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FORMATION OF ASYMMETRIC CELLULOSE ACETATE MEMBRANES

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ABSTRACT

Cellulose acetate membranes were prepared from casting solutions containing dioxane as a solvent and varying concentrations (up to 6%) of maleic acid as an additive. Coagulation took place in water at different temperatures. The effect of these variables on membrane structure and membrane properties is related to two phenomena of phase separation in the system cellulose acetate/dioxane/water, viz. gelation in the toplayer and liquid-liquid phase separation in the sublayer of the membrane. We adopted a solution transport model which correlates membrane flux with the skin thickness and membrane salt rejection with the compactness (microstructure) in the skin. Effects of variables such as maleic acid concentration and coagulation temperature on the position of curves in the phase diagram and on membrane properties are discussed. It is concluded that more work should follow on the kinetics of the phase changes mentioned.

INTRODUCTION

Asymmetric cellulose acetate membranes are known for over twenty years now (ref. 1). Cellulose acetate is still one of the most important polymeric materials for the formation of RO membranes since the membranes prepared from it in a simple two-step procedure (coagulation and curing) have good desalting and high flux properties.

Asymmetric membranes are classically produced by the so-called phase-inversion process (ref. 2). In this process a homogeneous polymer solution is cast as a thin film followed by the immersion of the film in a nonsolvent coagulation bath. In this bath solvent diffuses out of and nonsolvent diffuses into the film and the polymer will precipitate forming a membrane. The fundamental question not yet solved is how coagulation conditions, structure formation and membrane properties are interrelated.

Many variables during membrane preparation have an influence on the resulting membrane structure and properties. Some of these variables are related to the

composition of the casting solution and others pertain to the coagulation conditions. Membranes produced under apparently identical conditions may vary appreciable in properties (ref. 3). Laborious methods of trial and error have been used to get improvements in preparation conditions. Some authors have tried to refine this approach by the use of numerical methods for the design of their experiments (refs. 4,5). But in this way optimal conditions may not be attained; one cannot avoid to make a choice between the variables to be changed and one may make a wrong choice.

A better understanding of the structure formation mechanism might offer a more efficient approach, since then it would become possible to select the right variables for an optimizing procedure. A second advantage of an advanced insight in structure formation might be the possibility of finding ways for a better reproducibility of the results.

In recent years the experimental evidence (refs. 6-9) was gathered in our laboratory that the coagulation process can be specified separately for the formation of the skin and for the sublayer of a membrane in terms of the two different types of phase separation that occur in polymer solutions of high and medium concentrations. Some of these phase separation results form the rationalization for the selection of the variables investigated in this study. The aim of the present study is to get a better understanding of how these variables influence the membrane properties.

PHASE SEPARATION, MEMBRANE STRUCTURE AND MEMBRANE PROPERTIES

Phase separation and membrane structure

As mentioned above the coagulation process can be described in terms of phase separation phenomena occurring in polymer solutions. Two different types of phase separation can be distinguished (Fig. 1):

- liquid-liquid (l-l) phase separation at low and medium polymer concentration and a variable nonsolvent content and
- gelation or (micro)crystallization at high polymer concentration.

We will now discuss what happens during the formation of a membrane. The ultimately determining factor for the type of phase separation and therefore for the type of structure formed is the local polymer concentration in each layer of the polymer solution at the moment of precipitation (Fig. 2).

The polymer concentration in the toplayer will increase i) by evaporation of solvent before the immersion in the coagulation bath and ii) by solvent depletion from the toplayer which occurs extremely fast upon immersion in the coagulation bath (Fig. 2a). This increase in polymer concentration improves the conditions for gelation to occur. The gelation will also be effected by the penetration of nonsolvent upon immersion, or even before immersion: evidently, when the polymer solution is being cast in an atmosphere with a certain humidity, the penetration of nonsolvent can already start during the time of contact between the polymer

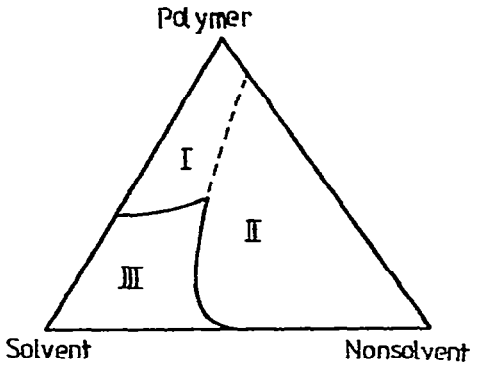


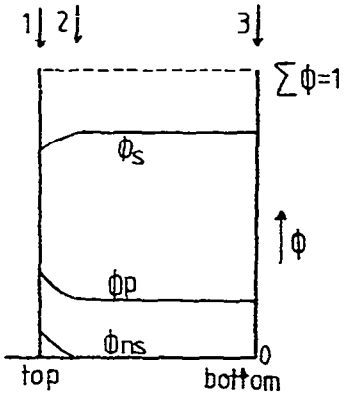
Fig. 1. Ternary phase diagram.
I gelation region
II l-l phase separation region
III homogeneous solution

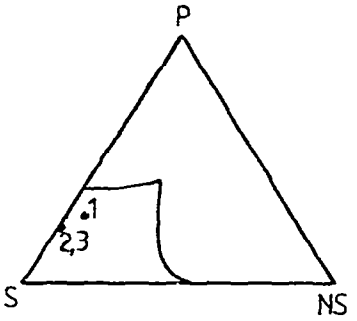
film and the air. It is obvious that the position of the solution-gel transition curve in the phase diagram is of extreme importance for skin formation. The higher the polymer concentration has become before the nucleation in the toplayer sets in, the more numerous and the smaller will be the nuclei. In this way a dense gel-layer will be formed and the resulting structure for the membrane is a dense skin (Fig. 2b).

As soon as the skin has formed, the diffusion of solvent out of the layers beneath this gellayer will be hindered. The denser this barrier is, the more diffusion will be delayed. This forms one of the characteristic differences in the formation of RO vs. UF membranes. Because of this delay of solvent diffusion the phase separation in the layers beneath the gellayer will take place at a much lower polymer concentration compared to that in the skin. This phase separation will be of the l-l phase separation type (Fig. 2c). The original polymer solution separates in spherical pores and conical voids containing mainly solvent and non-solvent, while the polymer solution between the pores increases in concentration and finally solidifies by gelation. In this way a porous sublayer is formed (Fig. 2d). Again one sees that it is extremely important to know exactly the position of the l-l phase separation curve, and to find out what is the effect of additives to the casting solution on the position of this curve in the ternary phase diagram. Fig. 3 shows the overall course of the top and bottom layers through the phase diagram during coagulation.

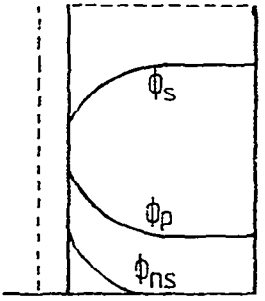
Selection of variables

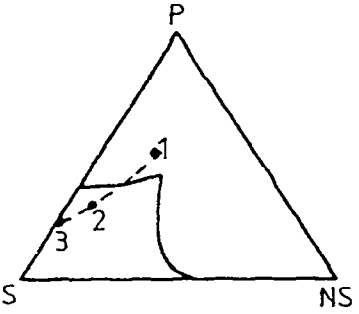
Altena (ref. 8) has shown that both gelation and l-l phase separation can occur in the system cellulose acetate/dioxane/water. The choice of this system was based on the frequent use of dioxane as a solvent in casting solutions. But casting solutions generally consist of more than two components (refs. 10-12): often a



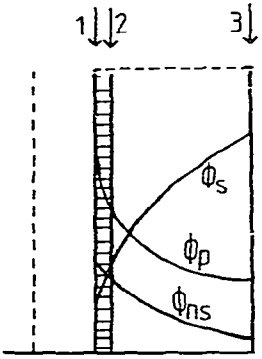


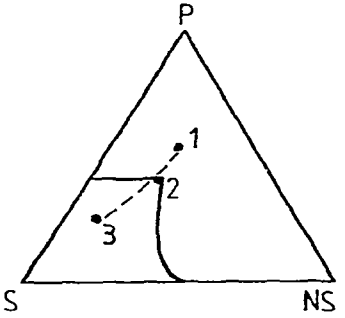
2a. $t=t_0$, time of immersion of the film in the coagulation bath (some evaporation of solvent out and some penetration of nonsolvent before immersion is assumed here).



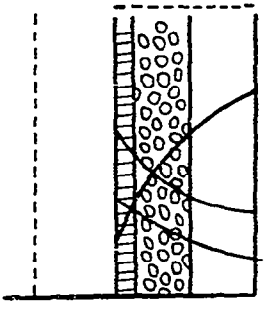


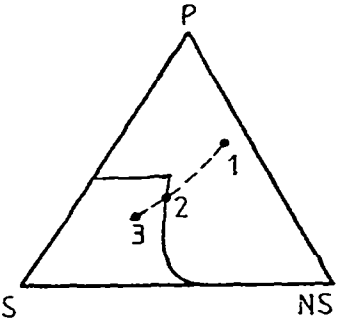
2b. $t=t_1$, start of the gelation process in the outmost toplayer.





2c. $t=t_2$, start of the l-l phase separation at point 2 below the skin.





2d. $t=t_3$, the coagulation process has proceeded halfway into the film (point 2) the bottom half is still fluid (between points 2 and 3).

Fig. 2. Concentration profiles and positions in the phase diagram for different points in the solution film at various times.

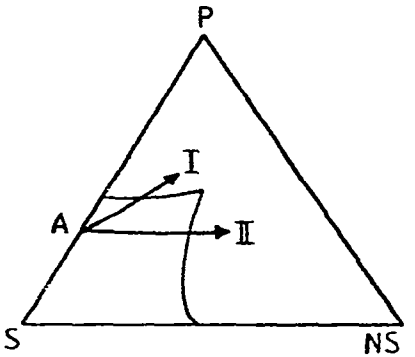


Fig. 3. Schematic course of the composition for the skinlayer (I) and the bottomlayer (II) of a polymer film with initial composition A upon immersion into a nonsolvent bath.

blend of two cellulose acetates with different acetyl content is used and acetone, dioxane, methanol and maleic acid form the solvents and the additives.

We have extended Altena's experiments by studying the influence of maleic acid (MA) on the phase separation phenomena in the system cellulose acetate/dioxane/water. Some of the results will be summarized here. The influence of MA content in the casting solution on the membrane properties is extensively reported in this study. In order to facilitate the interpretation of the results, acetone was omitted from the casting solution so that the effect of evaporation of acetone on the gelation process is avoided.

Phase separation phenomena are strongly influenced by the temperature. Lowering of the temperature far enough below the equilibrium phase line favours nucleation of a new phase, whereas growth of the nuclei is favoured at higher temperatures. For this reason the influence of the coagulation temperature on the membrane properties is also investigated.

Membrane structure and solution transport

In order to draw conclusions from flux and rejection data about the influence of preparation variables on structure formation (especially in the toplayer), we need a model interrelating membrane structure and transport of solution components. In our case of uncured RO membranes the following concept is used in which membrane structure parameters and membrane properties are coupled:
We assume that the flux is mainly determined by the thickness of the skin and that the rejection of the membranes is determined by the compactness of the skin. The term compactness may need some explanation. The skin layer consists of cellulose acetate segments participating in crosslinks -or microcrystalline domains- and segments which are less rigidly fixed in amorphous regions; in this concept a high compactness means a fine network of many small crosslink domains. Of course this

model of coupling flux values to skin thickness, and rejection values to compactness of the skin need not be universally valid. For instance curing in general gives effects on flux and rejection, which would not fit this model. In our case, however, of uncured membranes we find that flux and rejection are independently affected by preparation variables.

The thickness of the skin is determined by the thickness of the gellayer during membrane formation. This layer will become thicker: *i*) when the concentration for gelation is lower and/or *ii*) when the *l-l* phase separation curve is shifted to higher water concentrations (more to the right in the phase diagram); it then lasts longer for the *l-l* phase separation to become a competitive process in comparison to gelation.

The compactness of the skin is determined by the polymer concentration at which gelation sets in. The higher the concentration has become before nucleation sets in, the more numerous and the smaller will be the nuclei because of higher supersaturation.

Finally electron microscopy studies will show some effects of preparation variables on the morphology of the porous sublayer.

EXPERIMENTAL

Membrane preparation

Membranes were produced on a polyester nonwoven support by the use of a laboratory casting machine. The casting solution contained a blend of E 398-6 and 436-80S (Eastman Kodak) total polymer concentration 15% by weight, methanol 5%, MA 0-6% and dioxane. Cellulose acetate was dried before use. Reagent grade dioxane, methanol and MA were used without further purification.

The casting film thickness was 0.2 mm; the casting speed was 0.7 m/min. Coagulation was performed in pure water during 1 h at a temperature of 0 °C or during ½ h at a temperature of 22 and 32 °C. The membranes were tested without further treatment.

Reverse osmosis experiments

RO experiments were carried out at 20 °C, a pressure of 4 MPa and a feed concentration of 5000 ppm NaCl. Concentration polarization was at a minimum at the flow velocity used.

The membranes were pressurized during two hours before measurement. The concentration of NaCl in the feed and the product were determined by conductivity measurements.

Scanning electron microscopy (SEM)

The membranes used for the SEM experiments were hand cast on a glass plate and then immersed in the coagulation bath. Membrane samples were fractured at liquid nitrogen temperature and sputtered with gold. Cross sections were investigated using a Jeol JSM U3 electron microscope.

Cloud point measurements

Cloud points were measured by the method described earlier (ref. 13). Well degassed (liquid nitrogen temperature) solution samples in Pyrex tubes were made homogeneous by heating at a high enough temperature.

Phase separation points were usually determined by cooling or heating the samples in a thermostat bath at a rate of 1 ^{o}C per 10 minutes until turbidity appeared or disappeared.

RESULTS AND DISCUSSION

Phase separation experiments

The l-l phase separation experiments were performed with solutions of constant composition at varying temperatures. It was found that due to the presence of MA a lower temperature was needed to get phase separation. When this is compared to a system with varying composition at constant temperature, one may infer that more water is needed to cause l-l phase separation in the presence of MA than when MA is absent.
So one can expect that during membrane formation the l-l phase separation is delayed by the presence of MA.

Solutions of cellulose acetate in dioxane and maleic acid gelated when kept at higher temperatures for longer times, a phenomenon that was not observed in the absence of MA. From these observations it was concluded that gelation occurs more easily during membrane formation in the presence of MA.

Flux and rejection measurements

Flux and rejection data of membranes cast from solutions with different MA content and coagulated at different coagulation temperatures are given in Figs. 4 and 5.

The results for membranes coagulated at 0 ^{o}C (curves a. in figs. 4 and 5) can be explained as follows: due to the presence of MA gelation occurs at a lower polymer concentration in the toplayer. This means that gelation sets in at a lower supersaturation; the resulting skin will be less compact and a lower rejection should be expected. As is seen from Fig. 4a a decrease in rejection values

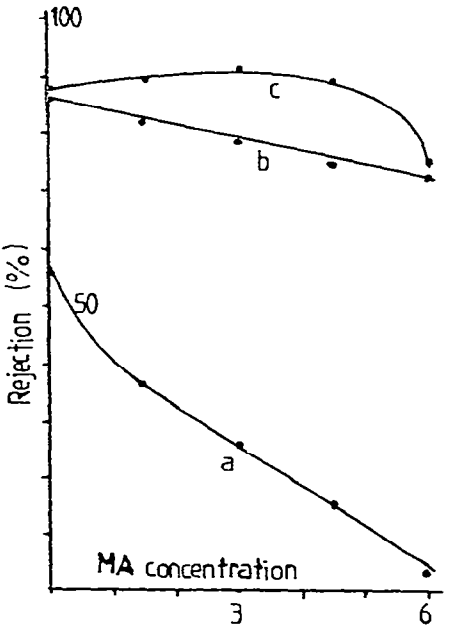


Fig. 4. Rejection values for different MA concentrations Coagulation temperatures: a) 0 °C; b) 22 °C; c) 32 °C.

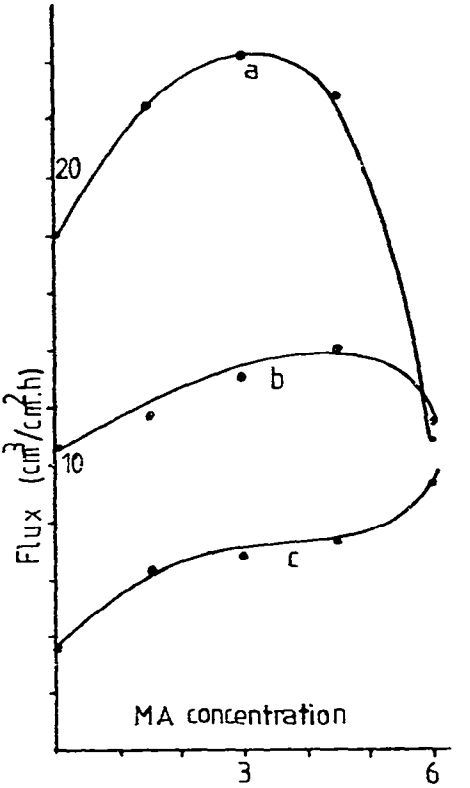


Fig. 5. Flux values for different MA concentrations.

is indeed found at increasing MA content.

The dependence of flux on MA concentration for membranes coagulated at 0 °C (Fig. 5a) shows a more complex relationship. We have seen that with increasing MA content gelation occurs at lower polymer concentration and l-l phase separation is shifted to higher nonsolvent content. Both effects would indicate an increase in gel thickness and therefore a reduction in flux values with increased MA content of the dope. It is obvious from Fig. 5a, at least at lower MA concentrations and also from Figs. 5b and 5c, that a different trend exists that favours flux increase with increasing MA content. This might be an effect originating from the kinetics of gelformation and l-l phase separation. For the take-over of l-l phase separation from gelation below the toplayer, not only the position of the equilibrium phase lines in the diagram is important, but also the nucleation and growth kinetics of both processes. Since we do not have relevant data on the phase separation

kinetics so far the rising branch in Figs. 5a-c still lacks explanation.

The relative position of curves a, b and c in Fig. 5, showing decreasing flux values for higher coagulation temperature (at constant MA content) reflects two considerations which already were mentioned earlier: *i*) at higher temperature nucleation becomes more difficult and the point of incipient gelation is shifted to higher polymer concentrations, *ii*) at higher temperatures *l-l* phase separation sets in at higher nonsolvent content. Both effects lead to a thicker gellayer, since solvent depletion can proceed to a larger extent before *l-l* separation takes over from gelation.

In Fig. 6 a schematic survey of the effects that a variation in MA concentration or in coagulation temperature, can have on the position of phase lines in the diagram and on the kinetics of phase changes is given.

The observed higher rejection values at higher coagulation temperatures (Figs. 4b and c) can also be explained by the fact that the nucleation is more difficult at higher temperatures. When the gelation point lies at higher concentrations a higher supersaturation is possible, resulting in a more compact skin. Membranes coagulated at 22 °C do indeed have a higher rejection than membranes coagulated at 0 °C. Moreover the decrease in rejection values at increasing MA concentrations is less pronounced. Membranes coagulated at 32 °C show an even higher rejection with a maximum value at intermediate MA concentrations (Fig. 4c).

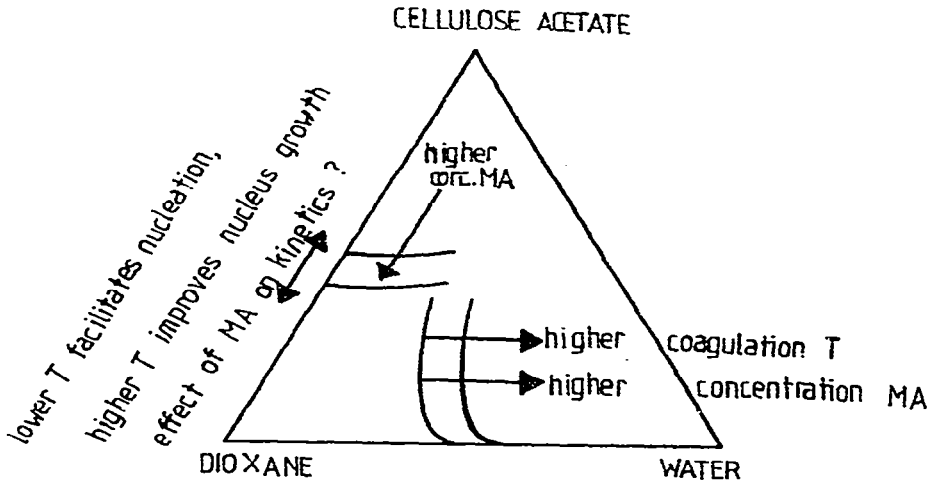
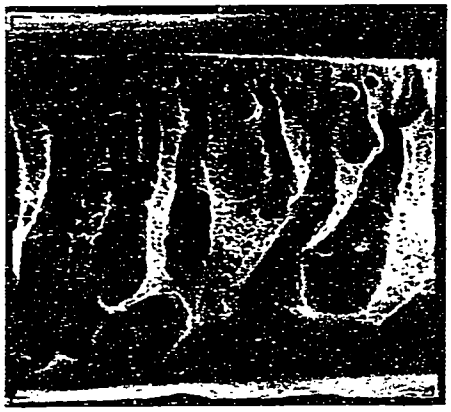


Fig. 6. Survey of effects on phase separation through variation in MA concentration and coagulation temperature.

Electron microscope experiment

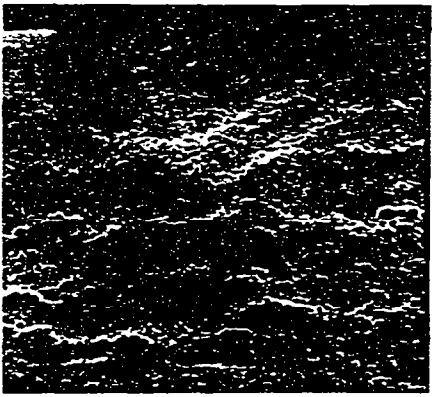
The electron microscope photographs (Figs. 7a, b) evidence that the number of pores in the sublayer is larger and the size is smaller at increasing maleic acid concentration. This can be explained by the fact that due to the presence of MA the L-L phase separation is delayed. In this way a higher concentration of polymer is reached when the phase separation sets in, so more nuclei can be formed, which grow more slowly. These nuclei correspond with the pores found in the resulting sublayer. Figs. 8a, b and c show that the number of conical voids is increased at increasing coagulation temperatures. This phenomenon was also observed by King et al. (ref. 14).



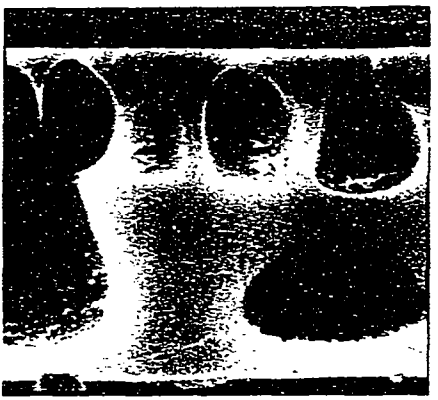
7a. 0 % MA.
Magnification 800

7b. 6% MA.
Magnification 900.

Fig. 7. Cross section of membranes prepared from casting solutions with different MA content, coagulation temperature 20 °C.



8a. Coagulation temperature 0 °C. Magnification 3000×



8b. Coagulation temperature 22 °C. Magnification 900

8c. Coagulation temperature 32 °C. Magnification 900×

Fig. 8. Cross section of membranes prepared from a casting solution containing 3% MA and coagulated at different temperatures.

CONCLUSIONS

This study shows that a detailed knowledge of phase separation phenomena can help to understand and improve membrane formation. Direct connections between preparation variables, membrane structure and membrane properties become apparent. Kinetics of phase changes occurring during membrane formation deserve more attention in the future.

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