Tensile Properties and Desalination Performance of Modified Cellulose Acetate Membranes

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The effects of annealing temperature on the mechanical properties and the desalination performance of cellulose acetate membranes have been investigated. A critical temperature T_c exists at which all membrane properties change abruptly. In addition, the effects of low concentrations ($10^{-4}-10^{-1}$ mol/l) of phenol in the solution on the mechanical properties and on the water content of the membranes have been established. At the same concentration at which the phenol uptake sharply increases, a significant decline of water content and mechanical properties have been found.

The results confirm close relationships between the physical properties and the desalination performance.

INTRODUCTION

During the last ten years a great amount of work has been performed to characterize more adequately the cellulose acetate (CA) membranes used in hyperfiltration or in ultrafiltration[1,2] and, if possible, to modify them. In particular, the asymmetric CA membranes first prepared by Loeb and Sourirajan,[2] combining a large water permeability and a high salt rejection, generated considerable interest among scientists in these membranes. The asymmetric membranes are generally assumed to consist of a porous matrix (100–150 μ thick) supporting a very thin dense layer (≈ 0.2 μ thick) on the air-dried surface formed during the casting procedure.[2–5]

Considerable emphasis has been placed on improving the desalination characteristics of CA membranes by modifying the membrane formulations[7–10] and/or by treating the membranes thermally.[11]

In addition to studies with salt solutions, the separation of small organic molecules such as alcohols and ketones from water solutions has also been tested.[12,13] Unusual behavior has been observed with phenol solutions. In fact, negative rejection for phenol and a decreasing water permeability have been found.[11,14-19] This decrease of water permeability is pronounced at concentrations above 10^{-1} molar.

Relatively little work has been performed on the mechanical behavior of CA membranes in trying to correlate these properties with the transport behavior in hyperfiltration. Findley, in 1941,[18] studied the mechanical performance of compression-molded CA samples. Other authors[19-26] investigated homogeneously filled and unfilled films. Recently, Meinecke and Mehta[27-29] analyzed the influence of some processing variables on the properties of homogeneous CA membranes, relating physical properties such as birefringence, ultimate elongation, degree of orientation, and thermal treatment (annealing) with the transport characteristics of these membranes.

In the scientific literature, little work has been done in developing structural models which can correlate thermomechanical properties with desalination performances of polymeric asymmetric membranes. This can be due to the lack of a deeper knowledge of basic specific problems such as the T_g dependence from solvent uptake, thermomechanical history of the polymeric structural changes due to polymer–solvent interaction (plasticization), and the real structure of the dense skin and porous sublayer in these asymmetric membranes.

This paper reports the effect of annealing temperature and the influence of phenol on the tensile properties of asymmetric cellulose acetate membranes. An attempt is made to correlate these data with the desalination properties of the membranes.

EXPERIMENTAL

Experiments were performed with asymmetric CA membranes prepared from grade Cellit K700 cellulose acetate (39.1% acetyl) produced by Bayer AG in Leverkusen, West Germany according to the procedure reported in Ref. 30. These were annealed in water at different temperatures for about 10 minutes.

From these membranes, 1 cm × 8 cm strips were cut and tested for their tensile properties using an Instron Universal testing machine. The specimen was always completely immersed in water or the corresponding phenol solution depending on the kind of investigation. The grips were adequately modified to avoid slippage of the membranes during the deformation. In particular the elastomeric jaws made by Instron (cat. no. 2713-001) have been modified by cutting the roller brackets in two parts. The membranes were first fixed between these two pairs of emicylinders and then rolled around the rollers as in the

usual procedure for testing thin films. This modification allowed a better control of an eventual slippage of the membranes. The strain rate, $\dot{\epsilon}$, was 0.5 min^{-1} and the temperature was kept constant at 25°C. The data reported are averages of at least 10 experiments.

Permeability experiments were carried out at 40 atm using a hyperfiltration cell. All parts of the cell were built of 316 stainless steel, and the membranes were supported by finely porous sintered stainless steel plates located in the lower half cell.[31,32] The effective membrane area was 12 cm^2 and the experiments were carried out at 25°C.

RESULTS AND DISCUSSION

In Figure 1 a typical stress–strain curve of an asymmetric cellulose acetate membrane tested in water is reproduced. It appears that after an initial linear region there is a well-defined yield point and a large deformation before fracture. From the slope of the initial part of the curve, the Young's modulus, E, is obtained. The knee in the curve is the yield point and the corresponding values of σ and ϵ are the yield stress and yield strain, respectively. The corresponding values at the break point are the ultimate tensile strength, σ_u, and the elongation at break, ϵ_u.

The E values obtained by these experiments are smaller than the ones reported in the literature.[33] Moreover, the elongation at break is larger and the ultimate strength is smaller. All these data indicate that the membranes tested in this work are more plasticized than the ones used in previous research.
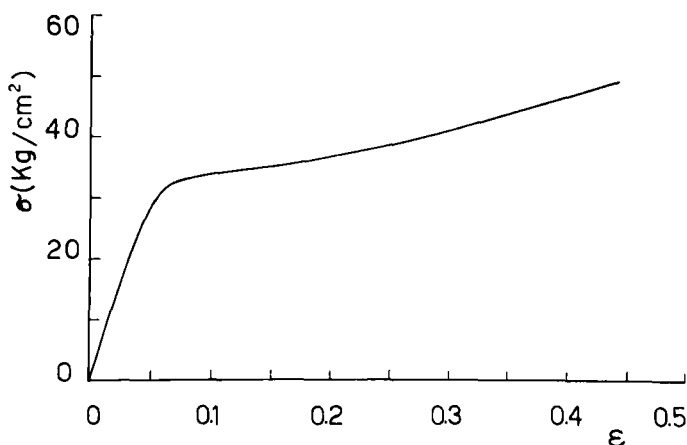

FIGURE 1   Typical stress–strain curve of CA membranes.

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It should be pointed out, however, that our experiments were performed with the membranes completely immersed in the solution, while the experiments carried out by others[33] were performed by clamping the membranes between wet filter papers to avoid drying of the specimen. To verify that this discrepancy is due to different experimental techniques, a few runs were made using the procedure described in the literature. With this experimental set-up the previously reported results[33] could be reproduced, indicating that clamping *the membranes between wet filter papers modifies the experimental findings.*

The two experimental techniques are not comparable. While membranes between wet filter paper may clamp, strain-enhanced sorption as well as bulk flow of liquid in deformation-defect zones within immersed membranes might influence the experimental results. For our purposes the immersion-technique is more reliable, and is the only one suitable for experiments with phenol solutions.

In Figure 2 the ultimate elongation (ϵ_u), the strength (σ_u), the elastic modulus (E), and yield stress (σ_y) are graphically reproduced as functions of the annealing temperature, T_a. All these parameters vary abruptly at a temperature, T_c, of about 75–80°C. At annealing temperatures either higher or lower than this critical value, all mechanical properties are practically constant. In particular, the modulus, the yield stress, and the strength are larger at an annealing temperature beyond T_c, while the elongation at break becomes smaller.

These phenomena are in agreement with permeability and selectivity data as shown in Figure 3, respectively. In fact, the steady-state water flux measured
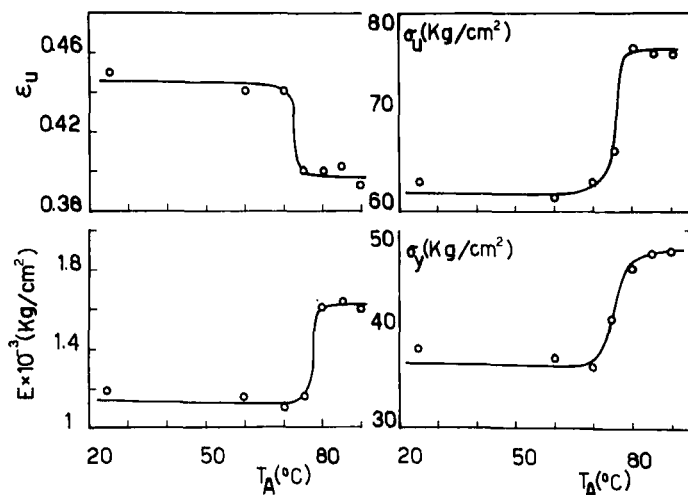

FIGURE 2   Tensile parameters of asymmetric CA membranes annealed at different temperatures T_a.

using asymmetric cellulose acetate membranes in hyperfiltration experiments also decreases sharply while the solute or salt rejection increases at annealing temperatures around T_c.

From these results it appears that a correlation exists between mechanical properties and membrane performance, particularly for permeability and selectivity. In fact, the increase in the elastic modulus of membranes annealed at $T > T_c$ can be interpreted as being due to the reduction of the porosity of the material. A similar explanation applies to the reduction of flow rate and the increase in the rejection coefficient of the membrane. The variation in rejection and water permeability is usually attributed to changes in the dense skin of the asymmetric membranes which represents only a very small part of the entire membrane (less than 0.2%). On the other hand, the mechanical properties,
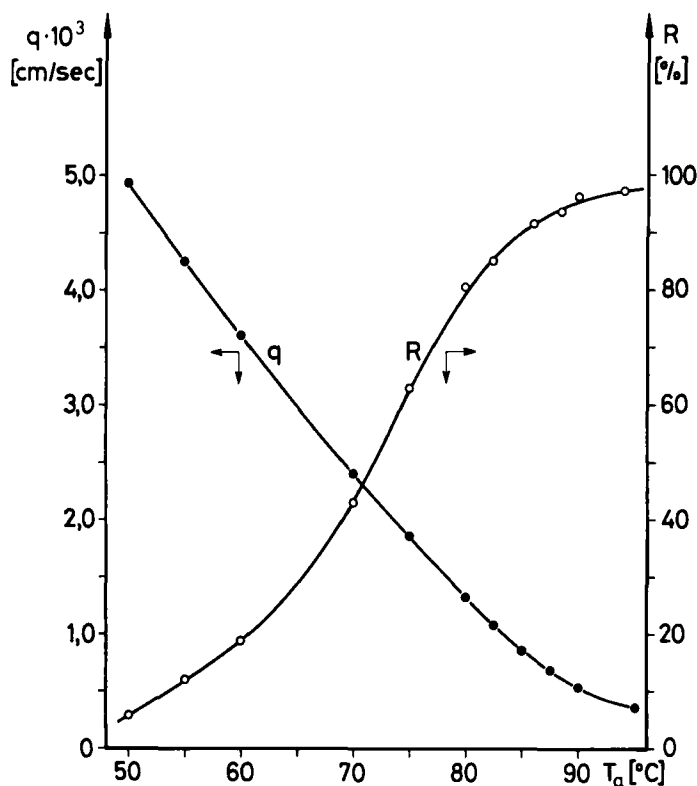

FIGURE 3 Volume flux, q and salt rejection, R, of asymmetric, paper-reinforced flat sheet cellulose acetate membranes (KALLE AG, Wiesbaden-Biebrich, Germany) as a function of annealing temperature T_a at $\triangle P = 100$ bar using 0.1 M NaCl brine solution (from W. Pusch.[36])

which are also strongly influenced by varying the annealing temperature, are always related to the overall thickness of the membrane sample.

Another interesting feature of CA membranes is the anomalous behavior in the presence of phenol solutions. These membranes, in fact, exhibit negative rejection for this solute. This behavior, moreover, seems to be time dependent. For a better understanding of this effect, phenol uptake in asymmetric CA membranes has been measured at different molar concentrations at 25°C.[11] From the data reported in Figure 4, it appears that at a phenol concentration of about 5×10^{-3}M the amount of phenol adsorbed increases sharply for both homogeneous and asymmetric CA membranes. In Figure 5 the amount of absorbed water in a homogeneous CA membrane is reported as a function of

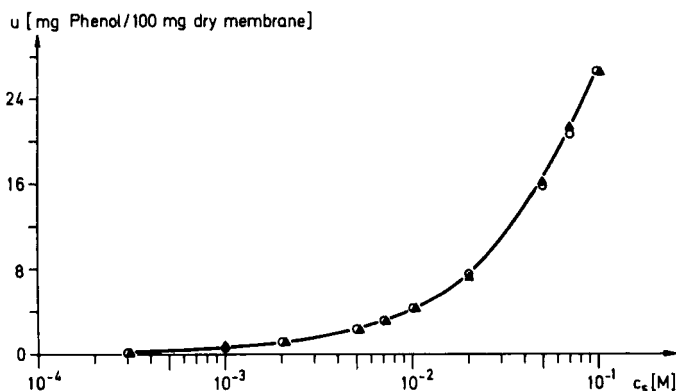FIGURE 4   Phenol uptake, u, of homogeneous (○) and asymmetric (▲) CA membranes as a function of phenol concentrations, c_s.[11]
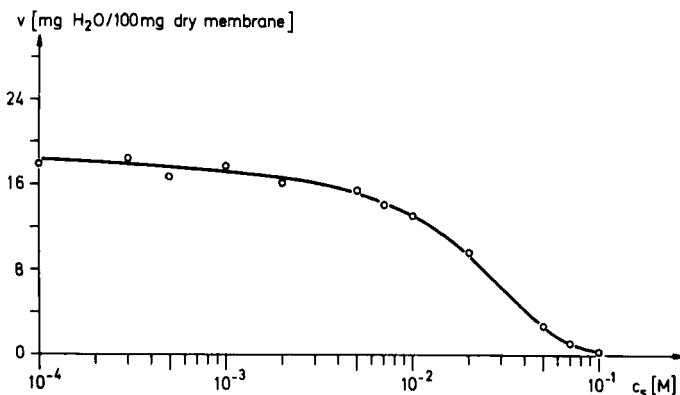

FIGURE 5   Water content, v, of a homogeneous CA membrane as a function of phenol concentration, c_s.[11]

the phenol concentration. It is interesting that at the same concentration at which the phenol uptake sharply increased, a significant decline of water content was found. Phenol interaction with the polymeric matrix appears to remove water from the matrix changing the physical properties of the membrane. Similar conclusions can be drawn from mechanical measurements.

In Figures 6 and 7 the mechanical parameters of CA membranes are reported which were obtained by immersing the membranes in solutions of different
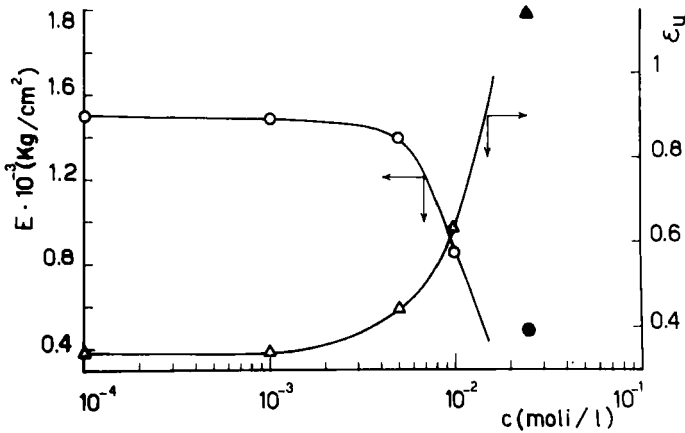
FIGURE 6   Young's modulus, E, and ultimate elongation, ϵ_u, of asymmetric CA membranes immersed in solutions of different phenol concentrations, c_s, as a function of phenol concentration. Open symbols are taken after 1500 min, full symbols after 1 min.
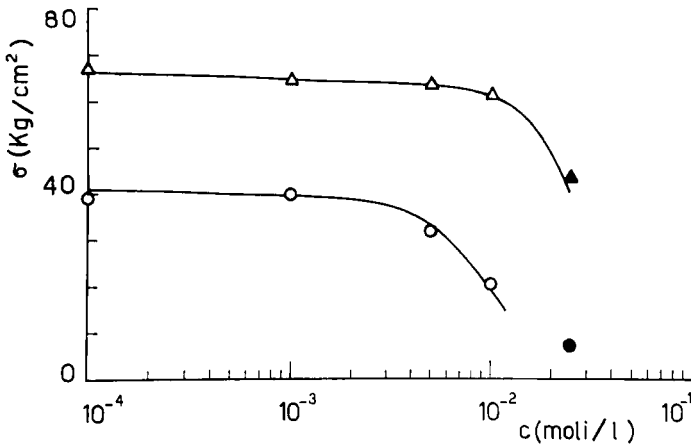

FIGURE 7   Yield stress ($\bigcirc$) and ultimate stress ($\triangle$) of asymmetric CA membranes immersed in solutions of different phenol concentrations, c_s. Open symbols are taken after 1500 min, full symbols after 1 min.

phenol concentrations. Most of the data reported were taken after 1500 minutes' immersion in a given phenol solution. For a phenol concentration of 0.025M, the data reported refer to an immersion period of about 1 minute, because at longer times the membranes were difficult to handle.

In Figure 6 the Young's modulus and the ultimate elongation are plotted versus molar concentration for a CA membrane annealed at 90°C. At about 5×10^{-3}M, a significant change of these parameters appears. The modulus decreases and ϵ_u increases, showing the plasticizing effect of phenol. The water content and the phenol uptake begin to change at the same concentration, as reported in Figures 4 and 5.

Reported in Figure 7 are the yield stress and the strength of CA tested in phenol solutions. As discussed for the other mechanical properties, both σ_y and σ_u are dependent on the phenol content for concentrations larger than 5×10^{-3} mol/l. The filled symbols represent data obtained after a residence time in solution of 1 minute while the open symbols were obtained after 1500 minutes. It should be noted that during this time no significant change in properties was observed and the data reported are an average of those obtained at different immersion times.

A narrow annealing temperature range thus exists in which the permeability, selectivity, and mechanical properties of asymmetric CA membranes change sharply. The desalination performance of these membranes has usually been attributed to the properties of the dense skin of the membrane. However, mechanical properties of these films are measured on the overall cross section, of the film. The possibility that a change in the physical properties of this skin would change the mechanical property of the entire film does not seem realistic. The model of a membrane formed by two parallel layers of materials with different properties would not explain our experimental data. A change of the mechanical properties of the skin layer would not yield the increase in the modulus shown in Figure 2 and also would not explain the increase in strength. However, a model which assumes a variation of physical properties of the entire membrane[34] is consistent with both the desalination performance and the mechanical data. It is also in agreement with recent studies on the structure of CA membranes which manifest a change of pore size distribution and transport parameters across the membrane.[35] A model correlating thermo-mechanical properties and desalination performances cannot be developed with our present knowledge. Thus, further thermomechanical experiments should be performed. A more detailed study on phenol- and water-sorption of CA membranes will be presented in a further paper.

Acknowledgements

References

1. C. E. Reid and E. J. Breton, *J. Appl. Polymer Sci.* **1**, 133 (1959).
2. S. Loeb and S. Sourirajan, *Advan. Chem. Sci.* **38**, 117 (1962).
3. S. Loeb and S. Manjikian, *Ind. Eng. Chem. Prod. Res. Develop.* **4**, 207 (1965).
4. S. Manjikian, *Ind. Eng. Chem. Res. and Develop.* **6**, 23 (1967).
5. R. L. Riley, J. O. Gardner, and V. Merten, *Science* **143**, 801 (1964).
6. R. L. Riley, U. Merten, and J. O. Gardner, *Desalination* **1**, 30 (1966).
7. R. Bloch and M. A. Fromer, *Desalination* **7**, 259 (1970).
8. S. Loeb and J. McCutchan, *Ind. Eng. Chem. Prod. Res. Develop.* **4**, 114 (1965).
9. R. E. Kesting, *J. Appl. Polymer Sci.* **9**, 663 (1965).
10. H. K. Lonsdale, U. Merten, and R. L. Riley, *J. Appl. Polymer Sci.* **9**, 1341 (1965).
11. W. Pusch, H. G. Burghoff, and E. Staude, *5th Int. Symposium on Fresh Water from the Sea*, **4**, 143 (1976).
12. R. Blunk, "A study of Criteria for the Semipermeability of Cellulose Acetate membranes to Aqueous Solutions", University of California Water Resources Center Report WRCC-88, 1964.
13. B. Keilin, *OSW Res. Dev. Progr. Rep. No. 117*, Aerojet-General Corp. (1964).
14. H. K. Lonsdale, U. Merten, and H. Tagami, *J. Appl. Polymer Sci.* **11**, 1807 (1967).
15. T. Matsura and S. Sourirajan, *J. Appl. Polymer Sci.* **15**, 2905 (1971).
16. T. Matsura and S. Sourirajan, *J. Appl. Polymer Sci.* **16**, 2531 (1972).
17. J. E. Anderson, S. J. Hoffman, and C. R. Peters, *J. Phys. Chem.* **76**, 4006 (1972).
18. W. N. Findley, *Proc. Amer. Soc. Testing Materials* **41**, 1231 (1941).
19. W. N. Findley, *Proc. Amer. Soc. Testing Materials* **41**, 914 (1941).
20. W. N. Findley, Creep Properties of Plastics, Int. Symposium on Plastics, ASTM Philadelphia (Feb. 1944).
21. R. N. Haward, *Trans. Faraday Soc.* **38**, 394 (1942).
22. R. D. Deamin, B. Baum, S. A. Margosiak and W. H. Holley, *Ind. Eng. Chem. Prod. Res. Develop.* **9**, 172 (1970).
23. Saline Water Conversion Report 1968, Office of Saline Water, Department of the Interior, 109.
24. Saline Water Conversion Report 1969-1970, Office of Saline Water, Department of the Interior, 99.
25. F. Klunker and P. Arriot, *AIChE Symp. Series*, **68**, 340 (1971).
26. T. A. Orofino, Office of Saline Water Res. Dev. Prog. Rept. No. 549 (1970).
27 E. A. Meinecke and D. V. Mehta, *Desalination*, **10**, 341 (1972).
28. D. V. Mehta and E. A. Meinecke, *Desalination*, **10**, 353 (1972).
29. D. V. Mehta and E. A. Meinecke, *Desalination*, **10**, 369 (1972).
30. S. Manjikian, S. Loeb, and J. W. McCutchan, *Proc. 1st. Int. Desalination Symp.*, paper SWD/12, Washington, D.C. (1965).
31. E. Drioli, F. Alfani and G. Iorio, *4th International Symposium on Fresh Water from the Sea* **4**, 115 (1973).
32. R. Gröpl and W. Pusch, *Desalination*, **8**, 277 (1970).
33. H. K. Lonsdale, U. Merten, R. L. Riley, and K. D. Vos, Reverse Osmosis for water Desalination, Annual Report April 16, 1964–April 15, 1965. Office of Saline Water, Research and Development Progress Report No. 150.
34. R. E. Kesting, in *Permeability of Plastic Films and Coatings to Gases, Vapors and Liquids*, H. B. Hopfenberg, Ed. Plenum Press, New York and London, p. 389 (1974).
35. C. Noel and L. Monnerie, *Proc. Fifth Internatl. Symposium on Fresh Water from the Sea*, Alghero, May 16–20, 1976, A. and E. Delyannis, Eds., published by the editors, Athens, 1976, Vol. 4, p. 125.
36. W. Pusch, *Proc. Symposium on Structure of Water and Aqueous Solutions*, Marburg, July 19–28, 1973, W. Luck, Ed, Verlag Chemie/Physik Verlag, Weinheim, pp. 541–562 (1974).