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Optical Polarizing Studies of Cellulose Acetate Membranes Prepared by Phase-Inversion

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Anisotropic spherical *cells* dispersed in an isotropic medium were observed, using polarizing microscopy, in asymmetric cellulose acetate (CA) membranes. Membranes CA-400 and CA-316 were prepared from ternary casting solutions of CA-acetone-formamide and CA-acetone-magnesium perchlorate/water respectively. The content of nonsolvent, formamide, was varied to yield membranes CA-400-22, CA-400-27 and CA-400-32 that show a decreasing number of larger anisotropic *cells* with the increase of nonsolvent content. The membranes CA-316 were subjected to a heat treatment—annealing—at varying temperatures yielding membranes CA-316-50, CA-316-68 and CA-316-86. The crystallinity observed was dependent on the temperature of this heat post-treatment. The selective permeation properties are correlated with the ratio of isotropic to anisotropic phases at the membrane skin surface. This ratio is in turn dependent on the casting solution composition-type and concentration of nonsolvent and on the annealing treatment. The results were interpreted considering that a lyotropic mesophase develops during the evaporation of the solvent after spreading the solution for film preparation. The ternary system is initially isotropic but as the polymer concentration (C) increases due to solvent evaporation, anisotropic droplets may appear at some value of $C \approx C^*$, where C^* is the critical concentration for the isotropic to liquid crystal phase transition in the CA/acetone (binary) system.

INTRODUCTION

Loeb and Sourirajan[1] cellulose acetate (CA) membranes, prepared by the so-called "phase-inversion" process,[2–4] are a land-mark in the recent development of membrane science and technology. This preparation process generates an asymmetric membrane composed of a thin layer (0.1 to 1 μm) supported by a highly porous sublayer (100 to 200 μm). The very thin skin is responsible for selective permeation characteristics, and therefore represents the actual membrane.

The phase inversion technique consists of:

(1) Preparation of a ternary casting solution: polymer-solvent-nonsolvent

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(2) Spreading of the solution as a film
(3) Solvent evaporation
(4) Gelation of the polymer film

Under controlled atmospheric conditions, the spreading of ternary solutions as thin films involves partial evaporation of the solvent from the film surface[5] with formation of a cloud point in this surface region leading to droplets that separate from the solution as a second interdispersed phase. The subsequent step yields a gel that constitutes a "phase inversion membrane".[3]

Membrane structure can be further modified by "annealing".[3–6] a post-formation treatment during which the polymer gel is exposed for a certain time period to hot water.

By variation of different preparation parameters membranes can be tailor-made for a given mass transfer task.

Kesting[3,4] investigated the mechanisms of membrane formation from a polymeric ternary solution composed of polymer-solvent-nonsolvent and studied the polymer desolvation through the steps involved in the casting process.

Matsuura[5] called the attention to the importance of the structure of the casting solution on the polymer desolvation process and on the membrane porous structure correlating specifically the size of polymer aggregates (polymer-nonsolvent) in the casting solution with the final membrane structure and its selective permeation performance.

It is well known[7–11] that binary solutions of CA with acetone, dimethylacetamide, and acetic acid form lyotropic liquid crystals for a given polymer critical concentration, depending on the solvent and on the degree of polymerization of the polymer.

Polarizing microscopy being a widely used technique to observe liquid crystalline behaviour[12–15] on cellulose and cellulose derivatives systems was used in our work to investigate the anisotropy of membranes prepared by phase-inversion from CA-acetone-nonsolvent.

The main objectives of our work were:

(a) The investigation of the effect of nonsolvents (type and concentration), and annealing temperature on the membrane anisotropy.

(b) The correlation of the surface textures observed with the selective permeation characteristics of the membranes.

EXPERIMENTAL

Membranes

Two series of cellulose acetate membranes, CA-400 and CA-316, were prepared according to the phase-inversion method described by Kunst and Sourirajan.[2] These series differ in the type of nonsolvent: formamide in CA-400 series and magnesium perchlorate/water in CA-316 series. In the homologous CA-400 series, the membranes differ in the formamide content. CA-316 membranes, prepared with a fixed

nonsolvent concentration, were annealed at three different temperatures. The formamide content and the annealing temperature are indicated as indices in the membrane code. Tables I and II list the details of the composition of the casting solutions and the film casting conditions for CA-400 and CA-316 respectively.

Membrane Characterization

CA-400 separation performance is characteristic of ultrafiltration (UF)—separation of macromolecules. CA-316 perform as reverse osmosis (RO) membranes—separation of salts and small organic molecules.

A first assessment of the permeation properties of UF/RO membranes is given by their water permeability (listed in Table III) defined by:

$$Lp = \frac{J_W \mu}{\Delta P} \tag{1}$$

where J_W is the water volume flux (ms^{-1}), ΔP is the transmembrane pressure (Pa), and μ is the viscosity (Pa.s).

TABLE I

Film casting conditions of CA-400 membranes

Membrane	CA-400-22	CA-400-27	CA-400-32
Composition of casting solution (wt %)			
Polymer: Cellulose acetate 398 (39.8% acetyl content)	17	17	17
Solvent: Acetone	61	56	51
Nonsolvent: Formamide	22	27	32
Temperature of casting solution (°C)		22–23	
Temperature of casting atmosphere (°C)		22–23	
Humidity of casting atmosphere (°C)		50–65	
Solvent evaporation time (min)		0.5	
Gelation medium		ice cold water (1–2 h)	

TABLE II

Film casting conditions and annealing temperatures of CA-316 membranes

Membrane	CA-316-50	CA-316-68	CA-316-86
Composition of casting solution (wt %)			
Polymer: Cellulose acetate 398 (39.8% acetyl content)		17	
Solvent: Acetone		69.2	
Nonsolvent: Magnesium perchlorate		1.45	
Water		12.35	
Temperature of casting solution (°C)		9–12	
Temperature of casting atmosphere (°C)		22–23	
Humidity of casting atmosphere (%)		50–65	
Solvent evaporation time (min)		1	
Gelation medium		ice cold water (1–2 h)	
Annealing temperature (°C)	50	67.5	86

TABLE III

CA-400 and CA-316 pure water permeabilities

Membrane	$Lp \times 10^{14}$ (m)
CA-400-22	1.1
CA-400-27	8.7
CA-400-32	22.5
CA-316-50	1.6
CA-316-68	0.9
CA-316-86	0.16
Membrane Surface Area (m^2)	13.2×10^{-4}
UF Pressure Range (Pa)	3×10^4 to 4×10^5
RO Pressure (Pa)	3×10^6
Temperature (°C)	25

Membrane selectivity is quantified by a solute rejection coefficient, f_A:

$$f_A = \frac{(C_A)_{\text{feed}} - (C_A)_{\text{permeate}}}{(C_A)_{\text{feed}}} \tag{2}$$

where C_A is the solute mass concentration in the feed and permeate streams.

UF membranes are characterized by a "molecular cut-off", which is the molecular weight of the solute with f_A higher than 0.9. RO membranes are characterized by the sodium chloride rejection coefficient, f_{NaCl}. Tables IV and V show the selectivities of CA-400 and CA-316 membranes, respectively.

The solutes used were polyethyleneglycols (PEG) and sodium chloride. The apparatus and experimental details have been reported previously.[16]

Optical Polarizing Microscopy Studies

Membrane samples were placed between slide and cover slide on a wet chamber and transferred at room temperature ($T \approx 25$°C) to the plate of an Olympus BH polarizing microscope. Observations were carried out with transmitted light under cross and parallel polars for several samples of the same membrane and at different regions of the

TABLE IV

Molecular cut-off of CA-400 membranes

Membrane	Mw Cut-off
CA-400-22	600
CA-400-27	6000
CA-400-32	10000
Membrane Surface Area (m^2)	13.2×10^{-4}
Transmembrane Pressure (Pa)	3×10^4
Feed Flow Rate ($m^3 s^{-1}$)	2.8×10^{-5}
Temperature (°C)	25
PEG Feed Concentration ($kg\,m^{-3}$)	0.6

TABLE V

Sodium chloride rejection coefficients of CA-316 membranes

Membrane	f_{NaCl}
CA-316-50	0.34
CA-316-68	0.68
CA-316-86	0.98
Membrane Surface Area (m^2)	13.2×10^{-4}
Transmembrane Pressure (Pa)	3×10^6
Feed Flow Rate ($m^3 s^{-1}$)	6.7×10^{-6}
Temperature (°C)	25
PEG Feed Concentration ($kg\,m^{-3}$)	3.5

microscope preparation. The photographs were taken with a Canon camera connected to the microscope. Membranes were always kept wet, otherwise their structure would have been damaged irreversibly.

RESULTS

CA-400 Membranes

Photographs of the skin layer of membrane CA-400-22, CA-400-27, and CA-400-32 are displayed in Figure 1 and show spherical *cells* dispersed in an isotropic medium.

For each membrane, average values of *cell* diameter, $\bar{d}$, and *cell* number, $\overline{nd}$, were calculated from direct measurements on several preparation photographs.

Membranes prepared from casting solutions with increasing formamide content yield skin surfaces with increasing *cell* diameters of 46 μm, 61 μm, and 68 μm, and decreasing *cell* number densities of 21 *cells*/cm^2, 5 *cells*/cm^2, and 1 *cells*/cm^2. A membrane prepared from casting solution without nonsolvent (17% CA and 73% acetone) and in the same casting conditions was observed and showed very small skin surface *cells*.

In Figure 1, observations with parallel (a) and cross (b) polars show that to each *cell* observed in (a) corresponds an optic-axis figure in (b), indicating that the medium is uniaxial in that region and that the polymer molecules are oriented inside the *cells* formed in the skin surface of the membrane.

Figure 2(a) shows an interference figure which suggests that the optic axis lies in the plane of the preparation. In Figure 2(b) the effect of a compensator ($\lambda = 530$ nm) can be observed. Starting from the center of the interference figure, it can be noted that in two opposite quadrants the interference colours rise with respect to that shown by the center, while in the other two they fall. The optical sign, considering the colours obtained, is positive.

CA-316 Membranes

Photographs I, II, and III of Figure 3 correspond to CA-316 membranes which were prepared in the same casting conditions but were annealed at different temperatures of

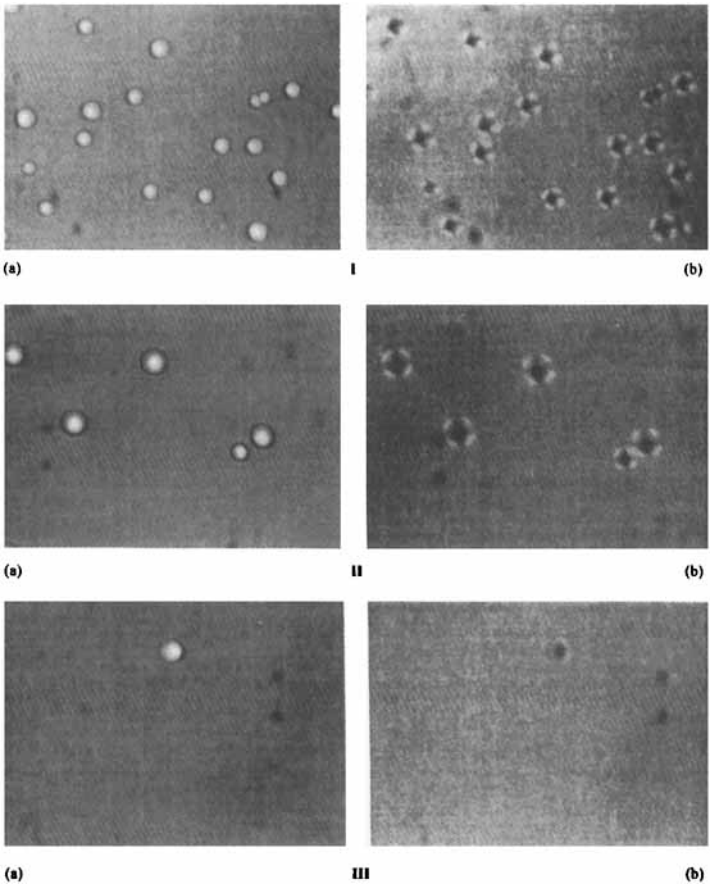
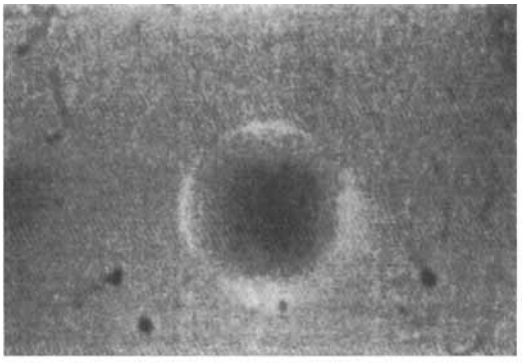


FIGURE 1 Optical observations on the skin layer of wet CA-400 membranes under (a) parallel and (b) cross polars I: CA-400-22. II: CA-400-27. III: CA-400-32. (× 45). See Color Plate VII.

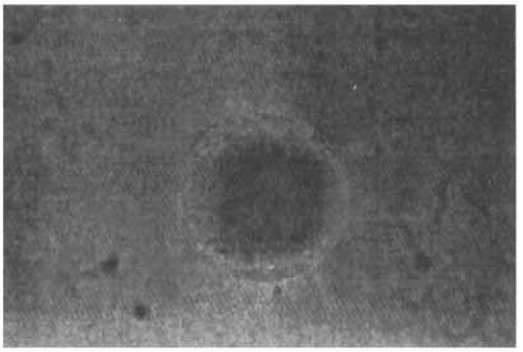
50°C, 67.5°C, and 86°C respectively. They present equally anisotropic spherical *cells* on the skin surface. In comparison to the ones of CA-400 membranes, these *cells* are smaller but exist in a much higher number density. Although not clear, it seems that annealing temperature does affect the skin surface anisotropy.

DISCUSSION

An early review of Kesting[4] presents electron microphotographs of Schultz and Asunmaa showing closely packed spherical *cells* at the skin membrane surface. Although the authors suggest a possible "microcrystalline nature" of the *cells*, no experimental evidence was ever presented. Furthermore, it is suggested that permeation takes place mostly through the intercellular amorphous region.



(a)



(b)

FIGURE 2 Optical observations on the skin layer of wet CA-400-27 membrane under (a) cross polars and (b) cross polars with a retardation plate, $\lambda = 530\,\text{nm}$. (× 250). See Color Plate VIII.

Polarizing microscopy observations shown in Figure 1(b), Figure 2(b), and Figure 3(b) are a clear evidence of the existence of anisotropic *cells* dispersed in the skin membrane face.

For the understanding of the above observations, the following hypothesis is proposed. In the film formation, immediately after spreading the polymer solution in the form of a film, evaporation of solvent starts at the air-solution interface. As a result of solvent loss, the critical concentration, C^*, for the isotropic to liquid crystal phase transition[7–11] is reached and a biphase with anisotropic droplets coexisting with an isotropic medium appears. After the immersion of the polymer film in the gelation medium (ice cold water), these droplets originate the observed *cells*, keeping their anisotropy.

The addition of a nonsolvent to the casting solution modifies solvent–solvent, solvent–polymer, and polymer–polymer interactions.

In CA-400 series, the strong hydrogen-bonding capacity of formamide coupled with its strong affinity for solvating CA, causes the swelling of the membrane with subsequent increasing in membrane porosity and permeability[3]. As displayed in Tables

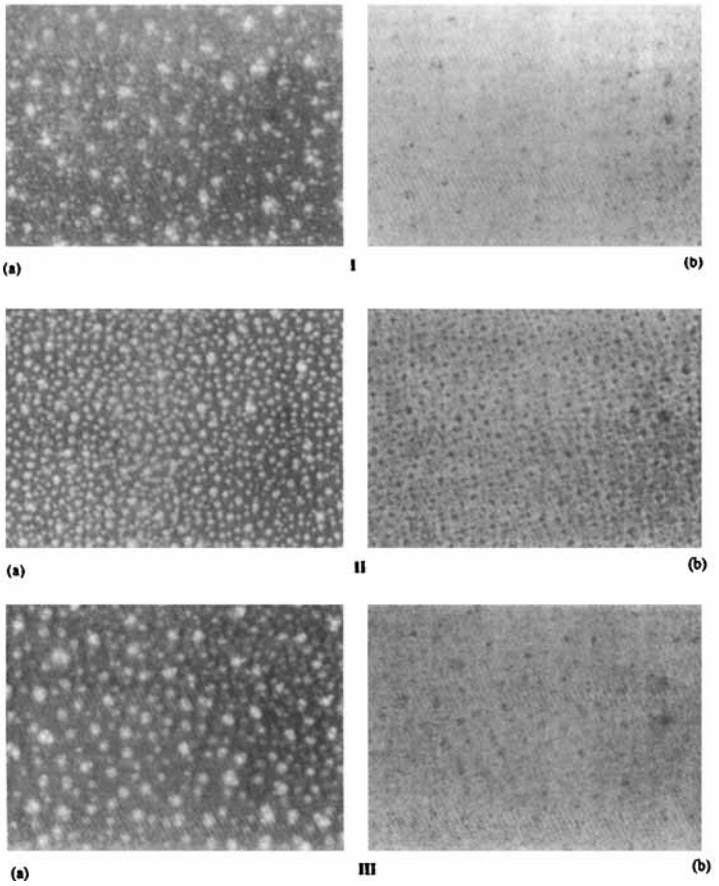


FIGURE 3 Optical observations on the skin layer of wet CA-316 membranes under (a) parallel and (b) cross polars I: CA-316-50. II: CA-316-68. III: CA-316-86. (× 50). See Color Plate IX.

III and IV, with increasing formamide content, membrane pure water permeability and molecular cut-off both increase through 1.1×10^{-14} m, 8.7×10^{-14} m, 22.5×10^{-14} m, and 600 Da, 6000 Da, 10000 Da respectively. This suggests also an increase in the ratio of isotropic (amorphous) to anisotropic phases with increasing formamide content, as depicted in Figure 1 through photographs I, II, and III respectively.

In CA-316 series, the salt $Mg(ClO_4)_2$ causes the aggregation of water molecules around the electrophilic cations (swelling action), considerably modifying the properties of the water[3] (used as nonsolvent and as gelation medium). The introduction of thermal energy, by heating a membrane in water, causes translational motion of the macromolecules allowing the approach of the polars groups to form virtual cross-links by dipole–dipole interactions[3] and, thereby, the incapacity of water to solvate them. This results in an irreversible "membrane shrinkage" (water lost) with subsequent decrease in permeability and increase in selectivity, particularly when CA membranes are heated above 68.6°C, the glass transition temperature. As displayed in Tables III

and V, with increasing annealing temperature CA-316 pure water permeability decreases and f_{NaCl} increases showing major variations from CA-316-68 to CA-316-86 transition (Lp goes from 0.9×10^{-14} m to 0.16×10^{-14} m and f_{NaCl} rises from 0.68 to 0.98). This shrinkage suggests a decrease in the ratio of isotropic to anisotropic phases. In Figure 3, photographs I to III do not show a clear tendency of increasing anisotropy with the annealing temperature, perhaps due to aggregation effects and/or optical resolution limitations. Further investigations on these membranes are in progress.

CONCLUSIONS

There is evidence of the existence of anisotropic *cells* in the surface of wet CA membranes prepared by phase-inversion.

The size and the density of these anisotropic *cells* are dependent on the casting solution, namely on the type and concentration of the nonsolvent, and on the annealing temperature.

The selective permeation properties could be correlated with membrane textures.

It is proposed that the anisotropy observed is the result of the formation of a mesomorphic (chiral nematic) phase during solvent evaporation when the polymer critical concentration for the isotropic to liquid crystal phase transition is reached.

Further investigations on *cell* formation mechanism and on the effect of annealing temperature in CA-316 textures are in progress.

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