference to a chemical reaction or a physical reaction in a process disclosed herein means that the chemical reaction or physical reaction proceeds to an extent that conversion of the starting material or substrate to product is maximized. Conversion may be maximized when greater than about 5, 10, 15, 20, 25, 30, 35, 40, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 or 100% of the starting material or substrate is converted to product.

[0048] The term “microporous” as used herein with reference to the hollow fiber membranes disclosed herein means the membranes have a pore size of from about 1 μm to about 15 μm , or about 2 μm to about 5 μm .

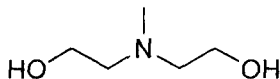
[0049] MEA as used herein refers to monoethanolamine:



[0050] AMP as used herein refers to 2-amino-2-methyl-1-propanol:

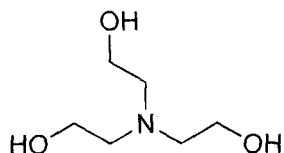


[0051] MDEA as used herein refers to methyldiethanolamine:

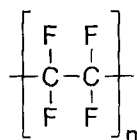


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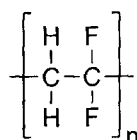
[0052] TEA as used herein refers to triethanolamine:



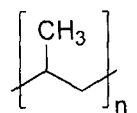
[0053] PTFE as used herein refers to polytetrafluoroethylene:



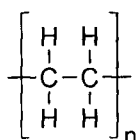
[0054] PVDF as used herein refers to polyvinylidene fluoride:



[0055] PP as used herein refers to polypropylene:

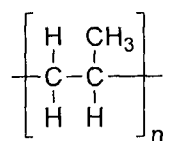


[0056] PE as used herein refers to polyethylene:

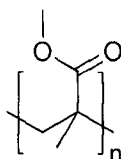


[0057] LDPE as used herein refers to low density polyethylene.

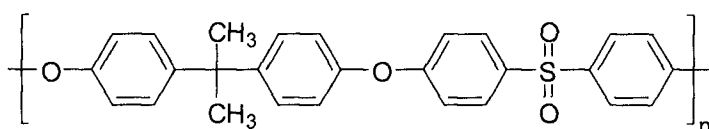
[0058] PP as used herein refers to polypropylene:



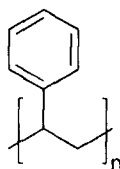
[0059] PMMA as used herein refers to poly(methyl methacrylate):



[0060] PSF as used herein refers to a series of polymers containing in their main chain mostly sulfone groups (SO₂) and ether groups, each linked to aromatic rings on both sides, with ether and sulfones alternating along the chain. For example, the following commercial polymers are both called polyethersulfones:



[0061] PS as used herein refers to polystyrene:



[0062] For example, the at least one suitable water soluble salt can have an average particle size of about 2 to about 15 μm , about 3 to about 12 μm or about 5 to about 10 μm .

[0063] For example, the mixture can comprise about 40 to about 60 % or about 45 to about 55 % by weight of the at least one suitable water soluble salt based on the total weight of the mixture.

[0064] For example, the conditions suitable to form the mixture can comprise:
mixing the at least one polymer suitable for melt extrusion with the at least one suitable water soluble salt so as to form a physical blend; and

feeding the physical blend into an apparatus suitable for melt blending the at least one polymer suitable for melt extrusion with the at least one suitable water soluble salt to form the mixture.

[0065] For example, the method can further comprise feeding the mixture into an apparatus suitable for converting the mixture into pellet form.

[0066] For example, the conditions suitable to form a hollow fiber membrane can comprise feeding the mixture into an apparatus suitable for melt extruding the mixture through a hollow fiber die.

[0067] For example, the hollow fiber die can have an inside diameter of about 1 mm to about 10 mm, and an outside diameter of about 1.5 mm to about 11 mm.

[0068] For example, the inside diameter can be about 5 mm and the outside diameter can be about 7 mm.

[0069] For example, the mixture can be fed into the apparatus suitable for melt extruding the mixture through a hollow fiber die is in pellet form.

[0070] For example, the conditions suitable for at least substantially removing the salt from the hollow fiber membrane can comprise leaching the hollow fiber membrane with water in a vessel at a temperature suitable for weakening the mechanical properties of the at least one polymer suitable for melt extrusion, for a time of about 120 min to about 160 min or about 160 min. For example, the time can depend upon the initial concentration of salt.

[0071] For example, the water in the vessel can be changed every about 15 h to about 30 min or about every about 20 min.

[0072] For example, the vessel can be suitable for continuous leaching of the hollow fiber membrane with water.

[0073] For example, the polymer suitable for melt extrusion can be chosen from thermoplastic melt-processable polymers, thermoplastic melt-processable copolymers, thermoplastic melt-processable elastomers, thermoplastic melt-processable composites, heat-curable thermoset polymers, heat-curable thermoset copolymers, heat-curable thermoset elastomers and heat-curable thermoset composites.

[0074] For example, the polymer suitable for melt extrusion can be chosen from polyolefins, polyolefin composites, vinyl polymers (such as polymethacrylates, polyvinyl acetates, or polyvinyl chlorides) polyacrylonitriles, polystyrene, polyesters, polyurethanes, nylons, and polyethersulfones.

[0075] For example, the polymer suitable for melt extrusion can be low density polyethylene (LDPE).

[0076] For example, the LDPE can have a density of about 910kg/m^3 to about 925kg/m^3 , about 915 kg/m^3 to about 920 kg/m^3 or about 919 kg/m^3 .

[0077] For example, the LDPE can have a melt index of about 0.8 g/10 min to about 7.5 g/10 min, about 1 g/10 min to about 5 g/10 min, about 2 g/10 min to about 4 g/10 min or about 2.3 g/10 min.

[0078] For example, the hollow fiber membrane can be leached with water at a temperature of about 10°C to about 60°C or about 60°C .

[0079] For example, the suitable water soluble salts can be chosen from alkali metal salts and alkaline-earth metal salts.

[0080] For example, the suitable water soluble salts can be chosen from alkali metal chlorides, alkali metal bromides, alkali metal iodides, alkali metal fluorides, alkali metal acetates, alkali metal carbonates, alkali metal phosphates, alkali metal sulfates and alkali metal nitrates.

[0081] For example, the alkali metal can be Li, Na, or K.

[0082] For example, the suitable water soluble salts can be chosen from alkali-earth metal chlorides, alkali-earth metal bromides, alkali-earth metal iodides, alkali-earth metal fluorides, alkali-earth metal acetates, alkali-earth metal carbonates, alkali-earth metal phosphates, alkali-earth metal sulfates and alkali-earth metal nitrates.

[0083] For example, the alkali-earth metal can be Mg or Ca.

[0084] For example, the suitable water soluble salt is sodium chloride.

[0085] Microporous and highly hydrophobic low density polyethylene (LDPE) hollow fiber membranes with inside and outside diameters of, respectively, 1.88-2.05

mm and 2.45-2.79 mm were successfully prepared via a solvent-free method, combining melt extrusion and salt-leaching techniques. NaCl particles with particle size of 1-10 μm were mixed with LDPE granules to produce a blend of 35, 40, 50, 60, 65 and 68 wt% of salt. The microporous structure was produced by leaching the salt particles from the hollow fiber matrix via immersion in water at 60°C. It was observed that leaching increased with time and with initial salt content, so that after 160 min immersion in water a reduction of 3, 6, 20 and 100% in salt content was obtained for hollow fiber membranes with initial salt content of 35, 40, 50 and 60-68 wt%, respectively. A remarkable increase in the water contact angles of hollow fiber membranes from 98° for LDPE hollow fibers fabricated without the addition of salt (blank sample) to 104°, 106°, 111°, 128°, 134° and 128°, respectively for hollow fibers with initial salt content of 35, 40, 50, 60, 65 and 68 wt%, is mainly attributed to the rough structure produced by removing imbedded salt crystals, which comprised a large number of micropapillas. The increase in surface roughness and porosity of hollow fiber membranes with the increase in initial salt content was confirmed by SEM and AFM analyses.

[0086] For example, the conditions suitable to form the mixture (comprising at least one polymer suitable for melt extrusion and at least one suitable water soluble salt) comprise melt blending at least one polymer suitable for melt extrusion with at least one suitable water soluble salt using, for example, the system shown in Figure 1 under conditions suitable to melt blend at least one polymer suitable for melt extrusion and the at least one water soluble salt.

[0087] For example, at least one polymer suitable for melt extrusion is mixed with, for example, from about 30 wt% to about 70 wt%, from about 35 wt% to about 70 wt%, from about 35 wt% to about 65 wt%, or from about 55 to about 65 wt% of at least one suitable water soluble salt to form a preliminary polymer-salt blend. The preliminary polymer-salt blend is fed into the extruder using the hopper (1). A person skilled in the art would readily understand how to choose a suitable temperature profile (for example from about 115°C to about 165°C, about 120°C to about 150°C, or from about 125°C to about 145°C) for the extruder zones, a suitable mass flow rate (for example from about 0.2 kg/h to about 0.8 kg/h, about 0.2 kg/h to about 0.6 kg/h or from about 0.3 to about 0.5 kg/h) and a suitable screw speed (for example

from about 15rpm to about 120 rpm, about 20 rpm to about 100 rpm or from about 40 rpm to about 65 rpm). For example, when the polymer suitable for melt extrusion is LDPE with a density of about 919 kg/m^3 (ASTM D792) and a melt index of about 2.3 g/10 min (ASTM D1238) and the suitable water soluble salt is NaCl with particle size of about 5-10 μm , the temperature is controlled at about 115°C for zone 1 (2), at about 135°C for zone 2 (3) and at about 140°C for zone 3 (4) and the die zone (5). After cooling in a water bath (6) fed by a fresh water spray (7) and emptied by salt-rich water drains (8) at a temperature from about 10°C to about 60°C or about room temperature, the extrudate is pelletized using a suitable method, for example using a PELL 2 pelletizer supplied by Berlyn Company to form pellets comprising the polymer-salt blend.

[0088] For example, the conditions suitable to form a hollow fiber comprising the polymer-salt blend comprise extruding the polymer-salt blend using, for example, the system shown in Figure 1. For example, pellets comprising the polymer-salt blend can be fed into the extruder using the hopper (1). A person skilled in the art would readily understand how to choose a suitable temperature profile for the extruder zones, a suitable mass flow rate and a suitable screw speed. For example, where the polymer suitable for melt extrusion is LDPE with a density of about 919 kg/m^3 (ASTM D792) and a melt index of about 2.3 g/10 min (ASTM D1238) and the suitable water soluble salt is NaCl with particle size of about 5-10 μm , the temperature is controlled at about 125°C for zone 1 (2), and a temperature of about 145°C to zone (2), zone 3 (4) and zone 4 (5); the extruder can be operated at a constant mass flow rate of about 0.2 kg/h to about 0.8 kg/h or about 0.4 kg/h; and the screw rate can be from about 15 rpm to about 120 rpm or about 60 rpm. The extrudate can be taken out of a hollow fiber die (10) with an inside diameter of from about 1 mm to about 10mm or about 5 mm, and an outside diameter of about 1.5 mm to about 11 mm or about 7 mm, and cooled in a water bath (6) fed by a fresh water spray (7) and emptied by salt-rich water drains (8) at a temperature of about 10°C to about 60°C or about room temperature. A take-up unit (11) can be used to control drawing speed at from about 200cm/min to about 300cm/min or about 250 cm/min.

[0089] For example, the conditions suitable for the removal of salt to proceed to a sufficient extent comprise placing hollow fibers comprising the polymer-salt blend into a suitable vessel, fully covering the hollow fibers comprising the polymer-salt blend with water, thoroughly sealing the vessel containing the water-hollow fiber mixture, and maintaining the vessel containing the water-hollow fiber mixture at a temperature of from about 10°C to about 60°C or about 60°C for a time of about 120 min to about 160 min, wherein the water in the vessel is changed every about 15 min to about 30 min or about 20 min.

[0090] For example, the polymer suitable for melt extrusion can be a suitable LDPE. The polymer can also be (polyolefins or polyolefin composites, vinyl polymers such as polymethacrylates, polyvinyl acetate, polyvinyl chloride, polyacrylonitrile or polystyrene, polyesters, polyurethanes, nylons, polyethersulfones, or any other thermoplastic polymer, copolymer, elastomer or composite, or any heat-curable thermoset polymer, copolymer, elastomer or composite). For example, the suitable LDPE can have a density of about 910 kg/m³ to about 925 kg/m³ or about 919 kg/m³ (ASTM D792) and a melt index of about 0.8 g/10 min to about 7.5 g/10 min or about 2.3 g/10 min (ASTM D1238).

[0091] For example, the suitable water soluble salt can be NaCl of a suitable particle size. The salt can also be a water-soluble alkali or alkali earth salt (alkali fluoride, chloride bromide, iodide, acetate, carbonate, phosphate, sulfate or nitrate), which melts at a higher temperature than the chosen polymer. For example, the particle size of the NaCl can be from about 1 μm to about 20 μm, about 2 to about 15 μm or about 5 to about 10 μm.

[0092] For example, the inside diameters of the microporous hollow fiber membrane can be from about 1 mm to about 3 mm or about 1.5 mm to about 1.9 mm. For example, the outside diameters of the microporous hollow fiber membrane can be from about 1.5 mm to about 4 mm or about 1.8 to about 2.3 mm.

[0093] For example, where the polymer suitable for melt extrusion is LDPE with a density of about 919 kg/m³ (ASTM D792) and a melt index of about 2.3 g/10 min (ASTM D1238) and the suitable water soluble salt is NaCl with particle size of about 5-10 μm, the water contact angles of the microporous hollow fiber membrane

can be from about 104° to about 140° depending on the salt content or about 128° to about 140°.

[0094] According to a further aspect, the present application includes a microporous hollow fiber membrane prepared by a method for preparing a microporous hollow fiber membrane, which comprises:

mixing at least one polymer suitable for melt extrusion with at least one suitable water soluble salt under conditions suitable to form a polymer-salt blend;

extruding the polymer-salt blend under conditions suitable to form a hollow fiber comprising the polymer-salt blend; and

leaching the hollow fiber comprising the polymer-salt blend in water under conditions suitable for the removal of salt to proceed to a sufficient extent.

[0095] The following non-limiting examples are illustrative of the present application:

EXAMPLES

Materials

[0096] The LDPE used in the work described herein was Novapol LA 0219-A (Nova Chemicals) with a density of 919 kg/m³ (ASTM D792) and a melt index of 2.3 g/10 min (ASTM D1238). NaCl (SODA-LO 20) with particle size of 5-10 µm was supplied by Main Street Ingredients.

Example 1: Fabrication of LDPE hollow fibers

[0097] The melt-extrusion system for LDPE hollow fibers fabrication is shown in Figure 1. LDPE hollow fiber membranes were produced using a HaakeRheomix TW-100 co-rotating twin-screw extruder. LDPE was mixed thoroughly with NaCl to form blends containing 35, 40, 50, 60, 65 and 68 wt% salt. The mixture was then fed into the extruder using the hopper (1) in two steps. In the first step, the mixture was melt blended above the melting point of LDPE to obtain a uniform polymer/salt blend. The temperature profile was controlled at 115°C for zone 1 (2) 135°C for zone 2 (3) and 140°C for zone 3 (4) and the die zone, i.e. zone 4 (5). After cooling down through a water bath(6) fed by a fresh water spray (7) and emptied by salt-rich water drains (8) at room temperature, the extrudate was pelletized using a PELL 2

pelletizer supplied by Berlyn Company (not shown). In the second step, the prepared pellets were fed into the extruder using the hopper (1) at a temperature of 115°C for zone 1 (2), 135°C for zone 2 (3) and 140°C for zone 3 (4) and zone 4 (5). The extruder was operated at a constant mass flow rate of 0.4 kg/h and a screw speed of 60 rpm. To produce a stable hollow fiber structure, the inside air pressure was controlled (9) to prevent collapse. The extrudate was taken out of the hollow fiber die (10) with an inside and outside diameter of 5 and 7 mm, respectively and cooled down through a water bath (6) fed by a fresh water spray (7) and emptied by salt-rich water drains (8) at 60°C. Finally, a take-up unit (11) was used to control drawing speed at 250 cm/min. A motor drive (12) is also shown in Figure 1.

[0098] The detailed specifications of microporous LDPE hollow fiber membranes fabricated by this method are given in Table 3.

Table 3

Characteristics	Blank LDPE	LDPE/35 wt% NaCl	LDPE/40 wt% NaCl	LDPE/50 wt% NaCl	LDPE/60 wt% NaCl	LDPE/65 wt% NaCl	LDPE/68 wt% NaCl
Fiber outer diameter (mm)	2.66	2.75	2.79	2.62	2.45	2.62	2.60
Fiber inner diameter (mm)	1.90	2.05	2.05	2.11	1.88	2.01	1.99
Fiber thickness (mm)	0.38	0.34	0.37	0.25	0.28	0.30	0.30

Example 2: Formation of porous structure in LDPE hollow fibers

Materials and Methods

[0099] The porous structure of the LDPE hollow fibers prepared by the method of Example 1 was formed by removal of salt particles using a water leaching technique. In an exemplary preparation, 30 mm of prepared hollow fiber samples were placed in small vials, fully filled with water. The vials were sealed thoroughly

and kept for 160 min in an oven at 60°C to enhance the leaching process. Water was changed every 20 min to avoid saturation.

[00100] The percentage of salt removal was determined by comparing the dry weight of each specimen before and after leaching, using a high-resolution Mettler AE 240 digital balance. In addition, the content of salt remained in/removed from LDPE hollow fiber membranes with different initial salt content was confirmed by thermo-gravimetric analysis (TGA) of fresh fibers (before leaching) and fibers after 160 min leaching with water (after leaching), using a TA Instruments TGA model Q5000 IR from ambient temperature to 950°C at a heating rate of 10°C/min under air.

[00101] The porosity of the hollow fiber membranes (P) was determined via density method using the relation (1):

$$P(\%) = 1 - \left(\frac{\rho_1}{\rho_0} \right) \times 100 \quad (1)$$

where ρ_0 is the density of nonporous LDPE hollow fiber (blank) and ρ_1 indicates the density of porous LDPE hollow fiber membranes with different initial salt contents. ρ_0 and ρ_1 were calculated by measuring the volume and the weight of hollow fiber samples using the relation (2):

$$\rho = \frac{W}{\pi L(R^2 - r^2)} \quad (2)$$

where W is the weight of the hollow fiber, R and r are the outer and inner diameters, respectively, and L is the length of the hollow fiber. The porous structure of hollow fiber membranes was visually investigated using a scanning electron microscope (SEM) (JEOL Ltd., JSM-840a).

[00102] Pore diameter distribution of fabricated LDPE hollow fiber membranes were calculated via digitizing and analyzing the SEM images using Image-Pro-Plus Version 5.0 software (Media Cybernetics Inc.).

Results and Discussion

[00103] Generally, leaching is a slow process. In order to accelerate this process, salt leaching was done at temperatures higher than room temperature (around 60°C). At such temperatures, solubility and diffusion are higher, and salt particles can more easily be removed from the fiber to diffuse into the water. The

structure of PE is weakened and thus, salt particles can be easier removed from the fiber to diffuse into the water by the open cell morphology. In addition, the continuous leaching system used in this work (Figure 1) can reduce the leaching time to a great extent.

[00104] Since the formation of a porous structure strongly depends on the amount of salt removed from the hollow fiber matrix, it is essential to determine the level of salt removed from LDPE/salt fibers. The amount of salt removed from LDPE/salt hollow fibers was obtained by comparison of the dry weight of each sample before and after leaching in water. The percentage of salt removal (% salt removal) was calculated according to the following relation.

$$\% \text{ Salt removal} = \left(\frac{\% \text{ weight loss}}{\% \text{ initial salt content}} \right) \times 100 \quad (3)$$

[00105] Figure 2 shows the percentage of salt removed from LDPE hollow fibers, fabricated using 35, 40, 50, 60, 65 and 68 wt% salt. The ultimate percentage of salt removal was found to increase with increasing initial salt content from 35 to 68 wt%, so that it reaches from about 3% and 5%, respectively for samples with initial salt contents of 35 and 40 wt% to about 100% for those containing 60-68 wt% NaCl. While not wishing to be limited by theory, this could be attributed to the increasing number of pathways formed by the interconnections of salt particles, as they get closer together with increasing salt content. The interconnecting pathways provide better access to water for leaching out the salt particles.

[00106] Figures 3-8 show the TGA curves of LDPE hollow fiber membranes with various initial salt contents. At a temperature range of around 300-500°C, a weight loss of about 70% is observed due to the polymer thermal degradation. After the complete degradation of polymer, the sample weight remains constant. The sample weight in this region (500-750°C) is equivalent to the content of salt in the corresponding sample. The lower contents of NaCl shown by TGA than those initially blended with the polymer are attributed to the loss caused during fabrication (Table 4). The second break at around 750°C corresponds to NaCl degradation. Considering the TGA curves, the following results can be obtained: 1. the real initial salt content for all samples is lower than those initially mixed with PE. While not wishing to be limited by theory, this can arise either from the loss of ultra-fine salt

particles from the hopper or due to their sticking inside the extruder. 2. for samples with an initial salt content lower than 60 wt%, the leaching duration is too long, so that even after 160 min continuous leaching, a significant amount of salt remains inside the polymer matrix. This can confirm that a percentage of the salt removal increases by increasing the initial salt content.

Table 4

Salt wt% before extrusion (in polymer/salt blend)	Salt wt% after 1 st extrusion step (blending)	Salt wt% after 2 nd extrusion step (fiber fabrication)	% salt loss at the 1 st extrusion step	% salt loss at the 2 nd extrusion step
35	27	25	22	7
40	37	36	7.5	2.7
50	42	44	16	4.7
60	56	53	7.1	3.5
65	59	57	9.2	3.3
68	61	59	10.2	3.3

[00107] Such observations were confirmed by comparing the SEM micrographs of LDPE hollow fibers with 0-68 wt% initial NaCl content (Figures 9, 10). It can be clearly observed that the structure of hollow fibers changed from dense and nonporous (Figures 9A-9C) to porous and highly rough in character with a large number of micropapillas on the surface (Figures 10A-10F). In addition, SEM micrographs of cross sections of hollow fiber membranes evidently show that the porous structure becomes more interconnected and perforated through the thickness of the hollow fibers, as the initial salt content increases from 35 to 68 wt%.

[00108] The values of density and porosity of LDPE hollow fiber membranes are presented in Table 5. In accordance with the SEM micrographs, the porosity of hollow fiber samples increases from 0% for blank LDPE hollow fibers to about 51% for LDPE hollow fiber membranes with initial salt content of 68 wt%. Furthermore, the density of hollow fiber samples varies in reverse proportion to the initial salt content and fiber porosity.

Table 5

Property Membrane	Density (g/cm ³)	Porosity (%)
Blank (neat)	0.92	-
35 wt% NaCl	1.17	9
40 wt% NaCl	1.04	13
50 wt% NaCl	0.93	26
60 wt% NaCl	0.72	49
65 wt% NaCl	0.72	49
68 wt% NaCl	0.70	51

[00109] Figure 11 shows the pore size distribution of LDPE hollow fiber membranes with complete salt removal (samples prepared using 60-68 wt% salt). For all membranes, the maximum pore diameters are in the range of 2-5 μm . In addition, the pore diameters slightly decrease with increase in the initial salt content.

Example 3: Roughness measurements of LDPE hollow fibers

Materials and methods

[00110] Atomic Force Microscopy (AFM) experimental apparatus: AFM studies were conducted in tapping mode at the interior surface of hollow fibers using a Nanoscope III equipped with a 1553D scanner (Veeco Instruments Inc.).

[00111] Sample preparation: The access to the interior surface of membranes was done by cutting them longitudinally in very narrow ribbons of less than 1 mm width and 5 mm length. The analysis was done on the membranes with 40 and 68 wt% initial salt content and the blank fiber, for comparison.

[00112] The roughness parameters in terms of mean surface roughness (R_a), maximum roughness and RMS (R_s) were determined by the Veeco NanoScope

Software version 5.30. R_a and R_s are calculated from: $R_a = \sqrt{\frac{\sum_{i=1}^N (Z_i - Z_{ave})^2}{N}}$ and

$$R_s = \frac{\sum_{i=1}^N |Z_i - Z_{cp}|^2}{N}$$

where N is the number of points in the measured surface area, Z_i is the vertical scanner tip position at a given position of the image, Z_{ave} is the average Z value and Z_{cp} is the Z value of the center plane.

Results and discussion

[00113] Figures 12A-12C shows AFM plots and the calculated of LDPE fibers. The scanning scale which is equivalent to the height of the peaks (micropapillars) of the surface rises from 600 nm for the blank sample to 7.1 μm for the sample with initial salt content of 60 wt%. In addition, the mean roughness (R_a) increases as the initial salt content rises, so that it reaches from about 70 nm for the smooth surface of the blank LDPE hollow fiber to about 157 nm for the membrane with 40 wt% of initial salt and to 681 nm for the membrane with initial salt content of 60 wt%.

Example 3: Contact angle measurements of LDPE hollow fibers

Materials and methods

[00114] The optical contact angle analyzer (OCA15 EC Plus, Dataphysics) was used to measure water contact angles of LDPE hollow fibers using the sessile drop method. The system employed a high resolution camera and specific software developed to capture and analyze the contact angle on very small and curved surfaces². For very precise measurements, water droplets of 0.15 μl were dispensed on both inner and outer surfaces of hollow fiber samples via an ultra-thin needle with an internal diameter of 0.18 mm. For each experimental condition, measurements were performed on at least three samples and on three different portions of each sample in order to ensure the reproducibility of the results. The reported data for contact angles is the average of three obtained values.

Results and discussion

[00115] Table 6 shows the static water contact angle of LDPE hollow fiber samples.

Table 6

Membrane	Contact angle (°)	Errors (°)
Blank (neat)	98.2	± 0.6
35 wt% NaCl	104.0	± 0.6
40 wt% NaCl	105.9	± 0.7
50 wt% NaCl	111.1	± 0.6
60 wt% NaCl	128.2	± 2.4
65 wt% NaCl	133.6	± 0.9
68 wt% NaCl	140.3	± 1.9

[00116] It can be clearly observed that contact angle rises with the increase in initial salt content, so that for the sample with 68 wt% initial salt content, the contact angles reaches 140°. This is attributed to higher surface roughness, caused by the increase in the number of micropapillas, and high porosity membrane structure form as the initial salt content increases. The surface of microporous LDPE hollow fibers can be considered as a composite comprising trapped air and rough LDPE. According to the Cassie and Baxter theory³, the contact angle of a hydrophobic rough surface comprising solid and air can be determined using the following relation:

$$\cos \theta_r = f_1 \cos \theta - f_2 \quad (4)$$

where θ refers to the contact angle of smooth surface, θ_r defines the contact angle of rough surface and f_1 and f_2 are respectively the fractions of solid and air in the composite surface. This equation predicts that increasing the fraction of air (f_2) would lead to the increase in the contact angle. Since the roughness and porosity increase by raising the initial salt content, more air can be trapped in the pores and surface valleys leading to the increase in the contact angle. This remarkable rise of contact angles by increasing the initial salt content, can arise from the lower tendency of the surface to wetting, and is considered as the "lotus effect" which can be mimicked in artificial highly hydrophobic surfaces^{16,17,18}. By increasing the initial salt content much rougher surface is obtained (Figures 12A-C), which can end up with less contact between the sample surface and the testing liquid.

Example 4: Mechanical properties of LDPE hollow fiber membranes**Materials and methods**

[00117] Mechanical properties of LDPE hollow fiber membranes including tensile strength, Young's modulus and stress at break were measured using a RSA-3 Dynamic Mechanical Analyzer (DMA) supplied by TA Instruments. During the test, the hollow fiber membranes were held with grips, while a crosshead pulls fibers in tension at constant rate of 10 mm/min until the fiber can no longer resist and it is torn.

[00118] Strain was measured by the apparatus and the load-strain curve was developed. By dividing the load by the cross-sectional area of the sample, the stress-strain curve for each hollow fiber membrane was obtained. The modulus of elasticity (Young's modulus), which indicates the stiffness of the material or its resistance against elastic strain, was then determined by the slope of the stress-strain curve in the elastic region.

Results and discussion

[00119] The stress-strain curves of LDPE hollow fiber samples, the corresponding tensile stress and strain at break, as well as the Young's modulus are depicted in Figure 13. Young's modulus of hollow fiber samples decreased with an increase in the initial salt content, from 152 MPa for the blank sample to 60 MPa for the sample with an initial salt content of 60 wt%. While not wishing to be limited by theory, this can be attributed to cracks formed in the hollow fiber structure due to the high osmotic pressure during the salt extraction process. For the hollow fiber membrane with an initial salt content of 40 wt%, the stress at break reduces to 31 MPa, compared to that of 35 MPa for blank hollow fiber. This value reduces to 18 MPa for the membrane with an initial salt content of 60 wt%. While not wishing to be limited by theory, this can be due to the porous and cracked structure formed during the long salt extraction process, as described earlier.

[00120] Furthermore, the reduction of tensile stress of hollow fiber membranes with an increase in initial salt content is the expected result of the addition of rigid particles to glassy polymers⁴. This deterioration in mechanical properties has been observed in the literature for porous polymeric membranes and rigid particle filled polymeric compounds^{13,36,37}.

Example 5: Preparation of LDPE fibers via literature conditions

[00121] Several polyethylene (LDPE) fibers were fabricated via melt-extrusion following the conditions given in the paper by Dangtungee and Supaphol³¹. The NaCl-containing fibers were then leached with water for a prolonged time (7 days), in order to verify the salt removal and the pore formation. The SEM micrographs of the corresponding samples (Figures 14b-e) showed that no matter the conditions used (salt content and particle size varying between 5 and 25 wt% and 45 and 125 μm , respectively), dense and non-porous fiber structures were formed, even after a long leaching period.

[00122] In contrast, the fiber of the present application prepared by melt-extrusion/160 min leaching, using 60 wt% NaCl of 5-10 μm , presented a highly porous structure with small pores, characteristic to a microporous membrane (Figure 14a). In addition to the SEM micrographs, BSE (Back-scattered Electron Detector) images and EDS (Energy-Dispersive X-Ray Spectroscopy) analysis also indicated the presence of NaCl in the leached fibers fabricated using the literature conditions³¹ (Figures 15A-D). Finally, TGA (thermogravimetric analysis) diagrams of the same fibers³¹ confirm the existence of salt particles after leaching (Figures 16A-D), in contrast to the example of the membrane of the present application where a significant difference is observed between the curves before and after leaching (Figure 16E).

Example 6: Comparison to untreated and treated PP membranes

[00123] Lv et al.³³ performed a solvent (cyclohexanone and methyl ethyl ketone mixture) based treatment of polypropylene (PP) membrane fibers by depositing a rough layer on the surface in order to improve its hydrophobicity and consequently, to reduce the wetting phenomenon. Membrane efficiency was tested by CO_2 absorption in aqueous solutions of monoethanolamine in a membrane contactor for 20 days. A comparison between untreated (commercially available) PP, treated (solvent casting method) PP and the LDPE membrane of the present application is shown in Figure 17. The LDPE membrane shows a more stable and efficient performance (higher absorption flux and less decrease in the flux during the time).

[00124] The person skilled in the art would understand that the various properties or features presented in a given embodiment can be added and/or used, when applicable, to any other embodiment covered by the general scope of the present disclosure.

[00125] The present disclosure has been described with regard to specific examples. The description was intended to help the understanding of the disclosure, rather than to limit its scope. It will be apparent to one skilled in the art that various modifications can be made to the disclosure without departing from the scope of the disclosure as described herein, and such modifications are intended to be covered by the present document.

[00126] All publications, patents and patent applications are herein incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference in its entirety. Where a term in the present application is found to be defined differently in a document incorporated herein by reference, the definition provided herein is to serve as the definition for the term.

FULL CITATIONS FOR DOCUMENTS REFERRED TO IN THE SPECIFICATION

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CLAIMS:

1. A method for preparing a microporous hollow fiber membrane, which comprises:

mixing at least one polymer suitable for melt extrusion with at least one suitable water soluble salt having an average particle size of about 1 to about 20 μ m under conditions suitable to form a mixture comprising about 35 to about 70 % by weight of the at least one suitable water soluble salt based on the total weight of the mixture;

extruding the mixture under conditions suitable to form a hollow fiber membrane comprising the mixture; and

leaching the hollow fiber membrane comprising the mixture in water under conditions suitable for at least substantially removing the salt from the hollow fiber membrane.

2. The method of claim 1, wherein the at least one suitable water soluble salt has an average particle size of about 2 to about 15 μ m.

3. The method of claim 1, wherein the at least one suitable water soluble salt has an average particle size of about 5 to about 10 μ m.

4. The method of claim 1, 2 or 3, wherein the mixture comprises about 40 to about 60 % by weight of the at least one suitable water soluble salt based on the total weight of the mixture.

5. The method of claim 1, 2 or 3, wherein the mixture comprises about 45 to about 55 % by weight of the at least one suitable water soluble salt based on the total weight of the mixture.

6. The method of any one of claims 1 to 5, wherein the conditions suitable to form the mixture comprise:

mixing the at least one polymer suitable for melt extrusion with the at least one suitable water soluble salt so as to form a physical blend; and

feeding the physical blend into an apparatus suitable for melt blending the at least one polymer suitable for melt extrusion with the at least one suitable water soluble salt to form the mixture.

7. The method of claim 6, further comprising feeding the mixture into an apparatus suitable for converting the mixture into pellet form.

8. The method of any one of claims 1 to 7, wherein the conditions suitable to form a hollow fiber membrane comprise feeding the mixture into an apparatus suitable for melt extruding the mixture through a hollow fiber die.

9. The method of claim 8, wherein the hollow fiber die has an inside diameter of about 1mm to about 10 mm, and an outside diameter of about 1.5mm to about 11mm.

10. The method of claim 9, wherein the inside diameter is about 5 mm and the outside diameter is about 7 mm.

11. The method of any one of claims 8 to 10, wherein the mixture fed into the apparatus suitable for melt extruding the mixture through a hollow fiber die is in pellet form.

12. The method of any one of claims 1 to 11, wherein the conditions suitable for at least substantially removing the salt from the hollow fiber membrane comprise

leaching the hollow fiber membrane with water in a vessel at a temperature suitable for weakening the mechanical properties of the at least one polymer suitable for melt extrusion, for a time of about 120 min to about 200 min.

13. The method of claim 12, wherein the time is about 160 min.

14. The method of claim 12 or 13, wherein the water in the vessel is changed every about 15 min to about 30 min.

15. The method of claim 14, wherein the water in the vessel is changed every about 20 min.

16. The method of claim 12 or 13, wherein the vessel is suitable for continuous leaching of the hollow fiber membrane with water.

17. The method of any one of claims 1 to 16, wherein the polymer suitable for melt extrusion is chosen from thermoplastic melt-processable polymers, thermoplastic melt-processable copolymers, thermoplastic melt-processable elastomers, thermoplastic melt-processable composites, heat-curable thermoset polymers, heat-curable thermoset copolymers, heat-curable thermoset elastomers and heat-curable thermoset composites.

18. The method of any one of claims 1 to 16, wherein the polymer suitable for melt extrusion is chosen from polyolefins, polyolefin composites, vinyl polymers (such as polymethacrylates, polyvinyl acetates, or polyvinyl chlorides) polyacrylonitriles, polystyrene, polyesters, polyurethanes, nylons, and polyethersulfones.

19. The method of any one of claims 1 to 16, wherein the polymer suitable for melt extrusion is low density polyethylene (LDPE).

20. The method of claim 19, wherein the LDPE has a density of about 910kg/m³ to about 925kg/m³.
21. The method of claim 20, wherein the density is about 919 kg/m³.
22. The method of any one of claims 19 to 21, wherein the LDPE has a melt index of about 0.8g/10 min to about 7.5g/10 min.
23. The method of claim 22, wherein the melt index is about 2.3 g/10 min.
24. The method of any one of claims 16 to 23, wherein the hollow fiber membrane is leached with water at a temperature of about 10°C to about 60°C.
25. The method of claim 24, wherein the temperature is about 60°C.
26. The method of any one of claims 1 to 25, wherein the suitable water soluble salt is sodium chloride.
27. The method of any one of claims 1 to 25, wherein the suitable water soluble salts is chosen from alkali metal salts and alkaline-earth metal salts.
28. The method of any one of claims 1 to 25, wherein the suitable water soluble salts is chosen from alkali metal chlorides, alkali metal bromides, alkali metal iodides, alkali metal fluorides, alkali metal acetates, alkali metal carbonates, alkali metal phosphates, alkali metal sulfates and alkali metal nitrates.

29. The method of any one of claims 1 to 25, wherein the suitable water soluble salts is chosen from alkali-earth metal chlorides, alkali-earth metal bromides, alkali-earth metal iodides, alkali-earth metal fluorides, alkali-earth metal acetates, alkali-earth metal carbonates, alkali-earth metal phosphates, alkali-earth metal sulfates and alkali-earth metal nitrates.

30. A microporous hydrophobic hollow fiber membrane comprising :

a porosity of about 10 to about 80 %;

a mean roughness (R_a) of about 100 nm to about 1000 nm;

a water contact angle of about 110 to about 140°; and

microporous pores having a diameter of about 0.1 to about 1000 μm .

31. A microporous hydrophobic hollow fiber membrane comprising :

a porosity of about 40 to about 60 %;

a mean roughness (R_a) of about 600 to about 800 nm;

a water contact angle of about 128 to about 140°; and

microporous pores having a diameter of about 1 to about 20 μm .

32. A microporous hydrophobic hollow fiber membrane comprising :

a porosity of about 49 to about 51 %;

a mean roughness (R_a) of about 650 to about 750 nm;

a water contact angle of about 128 to about 140°; and

microporous pores having a diameter of about 2 to about 5 μm .

33. A microporous hydrophobic hollow fiber membrane comprising :

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a density of about 0.70 to about 0.72 g/cm³;
a porosity of about 49 to about 51 %;
a mean roughness (R_a) of about 700 nm;
a water contact angle of about 128 to about 140°; and
microporous pores having a diameter of about 2 to about 5 µm.

34. A microporous hollow fiber membrane prepared by a method for preparing a microporous hollow fiber membrane, which comprises:

mixing at least one polymer suitable for melt extrusion with at least one suitable water soluble salt under conditions suitable to form a polymer-salt blend;

extruding the polymer-salt blend under conditions suitable to form a hollow fiber comprising the polymer-salt blend; and

leaching the hollow fiber comprising the polymer-salt blend in water under conditions suitable for the removal of salt to proceed to a sufficient extent.

35. The method of claim 34, wherein the conditions suitable to form the mixture comprise:

mixing the at least one polymer suitable for melt extrusion with the at least one suitable water soluble salt so as to form a physical blend; and

feeding the physical blend into an apparatus suitable for melt blending the at least one polymer suitable for melt extrusion with the at least one suitable water soluble salt to form the mixture.

36. The method of claim 35, further comprising feeding the mixture into an apparatus suitable for converting the mixture into pellet form.

37. The method of any one of claims 34 to 36, wherein the conditions suitable to form a hollow fiber membrane comprise feeding the mixture into an apparatus suitable for melt extruding the mixture through a hollow fiber die.

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38. The method of claim 37, wherein the hollow fiber die has an inside diameter of about 1mm to about 10 mm, and an outside diameter of about 1.5mm to about 11mm.

39. The method of claim 38, wherein the inside diameter is about 5 mm and the outside diameter is about 7 mm.

40. The method of any one of claims 37 to 39, wherein the mixture fed into the apparatus suitable for melt extruding the mixture through a hollow fiber die is in pellet form.

41. The method of any one of claims 34 to 40, wherein the conditions suitable for at least substantially removing the salt from the hollow fiber membrane comprise leaching the hollow fiber membrane with water in a vessel at a temperature suitable for weakening the mechanical properties of the at least one polymer suitable for melt extrusion, for a time of about 120 min to about 200 min.

42. The method of claim 41, wherein the time is about 160 min.

43. The method of claim 41 or 42, wherein the water in the vessel is changed every about 15 min to about 30 min.

44. The method of claim 14, wherein the water in the vessel is changed every about 20 min.

45. The method of claim 12 or 13, wherein the vessel is suitable for continuous leaching of the hollow fiber membrane with water.

46. The method of any one of claims 34 to 45, wherein the polymer suitable for melt extrusion is chosen from thermoplastic melt-processable polymers, thermoplastic melt-processable copolymers, thermoplastic melt-processable elastomers, thermoplastic melt-processable composites, heat-curable thermoset polymers, heat-curable thermoset copolymers, heat-curable thermoset elastomers and heat-curable thermoset composites.

47. The method of any one of claims 34 to 45, wherein the polymer suitable for melt extrusion is chosen from polyolefins, polyolefin composites, vinyl polymers (such as polymethacrylates, polyvinyl acetates, or polyvinyl chlorides) polyacrylonitriles, polystyrene, polyesters, polyurethanes, nylons, and polyethersulfones.

48. The method of any one of claims 34 to 45, wherein the polymer suitable for melt extrusion is low density polyethylene (LDPE).

49. The method of claim 48, wherein the LDPE has a density of about 910kg/m^3 to about 925kg/m^3 .

50. The method of claim 49, wherein the density is about 919 kg/m^3 .

51. The method of any one of claims 48 to 50, wherein the LDPE has a melt index of about $0.8\text{g}/10\text{ min}$ to about $7.5\text{g}/10\text{ min}$.

52. The method of claim 51, wherein the melt index is about $2.3\text{ g}/10\text{ min}$.

53. The method of any one of claims 45 to 52, wherein the hollow fiber membrane is leached with water at a temperature of about 10°C to about 60°C .

54. The method of claim 53, wherein the temperature is about 60°C.
55. The method of any one of claims 34 to 54, wherein the suitable water soluble salt is sodium chloride.
56. The method of any one of claims 34 to 54, wherein the suitable water soluble salts is chosen from alkali metal salts and alkaline-earth metal salts.
57. The method of any one of claims 34 to 54, wherein the suitable water soluble salts is chosen from alkali metal chlorides, alkali metal bromides, alkali metal iodides, alkali metal fluorides, alkali metal acetates, alkali metal carbonates, alkali metal phosphates, alkali metal sulfates and alkali metal nitrates.
58. The method of any one of claims 34 to 54, wherein the suitable water soluble salts is chosen from alkali-earth metal chlorides, alkali-earth metal bromides, alkali-earth metal iodides, alkali-earth metal fluorides, alkali-earth metal acetates, alkali-earth metal carbonates, alkali-earth metal phosphates, alkali-earth metal sulfates and alkali-earth metal nitrates.

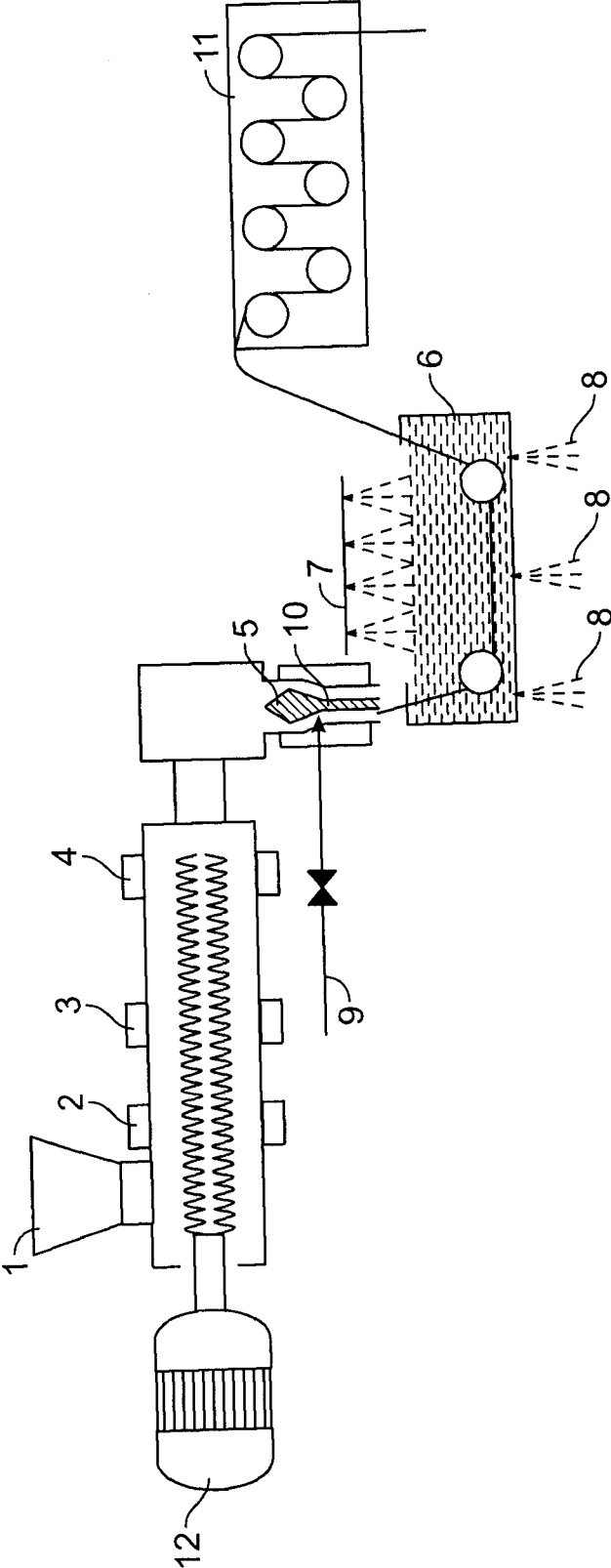


FIG. 1

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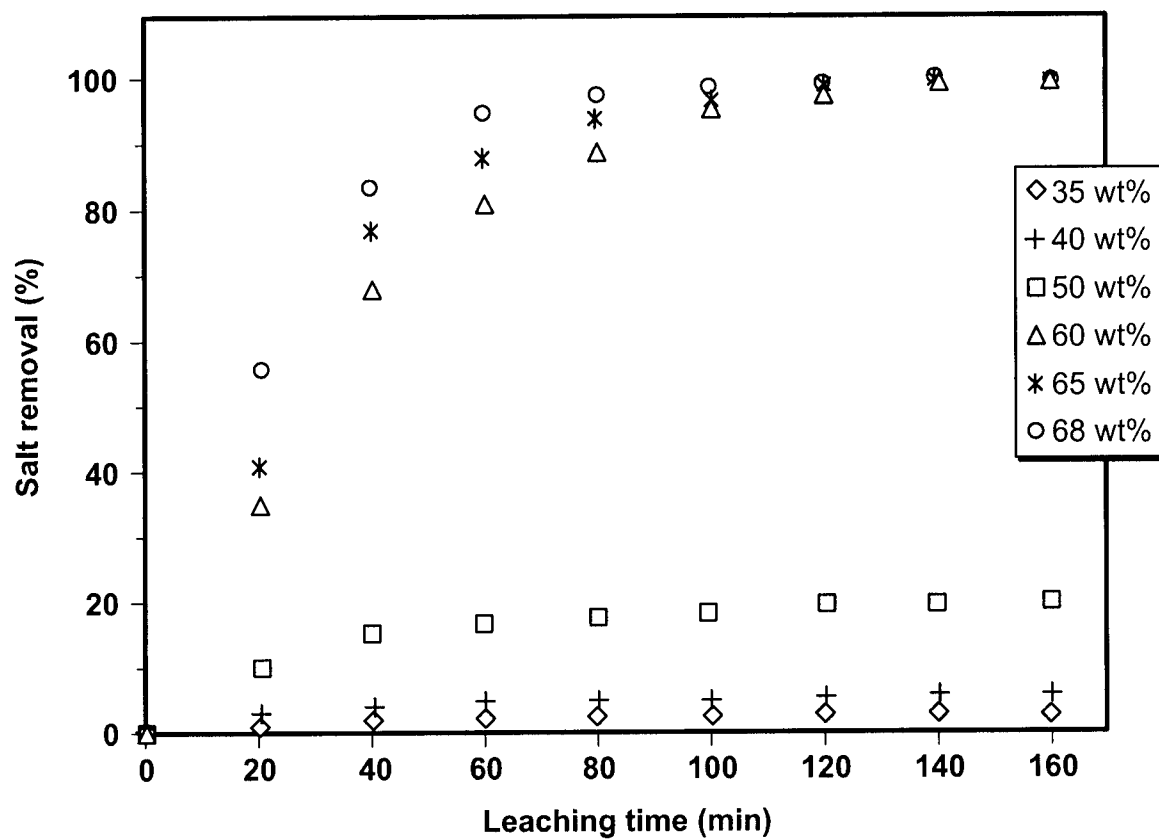


FIG. 2

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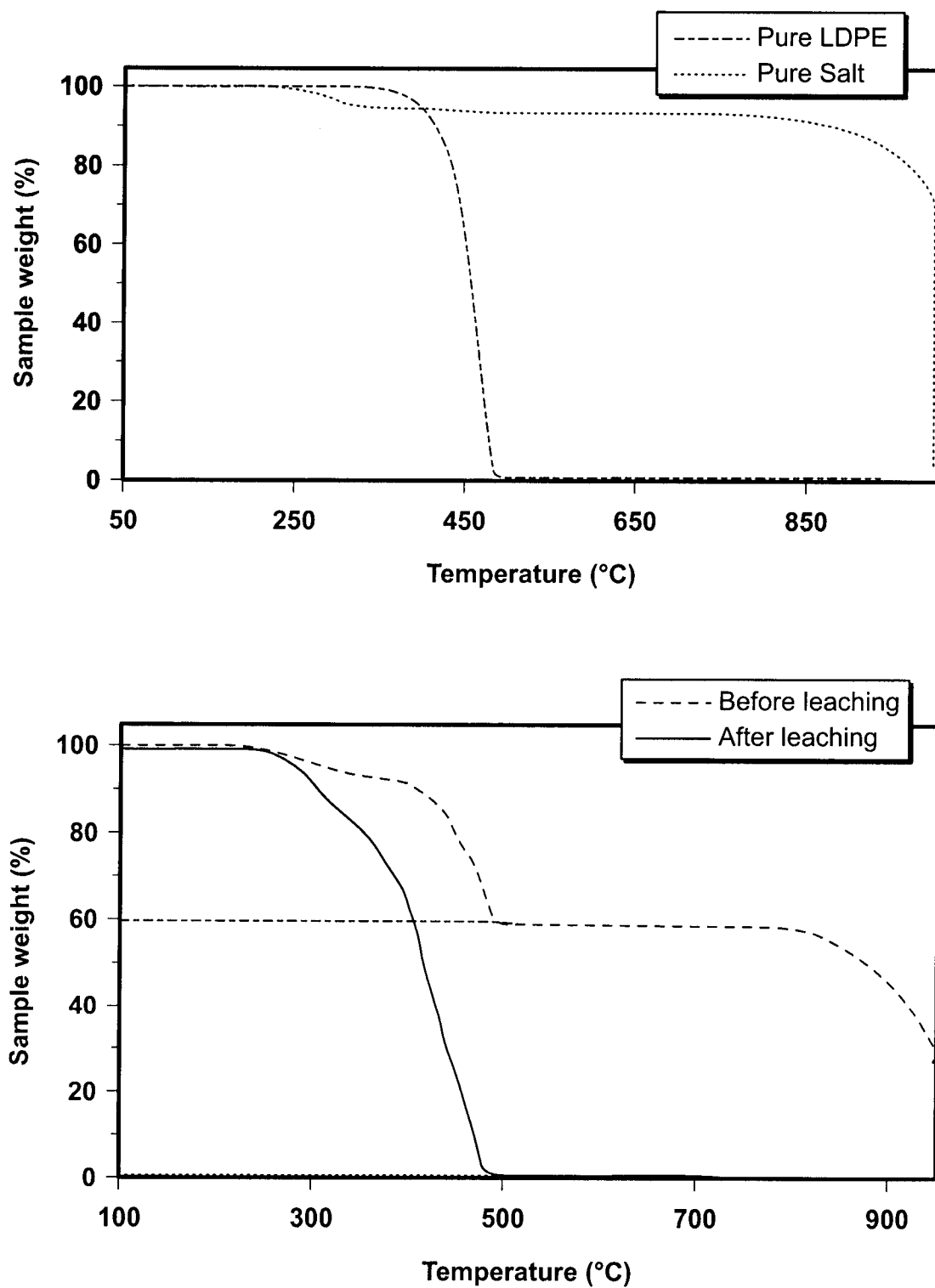


FIG. 3

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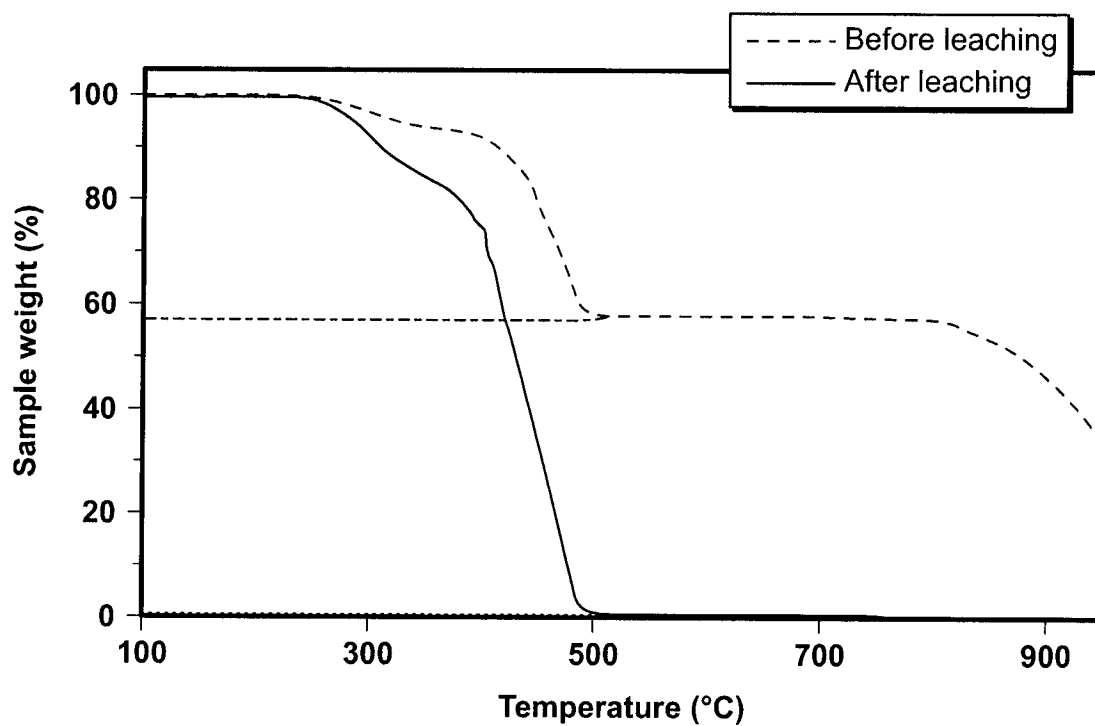


FIG. 4

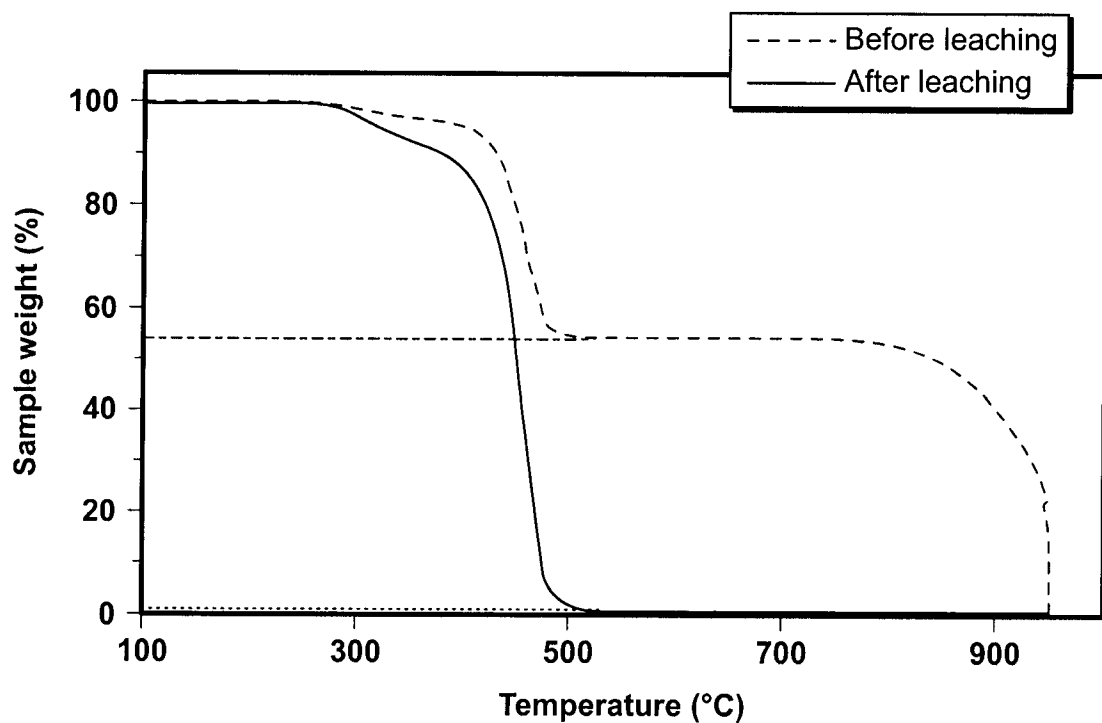


FIG. 5

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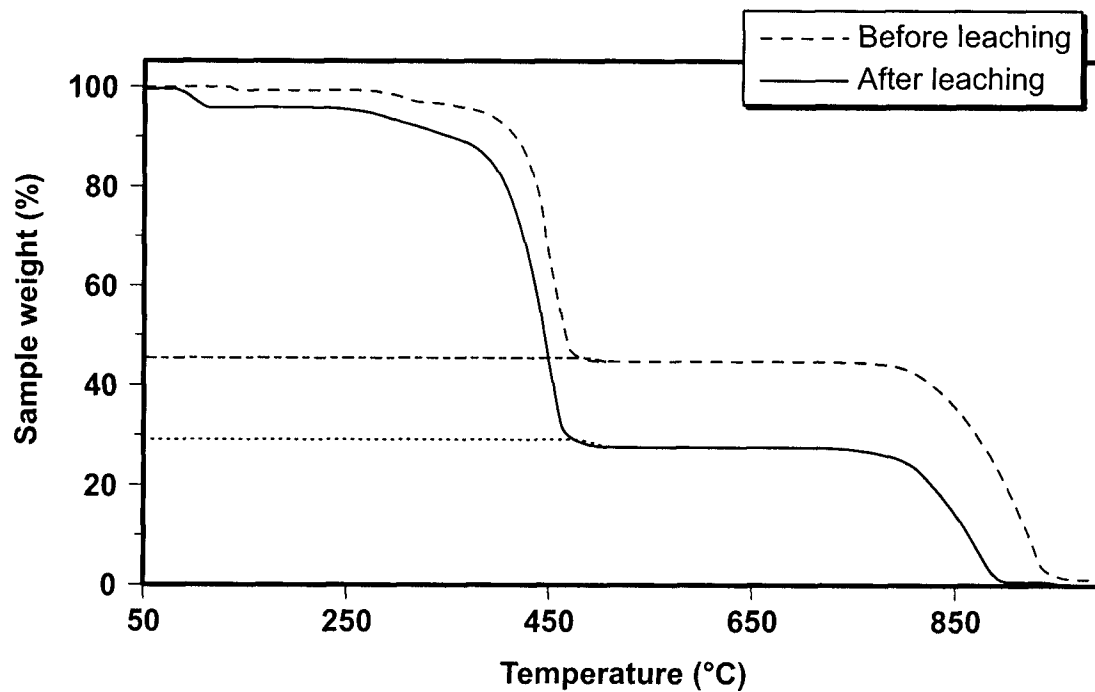


FIG. 6

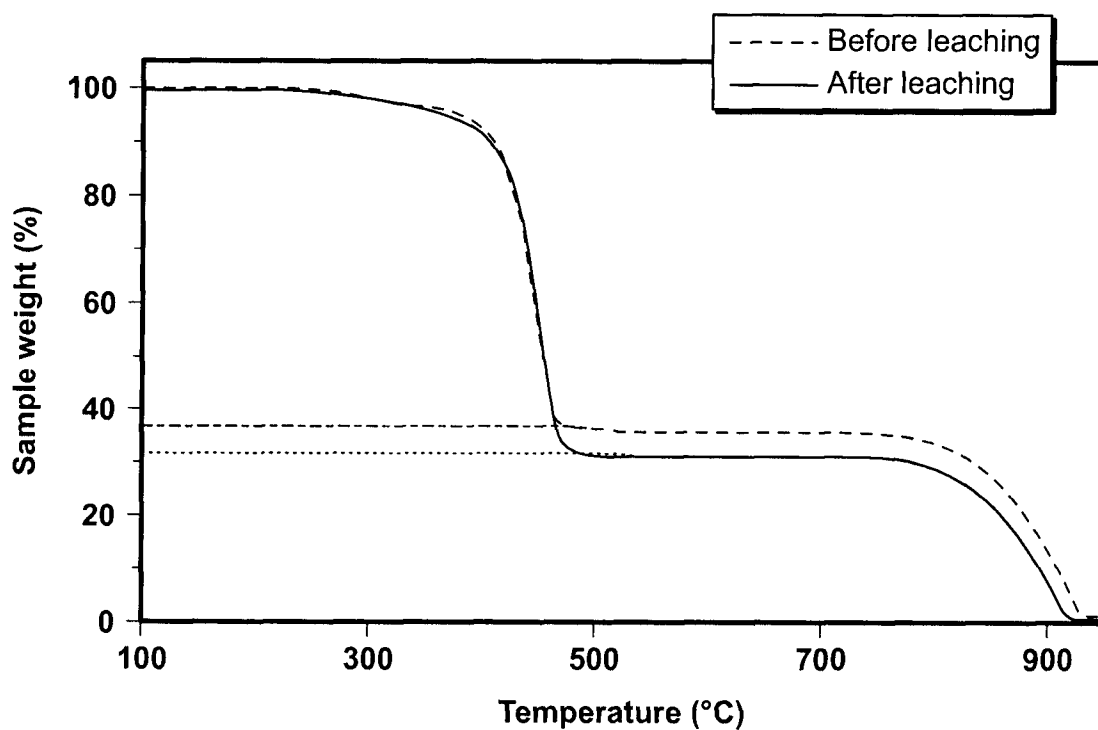


FIG. 7

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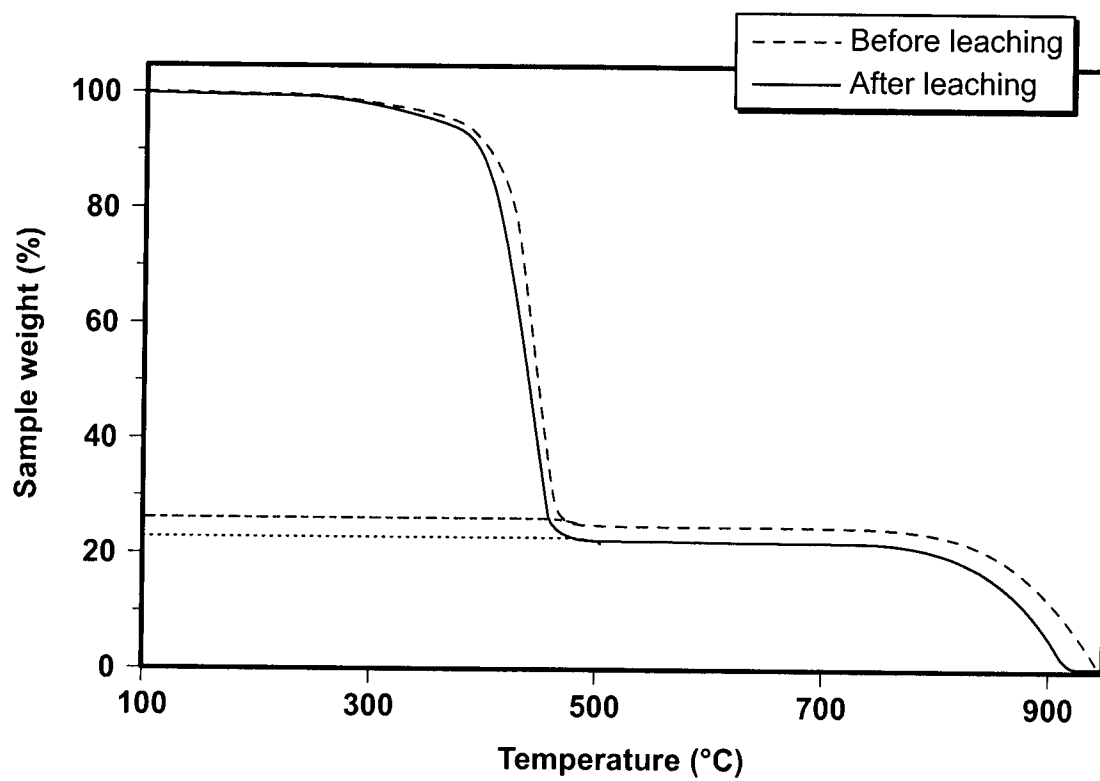


FIG. 8

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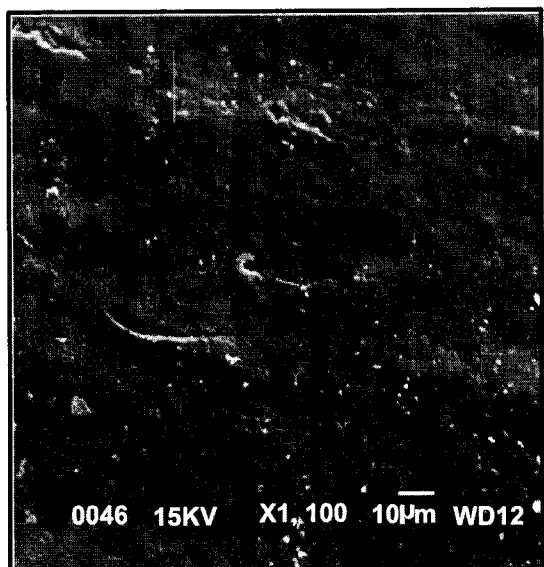


FIG. 9A

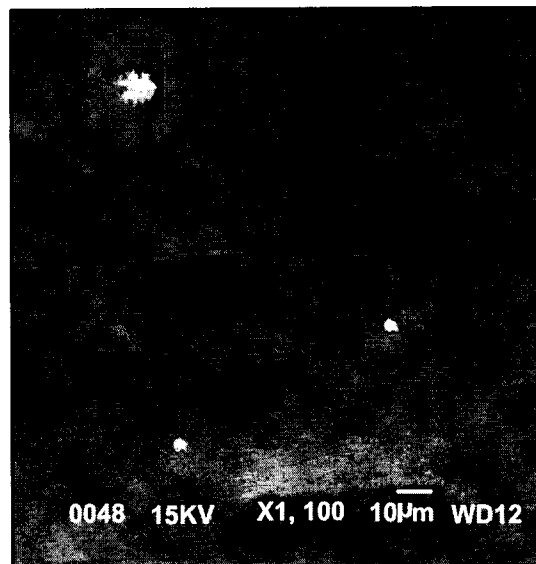


FIG. 9B

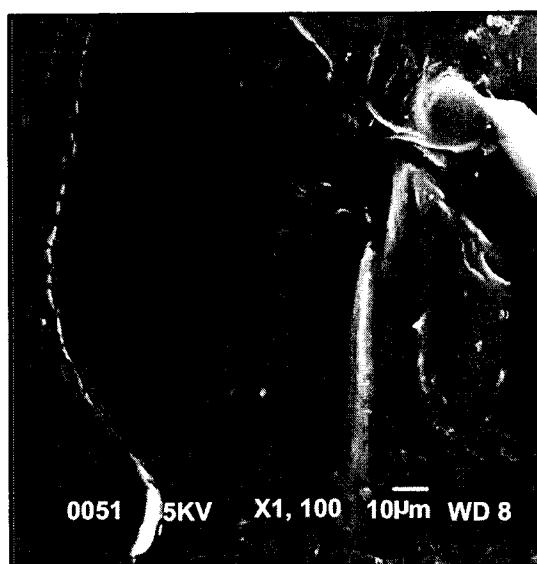


FIG. 9C

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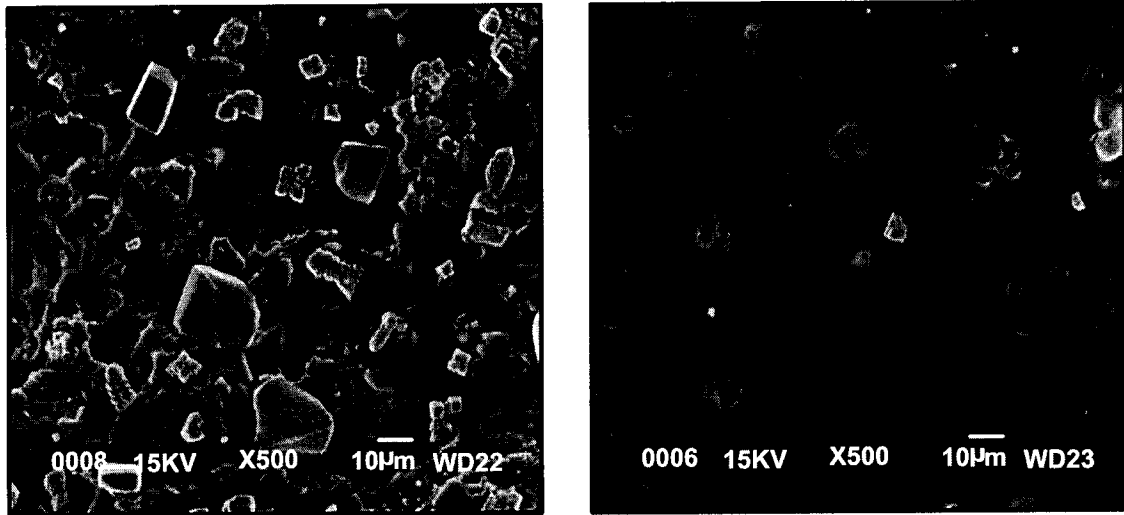


FIG. 10A

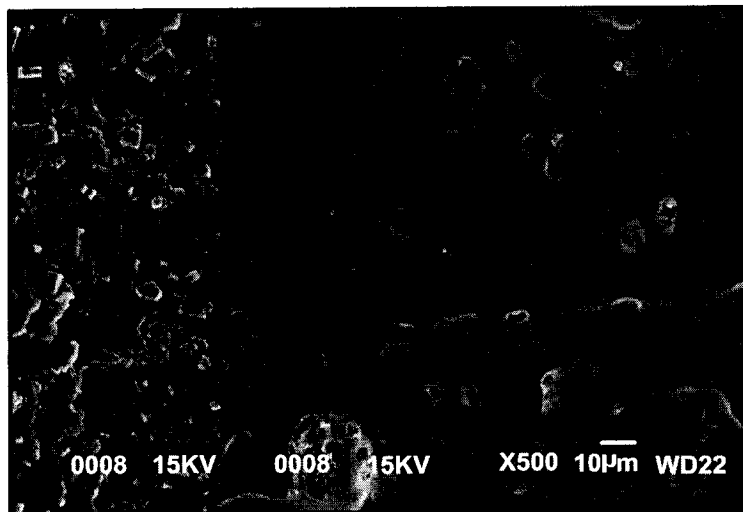


FIG. 10B

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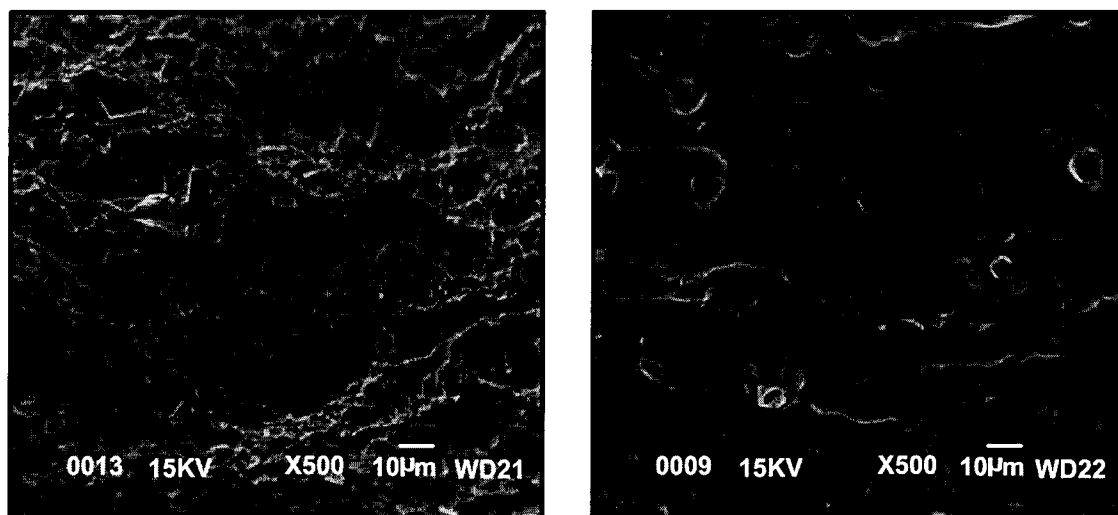


FIG. 10C

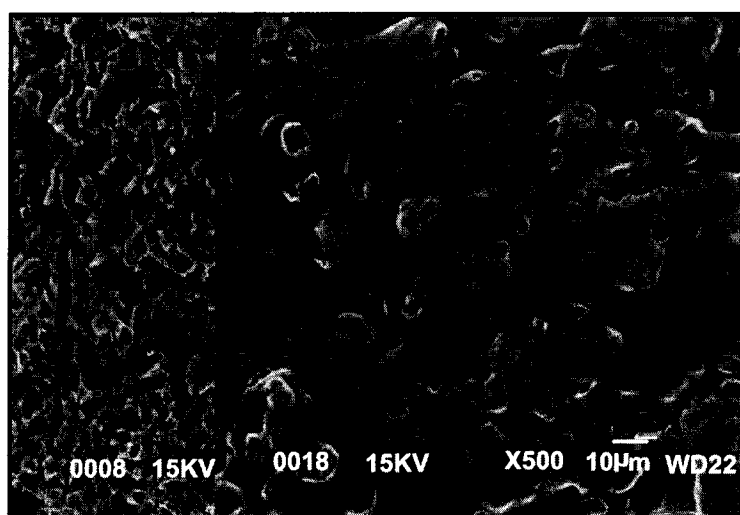


FIG. 10D

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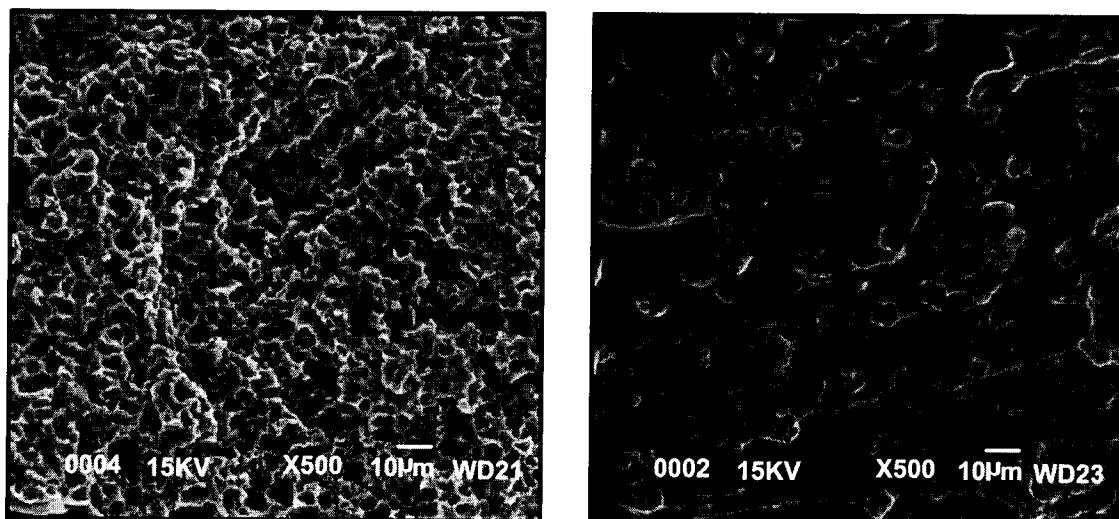


FIG. 10E

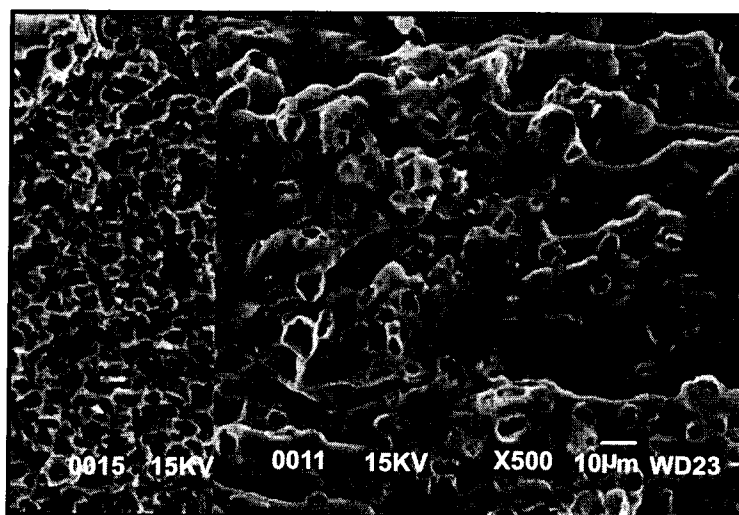


FIG. 10F

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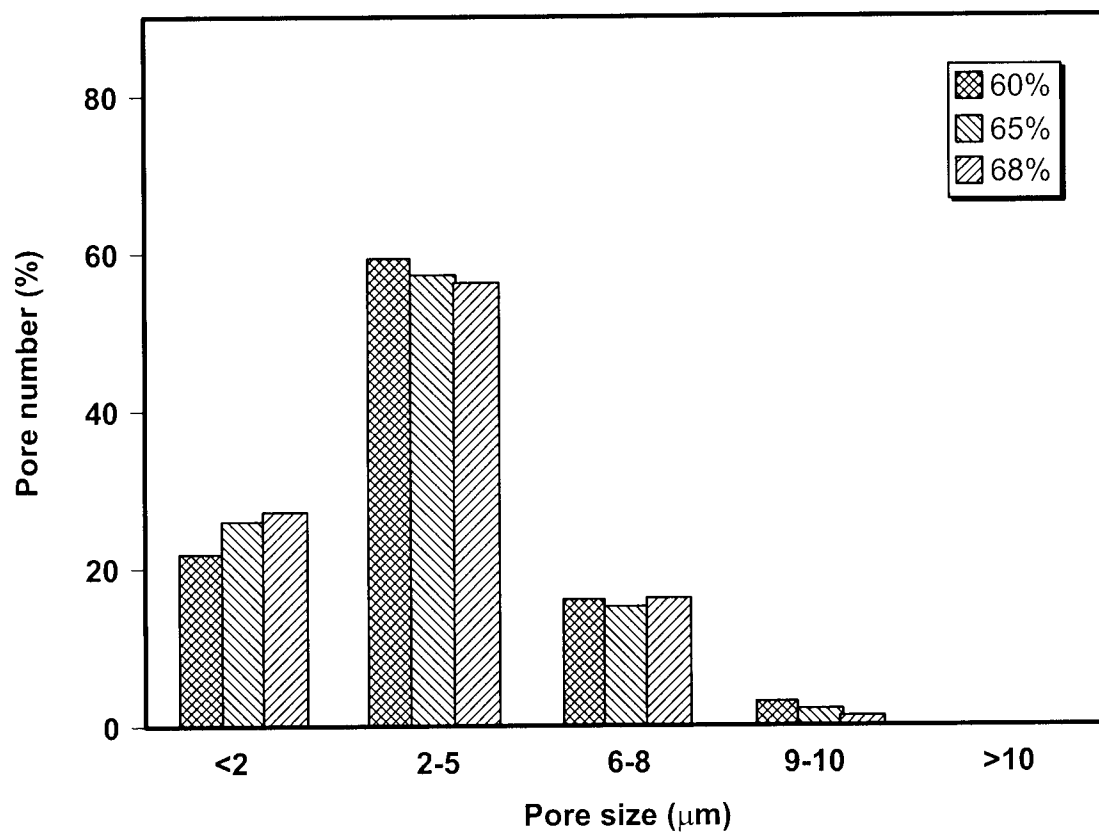


FIG. 11

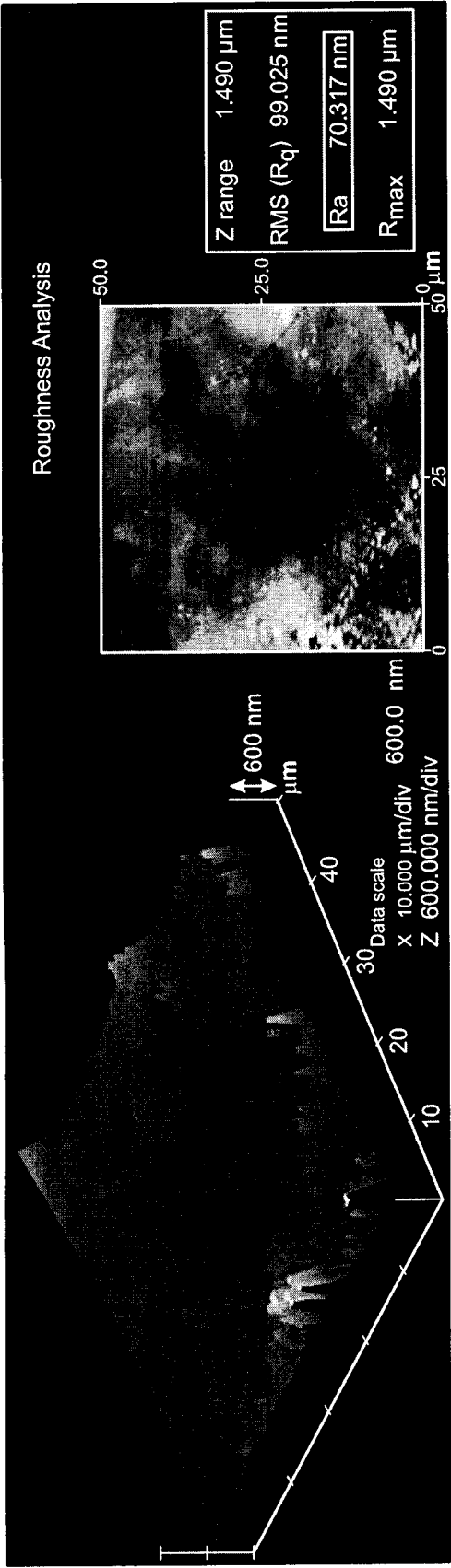


FIG. 12A

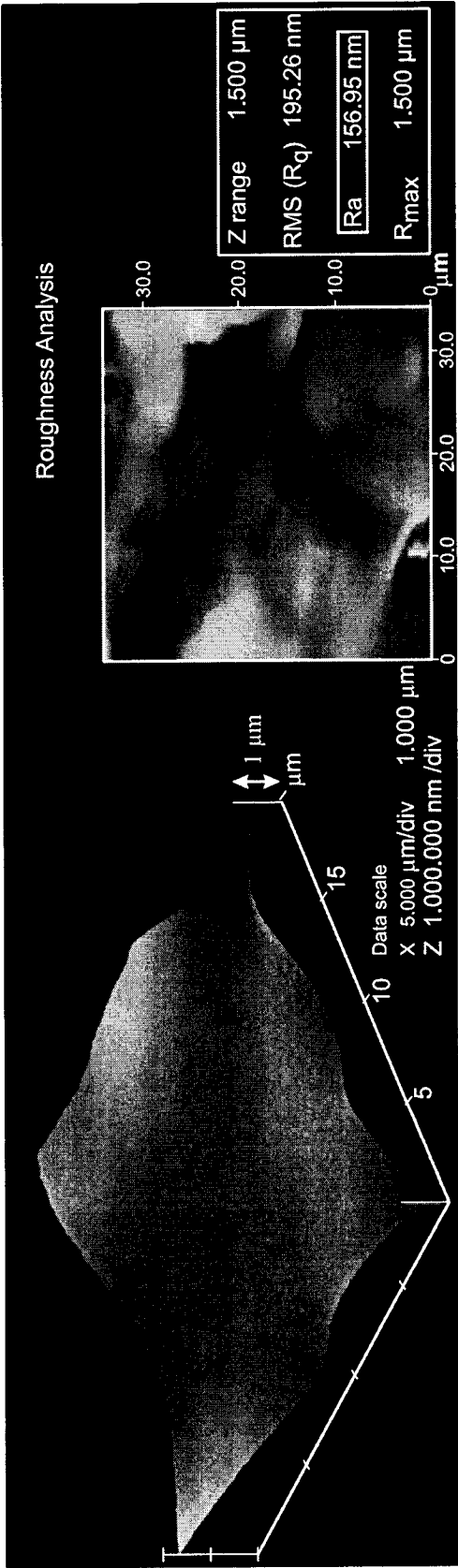


FIG. 12B

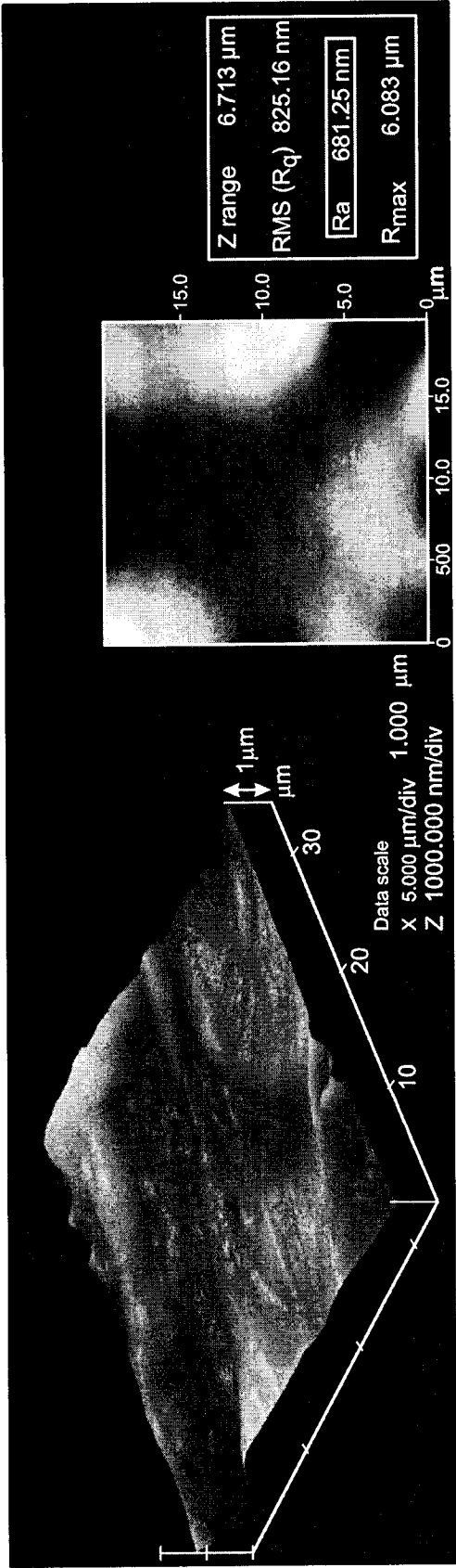


FIG. 12C

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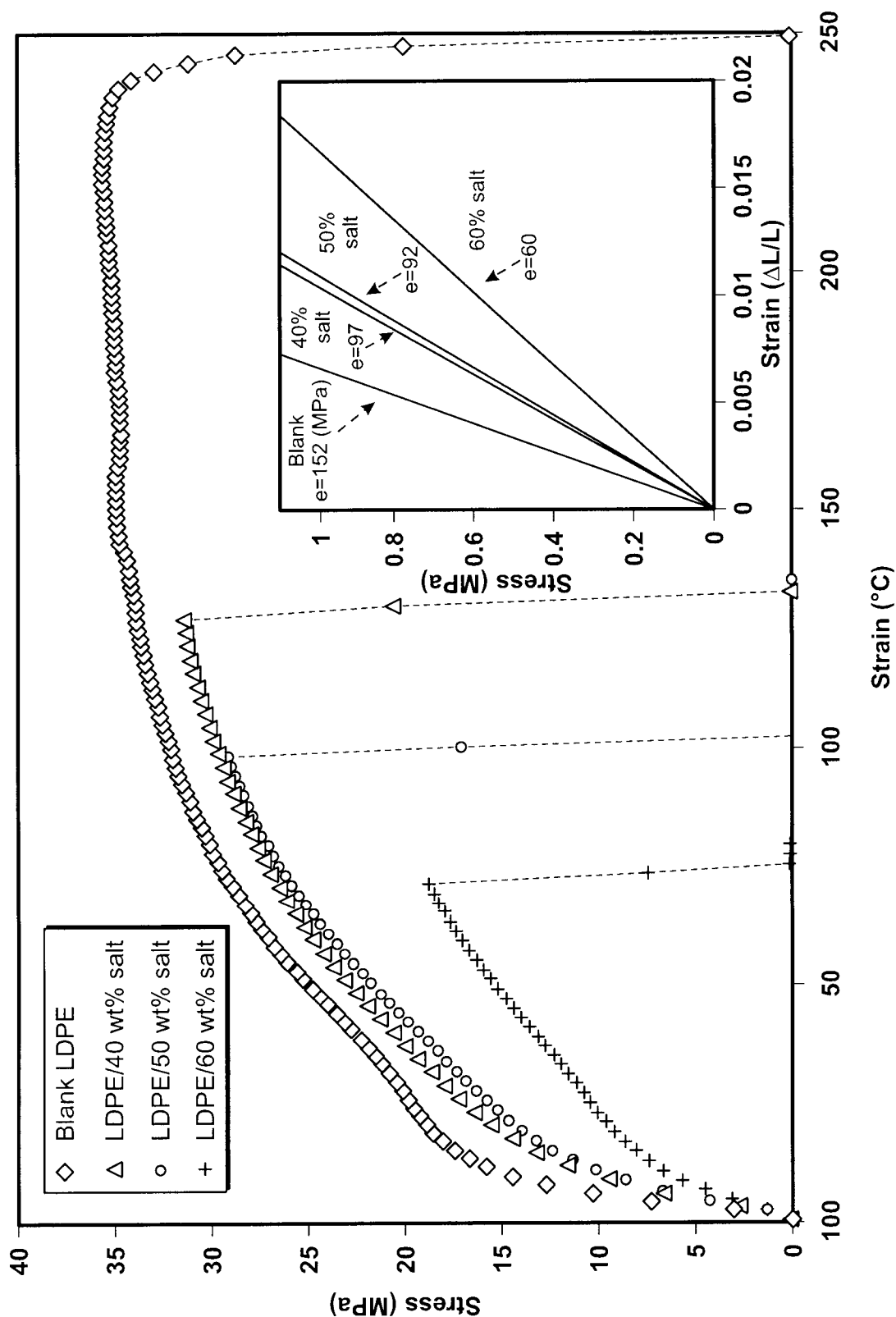


FIG. 13

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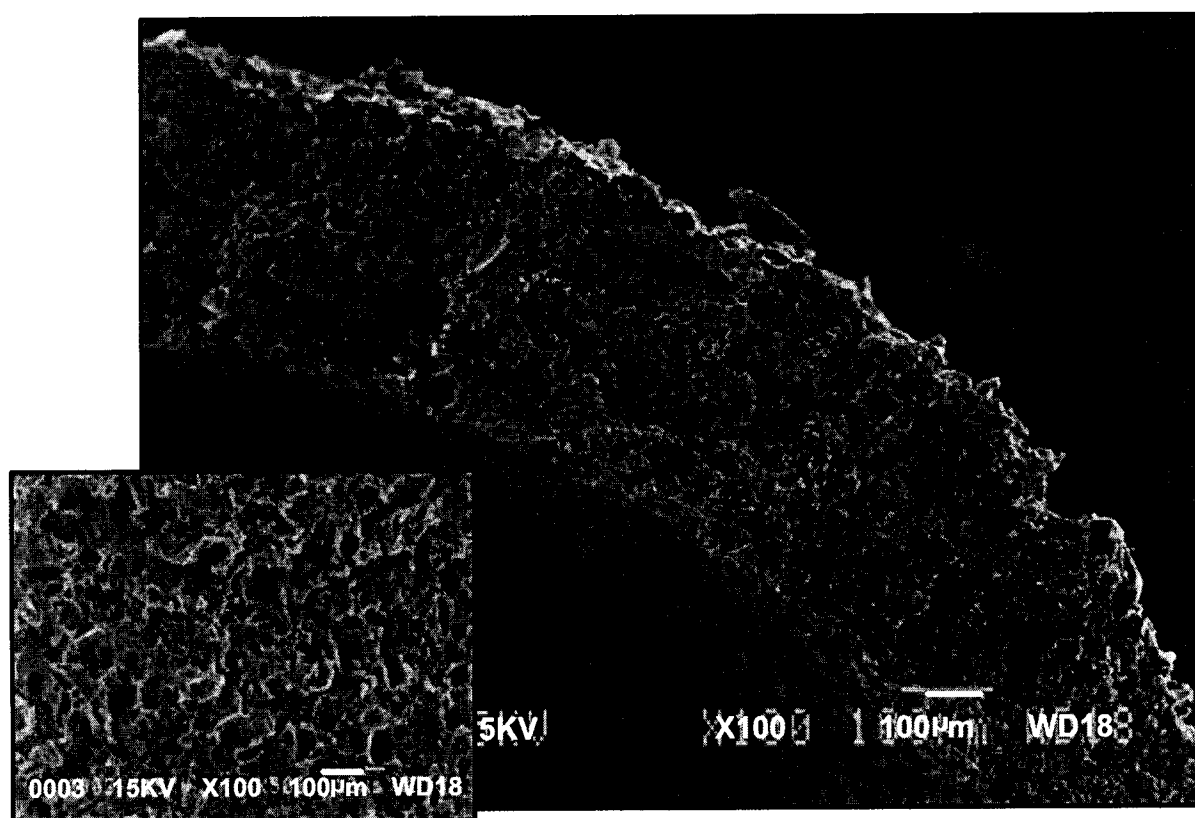


FIG. 14A

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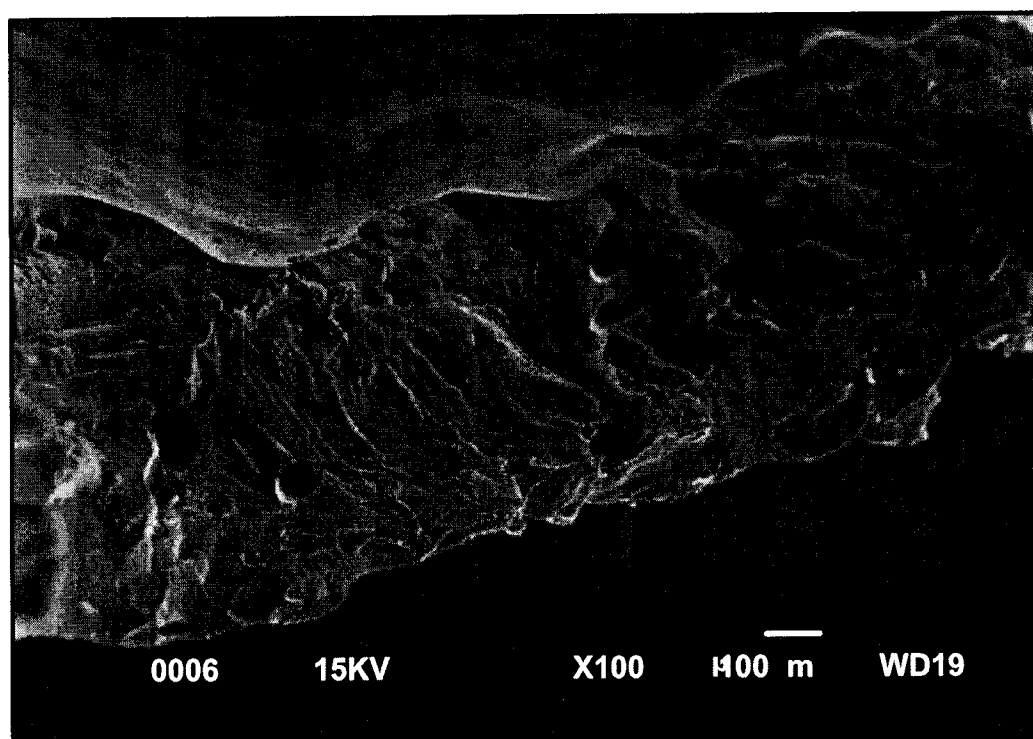


FIG. 14B

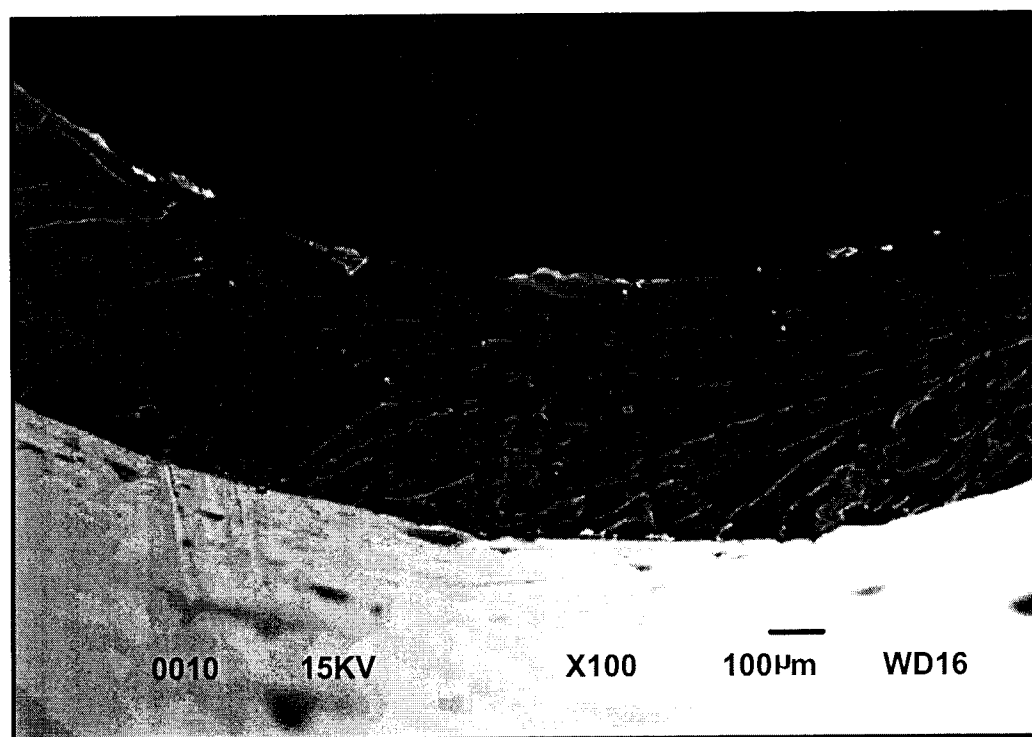


FIG. 14C

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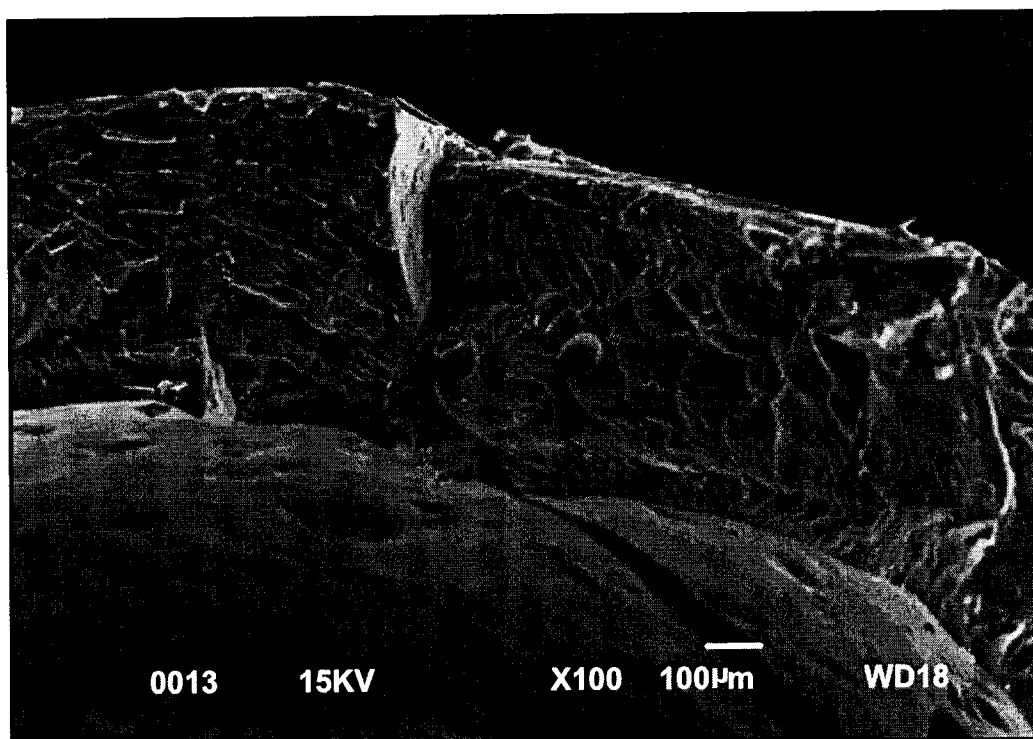


FIG. 14D

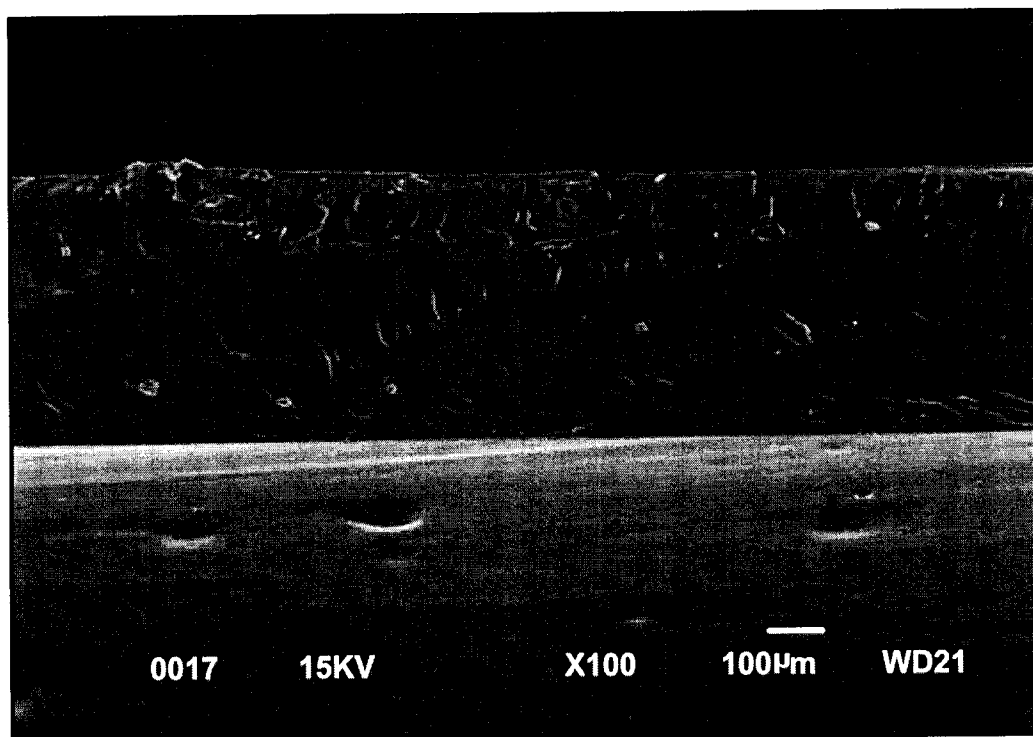


FIG. 14E

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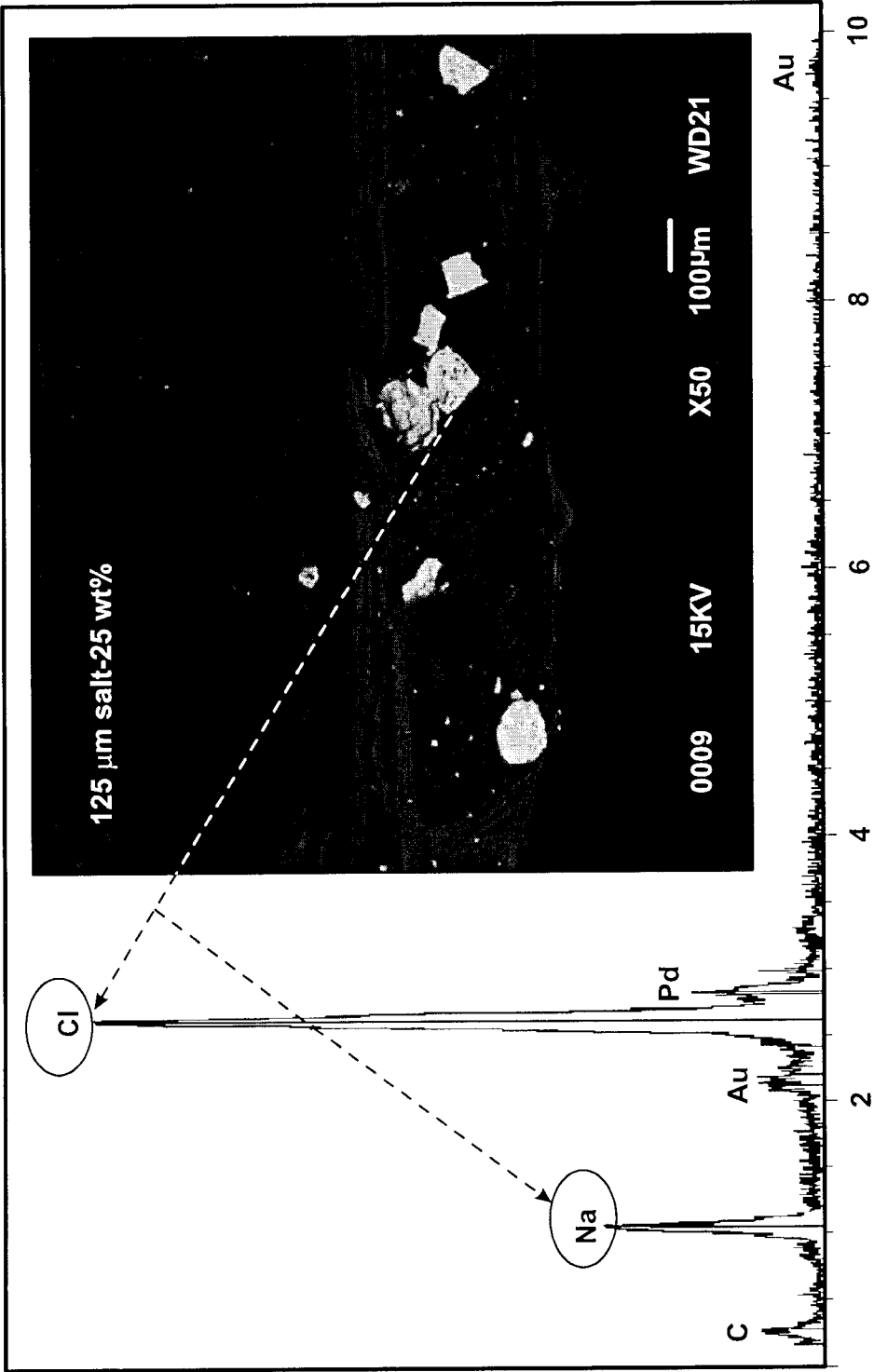


FIG. 15A

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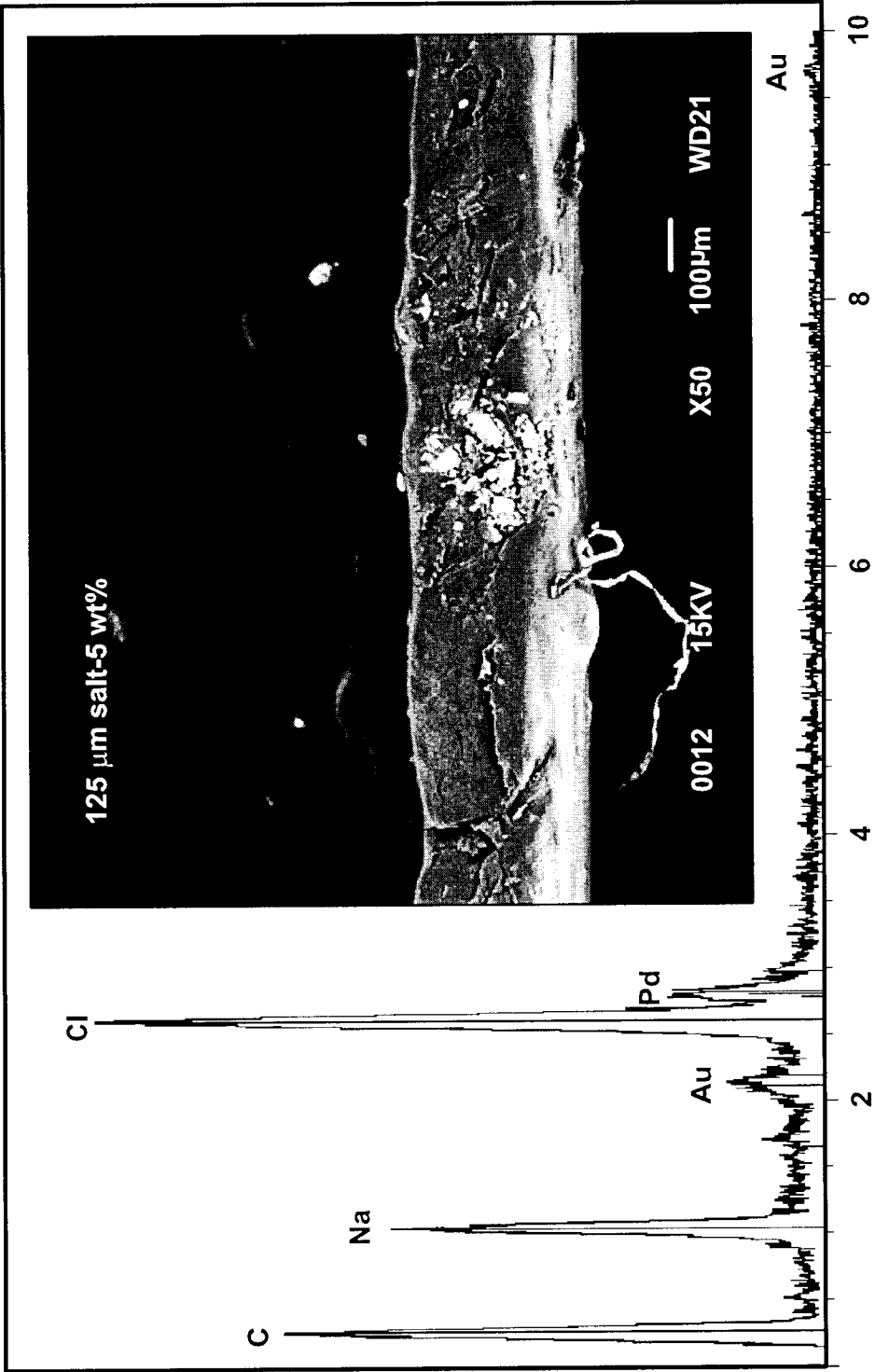


FIG. 15B

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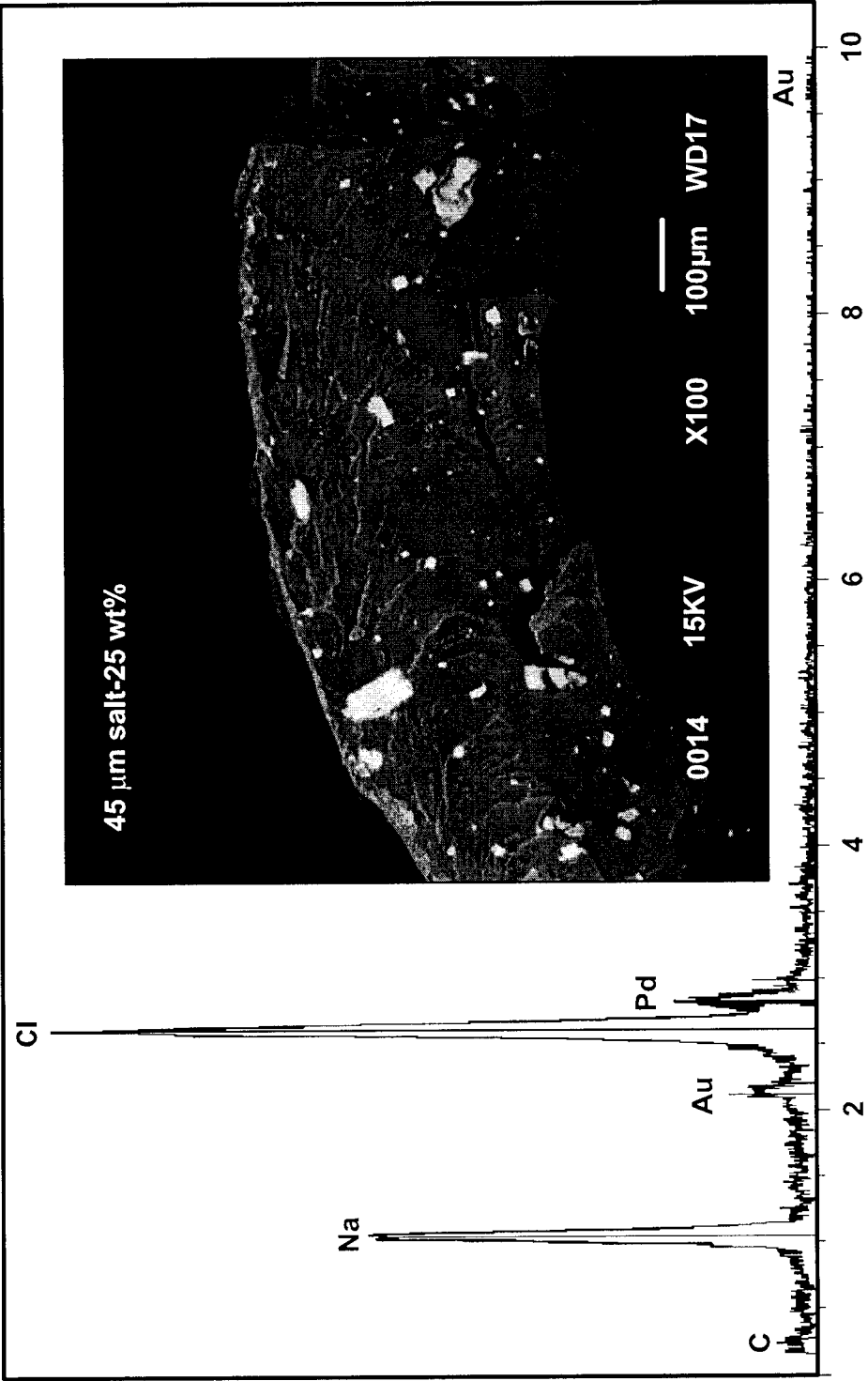


FIG. 15C

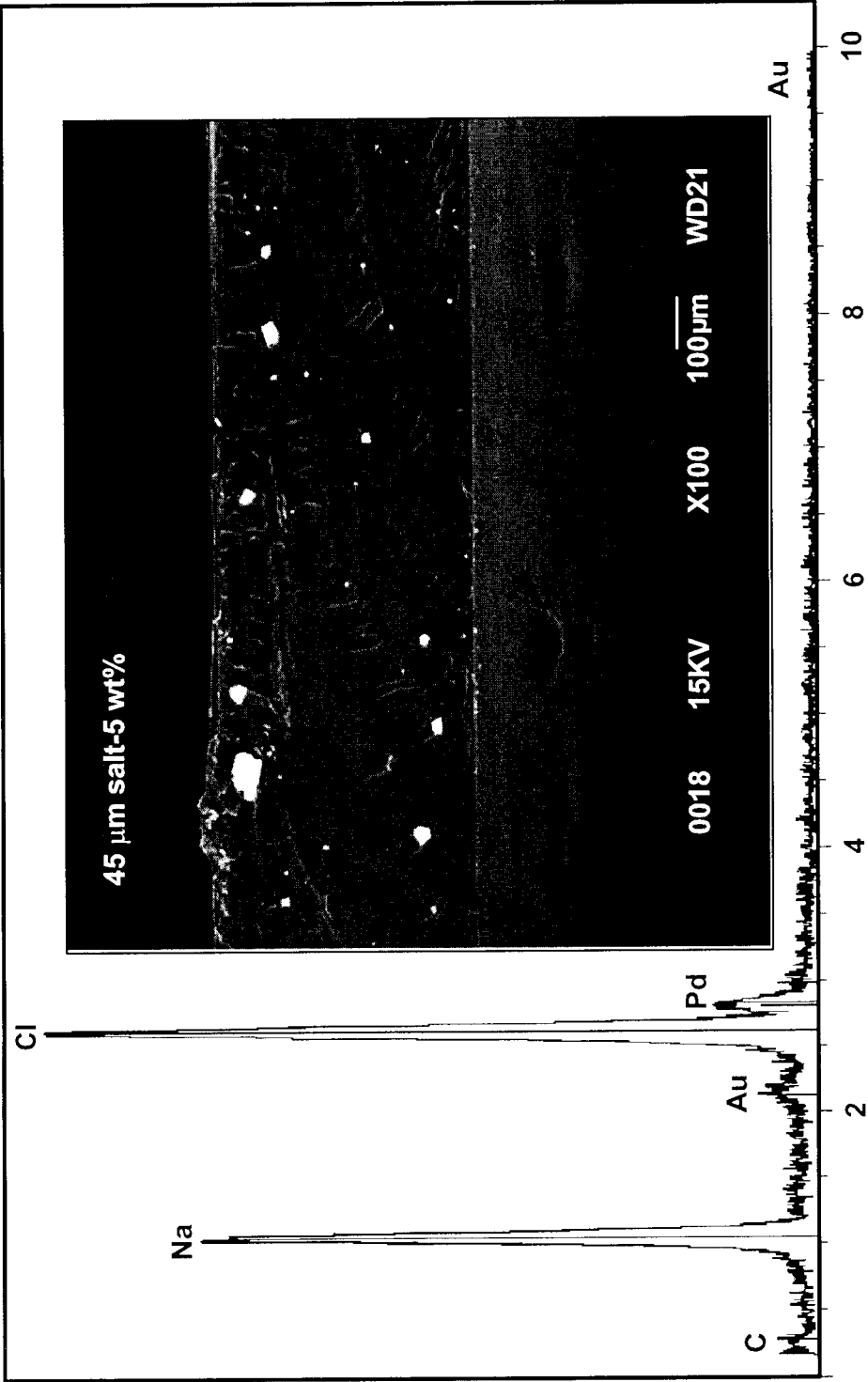


FIG. 15D

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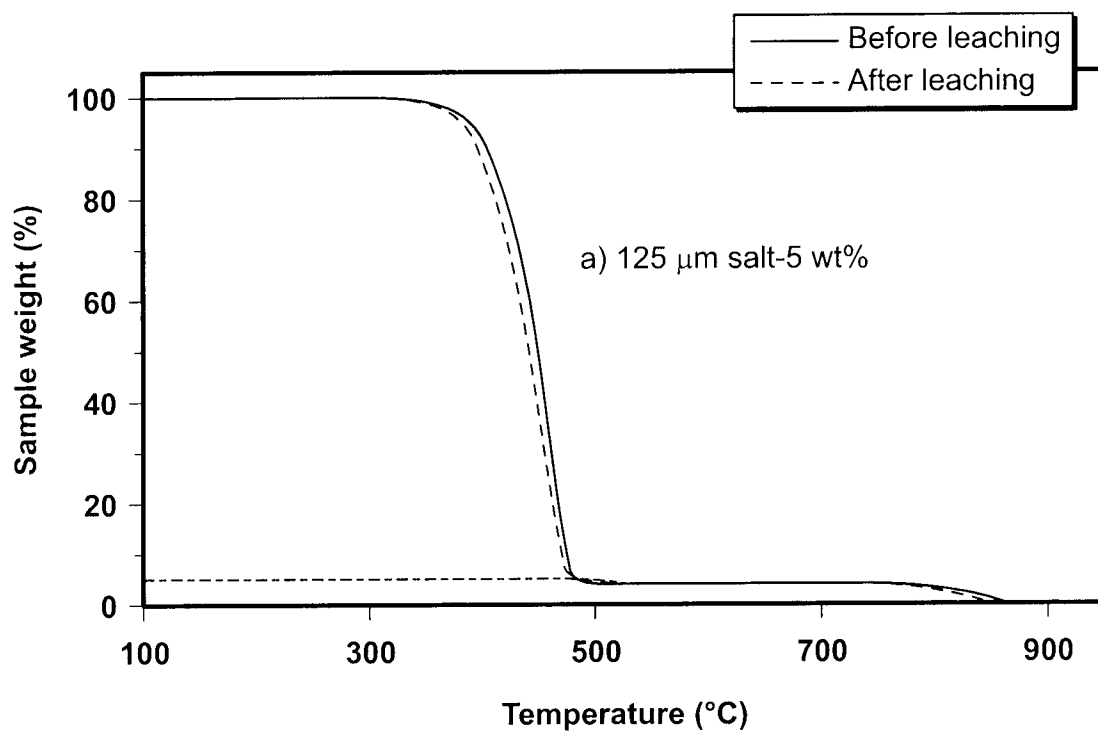


FIG. 16A

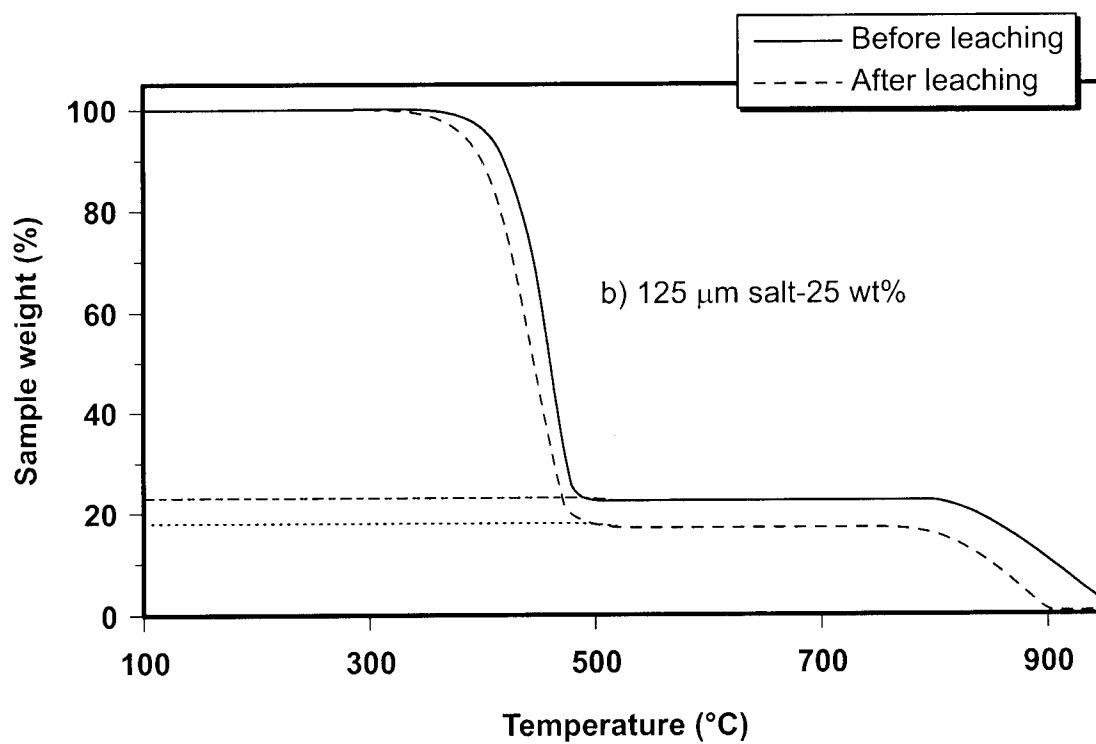


FIG. 16B

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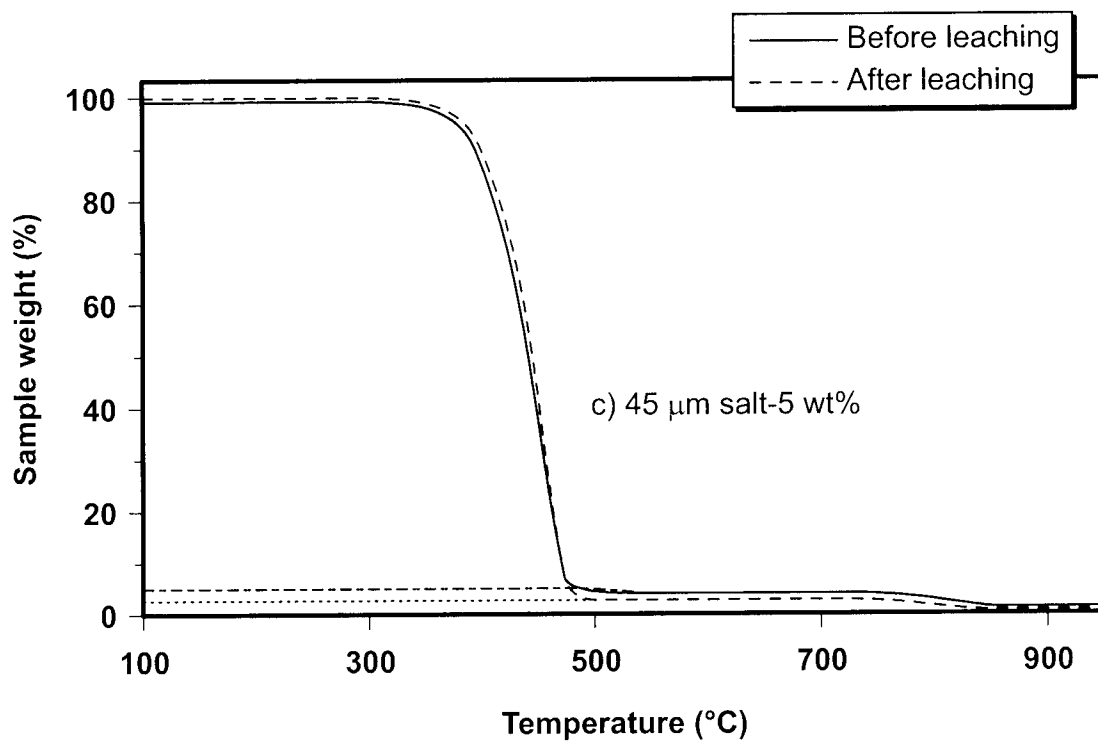


FIG. 16C

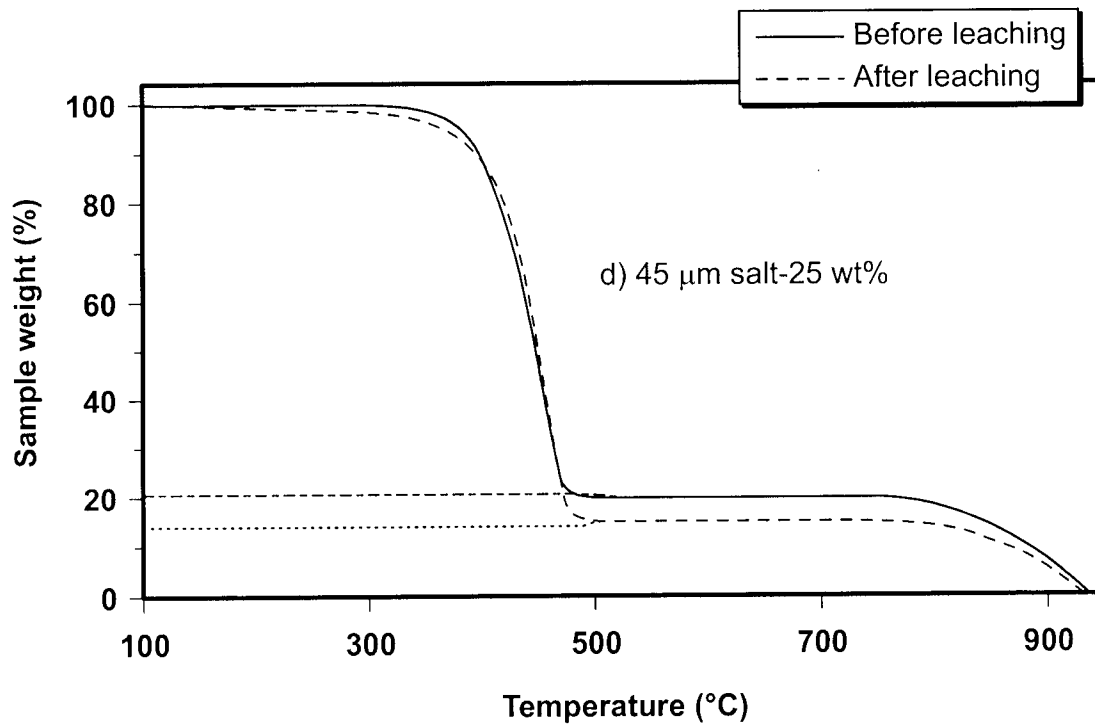


FIG. 16D

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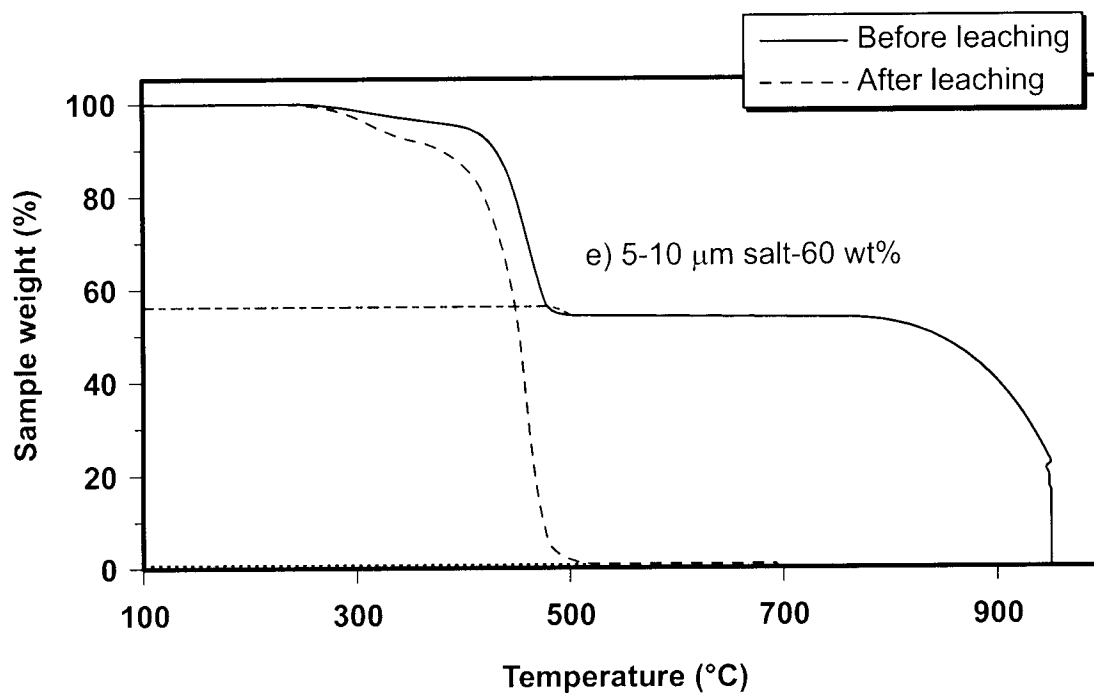


FIG. 16E

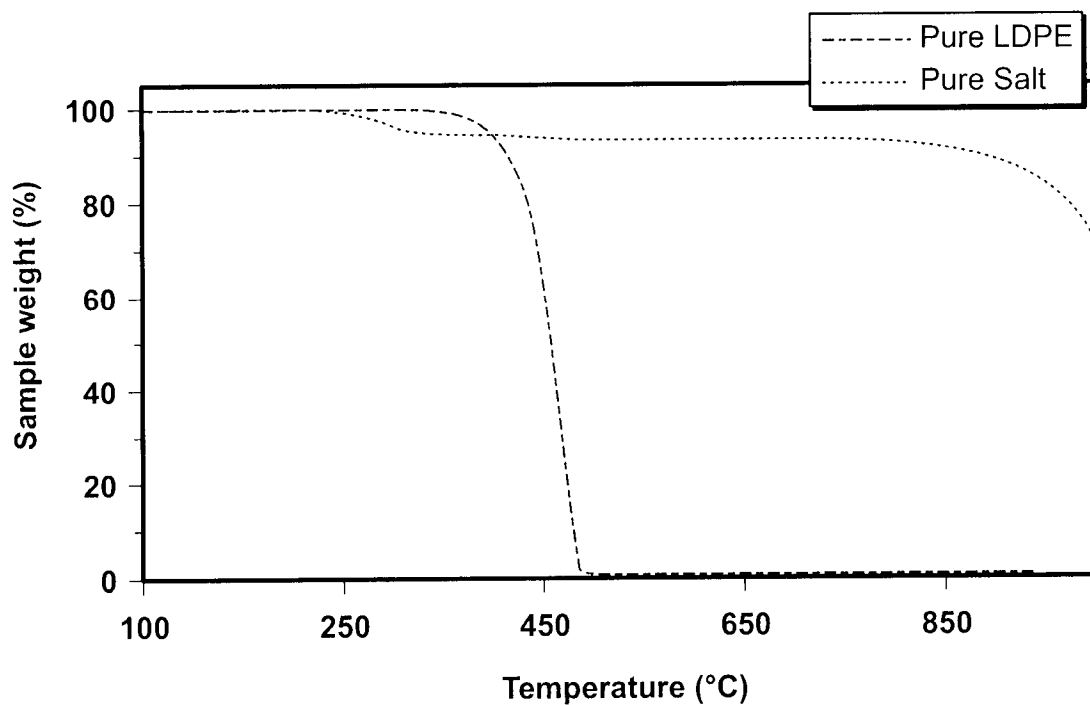


FIG. 16F

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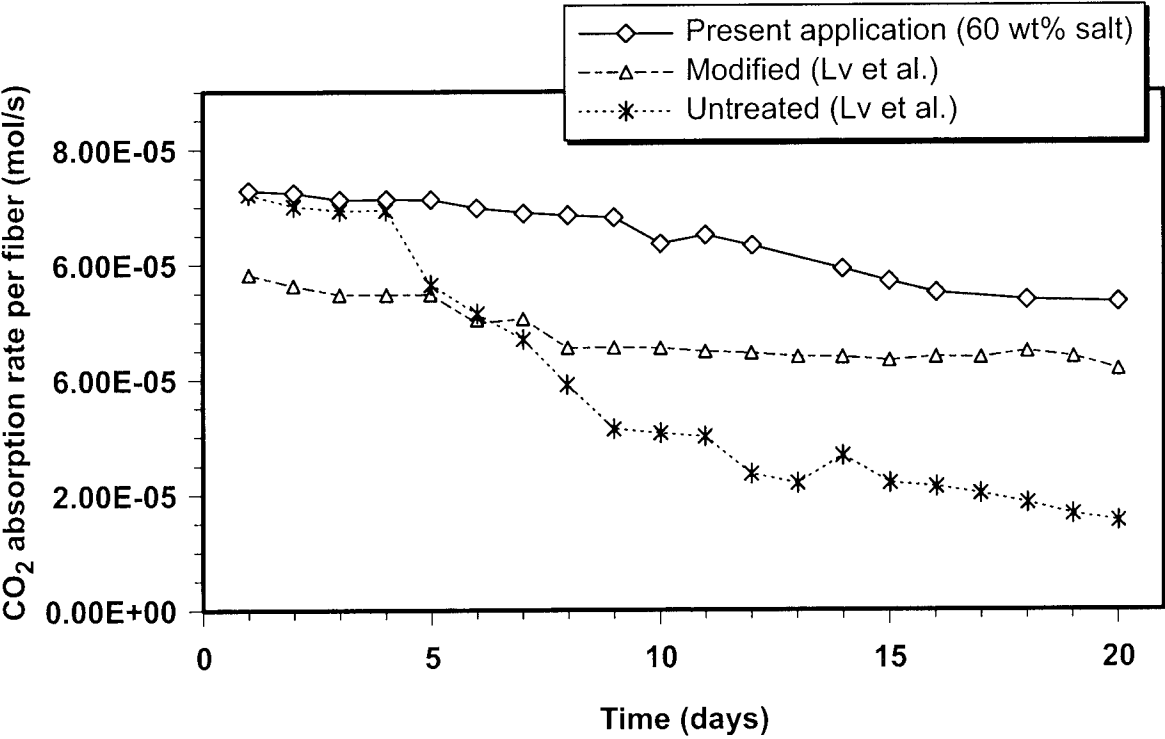


FIG. 17

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2013/000774

A. CLASSIFICATION OF SUBJECT MATTER IPC: B01D 67/00 (2006.01) , C08J 5/18 (2006.01) , C08J 9/26 (2006.01) , C08L 23/06 (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC																							
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC (2006.01): B01D 67/00, C08J 5/18, C08J 9/26, C08L 23/06 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Databases: EPOQUE (EpoDoc), Canadian Pents Database, Google Scholar Keywords: microporous, membrane, salt, fibre, fiber, hollow, leaching, polymer																							
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>US3640829 (ELTON) 8 February 1972 (08-02-1972)</td> <td>1-58</td> </tr> <tr> <td>Y</td> <td>* Column 3, lines 48-54; column 6, lines 21-24 and 41-49; column 8, lines 7-17 *</td> <td>19-23, 48-52</td> </tr> <tr> <td>Y</td> <td>US3214501 (STRAUSS) 26 October 1965 (26-10-1965) * Column 1, line 72 – column 2, line 11; column 3, lines 4-30 *</td> <td>19-23, 48-52</td> </tr> <tr> <td>A</td> <td>US4100238 (SHINOMURA) 11 July 1978 (11-07-1978) * The whole document *</td> <td>1-58</td> </tr> <tr> <td>A</td> <td>US4197148 (SHINOMURA) 8 April 1980 (08-04-1980) * The whole document *</td> <td>1-58</td> </tr> <tr> <td>A</td> <td>US3763055 (WHITE et al.) 2 October 1973 (02-10-1973) * The whole document *</td> <td>1-58</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US3640829 (ELTON) 8 February 1972 (08-02-1972)	1-58	Y	* Column 3, lines 48-54; column 6, lines 21-24 and 41-49; column 8, lines 7-17 *	19-23, 48-52	Y	US3214501 (STRAUSS) 26 October 1965 (26-10-1965) * Column 1, line 72 – column 2, line 11; column 3, lines 4-30 *	19-23, 48-52	A	US4100238 (SHINOMURA) 11 July 1978 (11-07-1978) * The whole document *	1-58	A	US4197148 (SHINOMURA) 8 April 1980 (08-04-1980) * The whole document *	1-58	A	US3763055 (WHITE et al.) 2 October 1973 (02-10-1973) * The whole document *	1-58
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.																							
<table border="0"> <tr> <td style="vertical-align: top;"> * Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="vertical-align: top;"> "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 </td> </tr> </table>			* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family																			
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Date of the actual completion of the international search 19 November 2013 (19-11-2013)		Date of mailing of the international search report 20 November 2013 (20-11-2013)																					
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476		Authorized officer Kevin Anderson (819) 953-1596																					

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US3640829A	08 February 1972 (08-02-1972)	BE757690A1 CA924467A1 DE2052831A1 FR2066196A5 GB1326442A JPS543901B1 US3770537A	19 April 1971 (19-04-1971) 17 April 1973 (17-04-1973) 29 April 1971 (29-04-1971) 06 August 1971 (06-08-1971) 15 August 1973 (15-08-1973) 28 February 1979 (28-02-1979) 06 November 1973 (06-11-1973)
US3214501A	26 October 1965 (26-10-1965)	None	
US4100238A	11 July 1978 (11-07-1978)	DE2611731A1 DE2611731C2 FR2304640A1 FR2304640B1 GB1506665A IT1058631B JPS51119069A JPS5720970B2	07 October 1976 (07-10-1976) 29 April 1982 (29-04-1982) 15 October 1976 (15-10-1976) 25 August 1978 (25-08-1978) 12 April 1978 (12-04-1978) 10 May 1982 (10-05-1982) 19 October 1976 (19-10-1976) 04 May 1982 (04-05-1982)
US4197148A	08 April 1980 (08-04-1980)	DE2751075A1 DE2751075C2 FR2373388A1 FR2373388B1 GB1592557A IT1089635B JPS5372070A JPS5939460B2	15 June 1978 (15-06-1978) 13 May 1982 (13-05-1982) 07 July 1978 (07-07-1978) 10 October 1980 (10-10-1980) 08 July 1981 (08-07-1981) 18 June 1985 (18-06-1985) 27 June 1978 (27-06-1978) 22 September 1984 (22-09-1984)
US3763055A	02 October 1973 (02-10-1973)	None	