Preparation of High Density Cellulose Membrane

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1. NTRODUCTION

The structure of porous membrane is related to the characteristics of the interacting polymer and solvent, components concentration, molecular weight, temperature, and storing time in solution. According to this, the high density membrane which have lower amount of pores is suitable for use in separation process of high pressure flux. The purpose of the present work is to form cellulose membranes from NMMO (*N*-methylmorpholine *N*-oxide) solution which have high density (low porosity) by investigate the effects of preparation parameters such as cellulose Degree of Polymerization, Cellulose Concentration, Coagulation bath condition and Drying condition to the porosity properties and membrane performance.

2. EXPERIMENTAL

Two cellulose pulp samples with DP 850 and 1200 are dried at 100°C in oven for 24 hours. 8%,10%,11% of cellulose and NMMO monohydrate with the addition *n*-propylgallate was place in glass flask and gently stirred for 30 minutes and dissolving was carried out by heating at 110°C for 1 hour under Nitrogen atmosphere. Cellulose NMMO solutions were cast into a membrane with a thickness of 30 μm on the glass plate then the casting solution was immersed into a coagulation bath for 24 hours then washed with water of 30°C for 30 minute. Finally, the samples were dry. All the samples prepared by above steps with some variation in condition process ie ;(additional 25% & 50% NMMO in coagulation bath, Coagulation bath temperature 20°C, 40°C, 60°C; drying condition 30°C; 50°C, dry vacuum 50°C. The membranes performance were characterized by dead-end filtration system. The pure water flux was measured under a pressure difference of 40 KPa at ambient temperature. The permeation flux, *J*, is calculated using Equation (1): in which *V* is the total volume of the water

$$J = \frac{V}{tS} \qquad (1)$$

permeated during the experiment (ml) ; *t* is the operation time (hour); and *S* is the membrane area (cm^2).The porosity, P_r, of membranes was measured using an area of 16 cm^2 cut out squarely, by measuring the thickness, *L* (cm), and the dried weight (i. e., cellulose weight), W_d (g), using Equation (2):

$$P_r = 1 - \frac{W_d}{16 L_p} \qquad (2)$$

where ρ is density of cellulose (1.561 g $N.cm^{-3}$ in this instance). The mean pore radius, *rf* (m), was evaluated by means of the water-flow-rate method by substituting the experimentally determined values of porosity, P_r as calculated by Equation (2) and permeation flux, *J* ($m^3.m^{-2}.s^{-1}$) calculated by Equation (1), and thickness of dry membrane, L_d (m), into Equation (3), that was derived on the basis of the straight through cylindrical pore model:
in which η_{H2O} ($N.s.m^{-2}$) is the viscosity of water, and ΔP ($N.m^{-2}$) is the load pressure. The thickness of each of the studied membranes was measured by using a micrometer graduated in 0.001-mm divisions.

$$rf = \sqrt{\frac{8\eta_{H2O} J L_d}{P_r \Delta P}} \qquad (3)$$

3. RESULT & DISCUSSION

A. The Effect of Pulp DP

Exp. condition	*J* = Flux ml	Membrane thickness	Porosity	2 *rf* = pore size
	hour.cm²	μm	(%)	(nm)
mix DP	1.25	36.2	38.0	16.16
DP 850	1.31	20.8	31.1	13.94
DP1200	1.35	27.5	41.3	14.33
8%	1.27	25.5	34.6	14.44
10%	1.31	20.8	31.1	13.94
11%	0.88	30.7	31.6	13.43
water	1.31	20.8	31.1	13.94
nmmo 25%	1.38	28.0	21.2	20.22
nmmo 50%	1.12	31.7	19.2	21.58
bath 20 C	1.31	20.8	31.1	13.94
bath 40 C	1.11	25.3	25.5	15.50
bath 60 C	1.34	30.9	26.3	18.72
dry 30 C	1.11	30.4	25.6	17.08
dry 50 C	1.22	37.1	27.2	19.09
dry 50 C vacuum	1.31	20.8	31.1	13.94

The high DP of pulp result in higher porosity (low density) and water permeability of membrane. Polymer with high degree of polymerization will have longer chain and larger molecule compare to a polymer with low degree of polymerization. This long and large chain make more entangle occur between polymer chain but less chain mobility which cause NMMO difficult to break the entangled cellulose hydrogen bond during dissolution process result in less homogenous casting solution. Moreover this long chain and lesschain mobility avoid polymer chain to arrange closer each other during coagulation process induce more porous part on membrane.

B. The Effect of Cellulose Concentration in casting solution

Increasing cellulose concentration from 8% to 11 %, the porosity, pore size and water permeated (flux) decrease whereas increasing concentration from 10 % to 11% give similar porosity but the smaller pore size yield in lower flux. This can be explain by increasing polymer concentration is related to increase of polymer chain amount per unit area and yield in decrease of free space (pore) in membrane.

C. The Effect of NMMO in Coagulation Bath

The porosity is decrease from 31% to 19 % while mean pore size increases from 13.94 nm to 21.58 nm when the NMMO % wt content in coagulation bath temperature increases from 0% (water only) to 50% wt NMMO. There are two different mechanisms have to be considered as far as the liquid-liquid demixing of polymer solutions is concerned that is nucleation growth mechanism (NG) and spinodal mixing (SD). This membranes are believed to be the result of the NG mechanism for the slow solidification process and the uniform sponge-like pore structure.With increasing NMMO concentration, the diffusion rate decreases so as inhibit the nucleation formed but provide a longer time for nuclei to growth, thus this yield in more denser with bigger pore size membrane structure.

D. The Effect of Coagulation Bath temperature

Bath temperature 40^{o}C to 60^{o}C caused higher porosity and pore size. Because the coagulant is pure water, the solidification process is very rapid due to the high diffusion rate of NMMO and water at high temperature. The non-solvent diffuses quickly and passes the spinodal line before nucleation takes place. Thus, the spinodal decomposition may be stopped instantly and a dense skin layer is formed. It is difficult for the coagulant to permeate the skin layer further. However, at the other side of the skin layer there is some polymer-poor phase which is the original location of the macrovoids arising from the lower mass transfer resistance along the direction of the thickness. However, in the case of a lower temperature of the coagulation bath, the solvent-coagulant exchange rate is lower at the beginning of the precipitation. Because of the large differential concentration between the solvent and the non-solvent, the water diffuses quickly at the upper side of the solution resulting in the solidification of the dense skin layer. On the other hand, the solvent has not enough driving force to diffuse through the dense skin as a result of the lower temperature. Thus the polymer-rich phase under the skin layer has enough time to merge and a dense structure is finally obtained

E. The Effect of Drying Condition

Drying at 30^{o}C result in lower porosity (more denser) and smaller mean pore size than drying at 50^{o}C.Vacuum condition applied during drying process result in smaller mean pore size of cellulose membrane. The vacuum condition applied during dying process accelerated the free water evaporation so that no macrovoids is reduced however this yield in smaller pore size caused by attraction force of vacuum reduce the pore size.

4. CONCLUSIONS

The parameter condition of cellulose membrane prepared through simple and environmentally friendly process from NMMO have effect to its porosity and pore size properties. Among these parameter condition the coagulation bath condition control give more influence to membrane morphology properties. In this study 10 % cellulose concentration of DP 850, Coagulation bath with 50% NMMO at 20^{o}C and drying vacuum at room temperature assumed to produce more dense membrane.

5. REFERENCES

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