Research Paper

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Effect of Solvent and Thermal Treatment on The Structure of Polyacrylonitrile Membranes

Engineering

KEYWORDS : ultrafiltration, polyacrylonitrile, polymeric membranes, thermal treatment

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ABSTRACT

Ultrafiltration (UF) membranes were formed by phase inversion on a substrate. Used are 16 mass% polymer solutions of polyacrylonitrile (PAN) copolymer (acrylonitrile-methylcrylate-2-acrulamide-2-methyl-propane-sulfonic acid) with solvents Dimethyl sulfoxide (DMSO). The membranes were thermally treated at various temperatures for time 10 min. It was proved that to industrial application the membranes is necessary to be thermally treated at 60oC. Defined are technological characteristics in relation to water and calibrants Albumin and α Chymotrypsin.

1. Introduction

The use of polyacrylonitrile membranes in the baromembrane technology (UF, MF) is preferred. They are dominant due to their resistance during exploitation. In recent years, the polyacrylonitrile membranes are object of specific interest of medical and biochemical researchers due to their biocompatibility. The material is economically effective for treatment and simple for technological maintenance in wide pH interval (2 – 11) and temperatures up to 70°C.

The method of phase inversion appears to be dominant [1 Kools, W.F.C. (1998)] for preparation of membranes from polymer solutions. Using the copolymer system acrylonitrile methylcrylate-2-acrulamide-2-methyl-propane-sulfonic acid is solubility in different solvents. Until now we have not encountered reports of the receipt and use of flat asymmetric UF membranes on a substrate from solution of this material with DMSO by dry-wet phase inversion. Preparation of industrially useful UF membranes are composed of several successive phases. The result from each stage depends on many conditions and each has stronger or weaker effect on the structure and characteristics of the membrane.

Thermal treatment is stage of preparation of UF membranes for application in membrane modules and systems [2] and the used temperature should be close to the temperature of the glass transition (Tg) of polymer. Aim is:

- the elimination of tension in the polymer structure gained in phase inversion, through relaxation processes that create changes in the selective layer and in depth;
- fixing the structure of membrane, which increases the resistance at the operating pressure and periodically washing at about 60°C;

The reason is to condition the membrane structure under the conditions of technological implementation, although accompanied by decrease of permeability but with increased retention [3]. Jung et al. [4] used thermal treatment at various temperatures in presence of additives as an opportunity for modification in the technological properties of PAN membranes.

The characteristics of acrylonitrile copolymers and the technology of membrane formation define practically an amorphous structure. This means that the ratio between the different phases would not be a factor affecting the membrane structure during the thermal treatment.

Using the copolymer system acrylonitrile methylcrylate-2-acrilamide-2-methyl-propane-sulfonic acid in this article we indicating a possibility for obtaining membrane from solutions of 16 mass% PAN/DMSO and the influence on thermal treatment of the structure and the technological properties of the membranes.

2. Experimental

2.1. Materials

The membranes were obtained from solutions with polymer concentration of 16 mass% polyacrylonitrile fibers obtained from ternary copolymer acrylonitrile-methylacrylate-2-acrylamide-2-methyl-propane-sulfonic acid, product of "LUKOIL Neftochim Bourgas" Co. with solvent DMSO p.a., produced by „Fluka", Switzerland. PAN has Tg=78°C and degree of crystallinity about 4-5 %.

Calibrants for the selectivities characterization at pressure of 0.3 MPa was used Albumin fraction V (from bovine serum) for biochemistry with molecular mass 76 000 and α Chymotrypsin (from bovine pancreas) cryst. lyophilized 350 U/mg for biochemistry with molecular mass 25 000 – products of „Merck"- Germany .

2.2. Preparation and thermal treatment of membranes

For membrane formation, the solution was dispersed uniformly on to a substrate of double calandered polyester matt, brand FO-2403, product of „Velidon Filter", Germany. The membranes were prepared by dry-wet phase inversion method in a precipitation medium – deionized water in 25°C. Deionized water was used also for the following washing.

The thermal treatment of samples of the membrane was carried out in water medium at 60° and 80°C for 10 min , with fixation of the membrane on a metal grid.

2.3. Characterization techniques

The studies on the membranes' transport and selective properties was performed using a Ultrafiltration laboratory cell SM-165-26 produced by "Sartorius", England, under increasing and decreasing pressure from 0.1 to 0.5 MPa.

Membranes' selectivities were measured with samples of the filtrate retained by them, on a spectrometer UV/VIS, "UNICAM" 8625 at wavelength for Albumin λ=280 nm and α Chymotrypsin – λ=215 nm.

The membranes structures was visualized by SEM with a scanning electron microscope JSM-5510 (JEOL, Japan).

The dynamic rheological characteristics of the polymer solution were determined on a rotational viscometer type - REOTEST II -2.1(Germany). The temperature control was done with a thermostatic bath at 25 ±0.1°C.

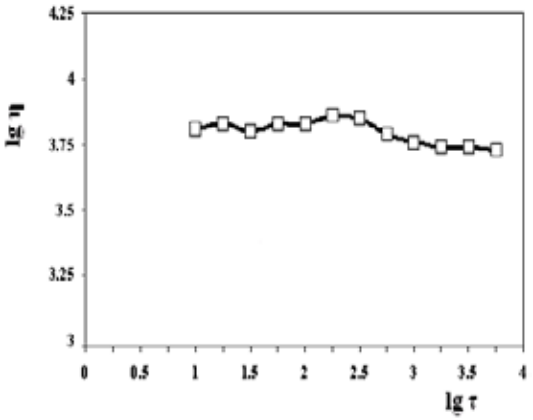
3. Results and discussion

Based on initial studies are used stable solution with a polymer concentration of 16 mass% PAN in DMSO. The rheological properties of the polymer solution was determining by measuring the dynamic viscosity at 25°C (Fig. 1).

The structure of the solution directly affect their viscosity determined as a result of the influence of the tangential shear stress

(τ). The flow curves of test solution is similar and characteristic of non-newtonian fluids. These results support their homogeneity. This is necessary condition to the polymeric solution for forming pore structure by phase inversion [5].

Fig.1 Flow curves of the polymer solution 16mass% PAN/ DMSO.



From the polymer solution by the phase inversion are formed membranes, samples of which are thermally non-treated, thermally treated at 60oC and 80oC for 10 min. The thermally treatment is a process that removes the tension in the polymeric structure through of relaxation processes in the region of the glass transition temperature of the polymer and creates the conditions for changing the structure of the membranes. Stage in the technology for the preparation of membranes is extensive washing and excludes residue from solvent which may be involved in the process of thermally treatment. Changes in structure that occur are only as a result of thermally treated.

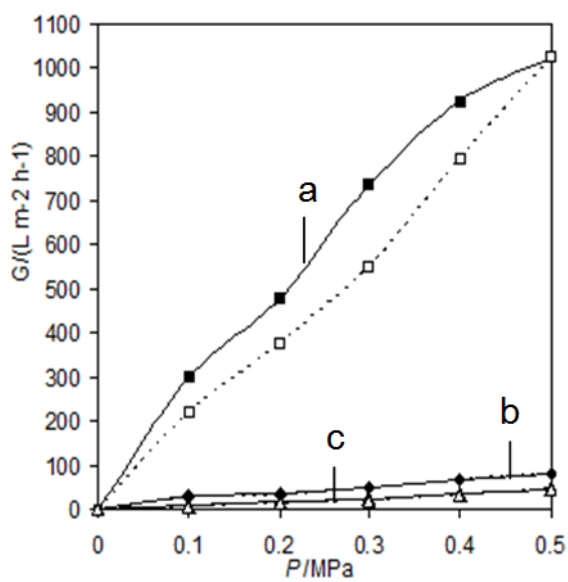


Fig. 2 Hysteresis curves of membranes: (a) - thermally non-treated, (b) - treated at 60°C, (c) - treated at 80°C.

Immediately after the coagulation, the membrane is with asymmetric structure with well structured and with deeper penetrating selective layer (Fig. 3a), as well big internal macropores.

The thermally non-treated structure of the membranes had quite high water permeability at all pressures (Fig2), twice higher than that towards α Chymotrypsin and almost the same selectivity and permeability towards Albumin at 0.3 MPa (Table 1).

Membranes	Permeation water flux, (L $m^{-2} h^{-1}$)	Permeation flux, Galb/ (L $m^{-2} h^{-1}$)	Albumin selectivity, φalb/ (%)	Permeation flux, Gtrips/ (L $m^{-2} h^{-1}$)	α Chymotrypsin selectivity, φtrips/(%)
obtained with DMSO thermally non-treated	735	45	96	92	69
obtained with DMSO treated at 60 °C	52	32	92	40	58
obtained with DMSO treated at 80 °C	24	7	76	10	54
obtained with DMF thermally non-treated	478	40	90	47	64
obtained with DMF treated at 60 °C	119	46	91	80	23
obtained with DMF treated at 80 °C	54	24	91	26	38

Table 1 Permeability and selectivity of all membranes to water, Albumin and α Chymotrypsin at 0.3 MPa.

Thermal treatment at 80°C (a temperature near the Tg of the polymer) for these membranes prepared using solvent DMSO, drastically reduced the permeability of water and calibrant to an extent of an inability to work. Permeability of water at 0.3 MPa is 480 $l.m^{-2}.h^{-1}$ and was reduced to 24 $l.m^{-2}.h^{-1}$, permeability of Albumin from 45 $l.m^{-2}.h^{-1}$ was reduced to 7 $l.m^{-2}.h^{-1}$. Selectivity of Albumin from 96% reduced to 76%, but for a low molecular weight α Chymotrypsin after treatment at 80°C selectivity decreased from 69% to 54 % at a satisfactory throughput of calibrant (Table 1).

Various results is obtained, when the membrane was treated at 60°C for 10 min. The temperature had not been chosen randomly. In membrane installations, the periodical regeneration is usually carried out at this temperature. This guarantees that the pore structure is effective and would not change during exploitation. After this temperature treatment, the membrane had optimal values for permeability, it can be seen from the data on the technological characteristics in Table 1. This feature, referring is on the SEM, can explain with the specifics of the primary structures (Fig. 3). At this temperature and duration of treatment, the selective layer is deformed to a greater extent through densification on the surface at membrane with DMSO (Fig. 3e). Probably in the membrane is generates a large internal stress, which causing rupture or pooling of pores, of which is due the slightly reduced on the selectivity. For that reason, this temperature is not suitable for fixing the structure of the membrane formed in DMSO.

For compared we use to known PAN membrane obtained from a solution of DMF in the same manner and under the same conditions. This membranes had optimal values for permeability and selectivity at thermally treated at 80°C.

The membranes obtained from solution with DMF and thermally treated at 60°C for 10 min did not reach stable structure. Figure 3(d) shows not so well arranged structure, compared to that on figure 3(f), which affect especially the selectivity towards α Chymotrypsin (Table 1).

In conclusion it can be said that the different results for the two membranes is determined by the physical structural changes that occur as a result of the different pore structure. Reason is the use of different solvents, as all other conditions are identical (characteristics of the polymer, the percentage of the solution, the conditions of the phase inversion).

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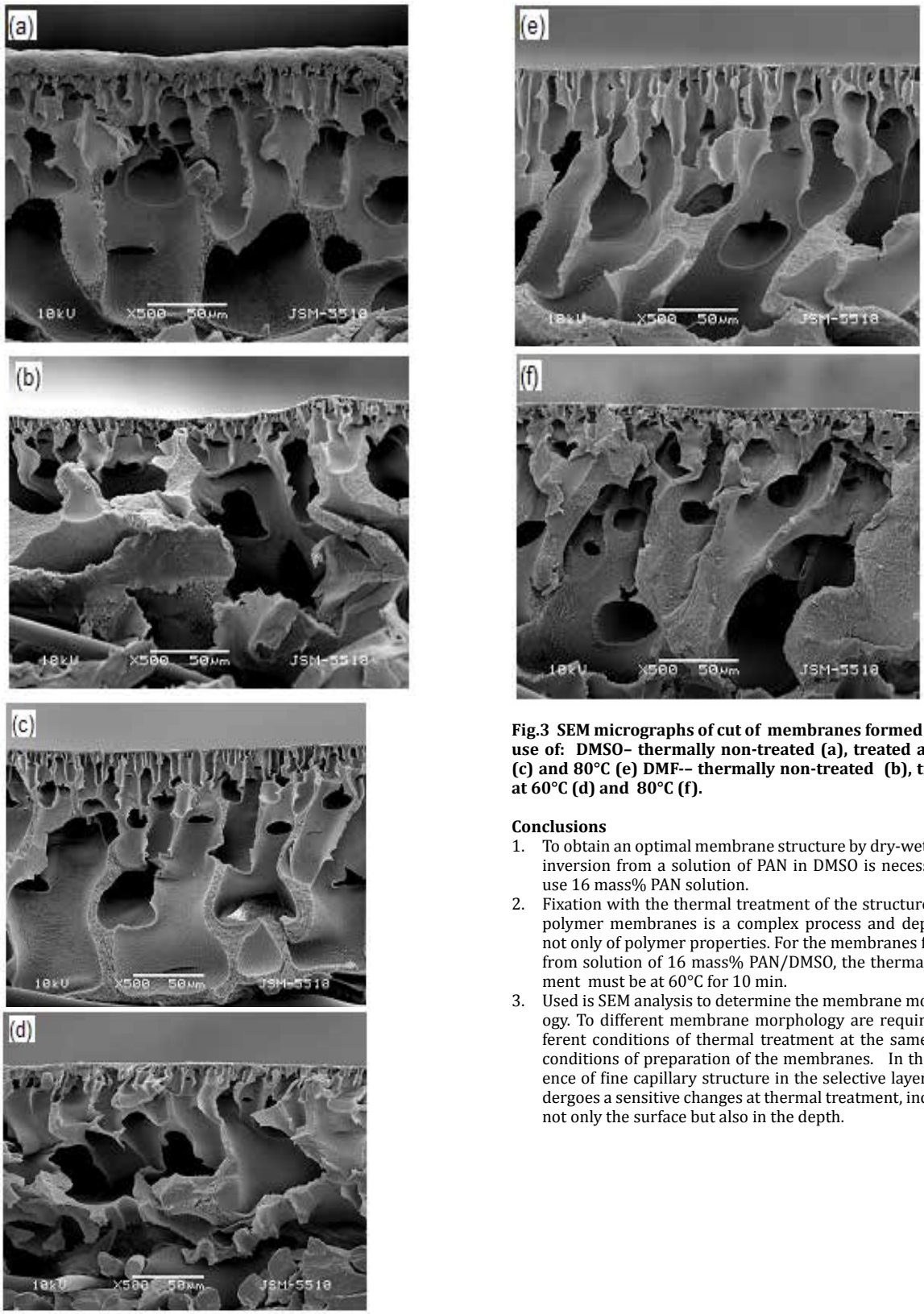

Fig.3 SEM micrographs of cut of membranes formed by the use of: DMSO– thermally non-treated (a), treated at 60°C (c) and 80°C (e) DMF-– thermally non-treated (b), treated at 60°C (d) and 80°C (f).

Conclusions

1. To obtain an optimal membrane structure by dry-wet phase inversion from a solution of PAN in DMSO is necessary to use 16 mass% PAN solution.
2. Fixation with the thermal treatment of the structure of UF polymer membranes is a complex process and depended not only of polymer properties. For the membranes formed from solution of 16 mass% PAN/DMSO, the thermal treatment must be at 60°C for 10 min.
3. Used is SEM analysis to determine the membrane morphology. To different membrane morphology are required different conditions of thermal treatment at the same other conditions of preparation of the membranes. In the presence of fine capillary structure in the selective layer, it undergoes a sensitive changes at thermal treatment, including not only the surface but also in the depth.

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