# A Mechanical Model for the Deformational Behavior of the Polymeric Membranes Operating in Pressure-Driven Processes

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SYNOPSIS

A mechanical model consisting of three elements (elastic, viscoelastic, and plastic) is proposed to describe the deformational behavior of a polymeric membrane operating in a pressure-driven process. The changes in the membrane thickness are proposed to be calculated from the experimentally obtained flux data. The advantages of a mechanical model over the conventional method of hysteresis area measurement as the mechanical stability of the polymeric membranes are discussed. © 1992 John Wiley & Sons, Inc.

## INTRODUCTION

The fluid flux $J$ through a porous membrane in a pressure-driven process may be described by the Kozeny–Carman relationship (1)[1]:

$$J = \frac{K}{\mu} \frac{\beta^3}{(1-\beta)^2} \frac{\Delta P}{l} \tag{1}$$

where $k$ is the Kozeny–Carman constant, $m^2$; $\mu$, the fluid viscosity, Pa s; $\beta$, the membrane porosity; $l$, the membrane thickness, $m$; and $\Delta P$, the transmembrane pressure, Pa.

Equation (1) shows that the fluid flux increases linearly with the increase in the transmembrane pressure. But, practically, the relationship flux vs. pressure almost always shows a negative deviation from linearity (Fig. 1)—an effect attributed to the deformation undergone by the membrane subjected to pressure. As a result of the deformation, the membrane thickness decreases, but, simultaneously, the membrane becomes compact, i.e., the porosity decreases. If the membrane had not undergone any deformation, the relationship flux vs. pressure would have followed the curve 0A (Fig. 1).

In a pressure-driven process, the polymeric membrane undergoes elastic, viscoelastic, as well as plastic deformations. Therefore, a mechanical model consisting of three elements might describe the deformational behavior of a polymeric membrane operating in a pressure-driven process (Fig. 2). Kurokawa et al.[2] observed the deformational behavior of a cellulose acetate membrane subjected to mechanical stress. The authors proposed a mechanical model consisting of two elements (elastic and viscoelastic) to describe the observed deformational behavior. Based on the model, they made an attempt to explain the flux-decline through the membrane under operating conditions. In our previous papers,[3,4] we discussed that the deformational behavior of a membrane subjected to mechanical stress is not the same as that of an operating one. Under operational conditions, there is a flux through the membrane and the permeating fluid exerts pressure on the pore walls counteracting the membrane compaction. Thus, the deformation of a membrane in a pressure-driven process is a resultant effect of the compressive pressure applied on the surface and that exerted on the pore walls by the permeating fluid. The membrane property may also be changed by the possible plasticizing effect of the permeating fluid. On the other hand, it is almost impossible to arrange direct observation on the membrane deformation under operational conditions. In the present paper, a mechanical model has been proposed to describe the deformational behavior of a polymeric membrane operating in a pressure-driven process. The changes in the membrane thickness are pro-

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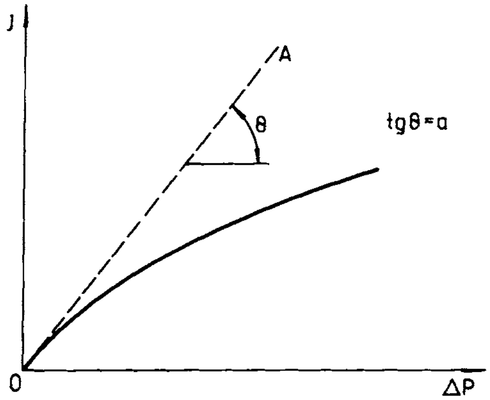


**Figure 1** Flux $J$ vs. pressure $\Delta P$ curve.

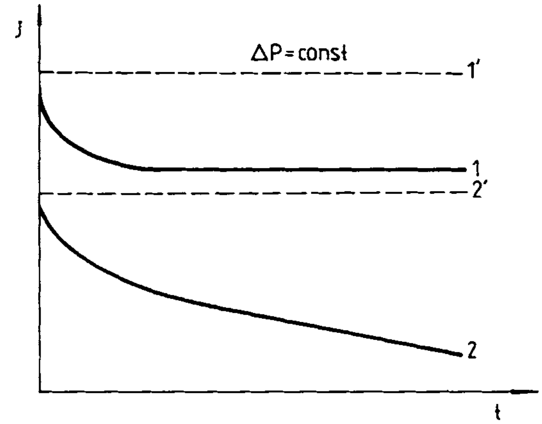


**Figure 3** Flux $J$ vs. operational time $t$ at a constant pressure: (1) a membrane with elastic and viscoelastic deformations only; (2) a membrane with elastic, viscoelastic, as well as plastic deformations.

posed to be calculated from the experimentally obtained flux data.

## THEORY

If the flux through the membrane is known, the change in the membrane thickness may be calculated with some approximation. Usually, the flux vs. operational period at a constant pressure is as shown in Figure 3.[5] If the membrane undergoes only elastic and viscoelastic deformations, the flux gradually decreases up to a certain value and then remains constant with the operational time (curve 1, Fig. 3). However, if the membrane undergoes the three types of deformations, the flux monotonously decreases with time (curve 2, Fig. 3). The discrete lines 1′ and 2′ show the expected constant fluxes, provided the membranes do not undergo any type of deformation. The constant values of curves 1 and 2 may be obtained from the curve 0A (Fig. 1) at the corresponding transmembrane pressure $\Delta P$. The curves 1′ and 2′ show higher flux than those of curves 1 and 2, respectively, even at $t = 0$, owing to the fact that at the moment of pressurization the membranes undergo at least some elastic deformation, which also brings about some compaction.

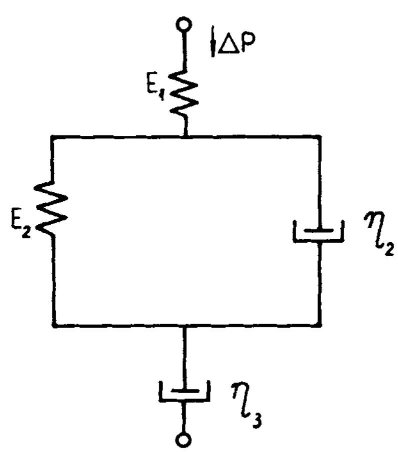


**Figure 2** A mechanical model consisting of three elements: $E_i$, moduli of elasticity; $\eta_i$, viscosity.

Assuming that the membrane material is practically uncompressible and the compaction is performed only at the expense of the pore volume, we have relation (2). Such an assumption is valid for soft porous substances[6]:

$$S(1-\beta_0)l_0 = S(1-\beta)l \qquad (2)$$

where $S$ is the membrane area, $m^2$; $\beta_0$ and $\beta$ are, respectively, the initial porosity and that at time $t$; $l_0$ and $l$ are, respectively, the initial membrane thickness, $m$, and that at time $t$. Combining eqs. (1) and (2), we have

$$l^3 - \left(J\frac{\mu d^2}{k\Delta P} + 3d\right)l^2 + 3d^2 l - d^3 = 0 \qquad (3)$$

with $d = (1-\beta_0)l_0$.

For the membranes with high porosity, the fourth term in eq. (3) may be neglected, and after a rearrangement, it is converted into a quadratic equation [eq. (4)]. We may accept that solution of eq. (4) for which $\beta$ has physical significance ($0 < \beta < \beta_0$):

$$l^2 - \left(J\frac{\mu d^2}{k\Delta P} + 3d\right)l + 3d^2 = 0 \qquad (4)$$

$\beta_0$ and $l_0$ are determined by a known method and the value of $\mu$ is collected from the reference books. The value of the Kozeny–Carman constant may be determined from the flux vs. pressure relationship (Fig. 1). As the curve 0A is expected for the undeformable membrane, the corresponding slope $a$ is given by eq. (5):

$$a = \frac{k}{\mu} \frac{\beta_0^3}{(1-\beta_0)^2 l_0} \tag{5}$$

or

$$k = a\mu \cdot \frac{(1-\beta_0)^2 l_0}{\beta_0^3} \tag{5a}$$

Now, knowing the value of $J$ at any time $t$ (from Fig. 3), the corresponding membrane thickness may be calculated from eq. (4). The calculated value of $l_0'$ at $t = 0$ will be different from the initial membrane thickness $l_0$ as the initial flux is measured after the membrane has already undergone at least some elastic deformation.

The membrane deformation $\epsilon$ is defined as follows:

$$\epsilon = l/l_0 - 1 \tag{6}$$

The relationship of deformation vs. operational period $t$ (corresponding to Fig. 3) would be as shown in Figure 4. These values of deformations may be used to determine the parameter of the mechanical model in Figure 2.

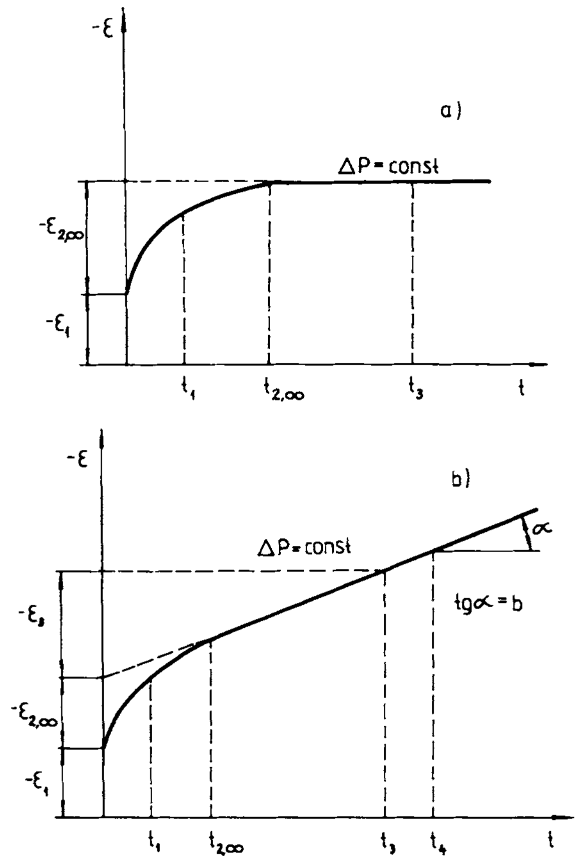


**Figure 4** Total deformation $\epsilon$ as a function of the operational time $t$ at a constant pressure: (a) a membrane with elastic and viscoelastic deformations only; (b) a membrane with elastic, viscoelastic, as well as plastic deformations.

## DETERMINATION OF THE PARAMETERS $E_1$, $E_2$, $\eta_2$, AND $\eta_3$ [FROM FIG. 4(b)]

The total deformation $\epsilon$ of the proposed model is the sum of the elastic deformation, $\epsilon_1$, viscoelastic deformation, $\epsilon_2$, and plastic deformation, $\epsilon_3$:

$$\epsilon = -\Delta P\{1/E_1 + 1[1 - \exp(-E_2 t/\eta_2)]/E_2 + t/\eta_3\} \tag{7}$$

with

$$\epsilon_1 = -\Delta P/E_1 \tag{7a}$$

$$\epsilon_2 = -\Delta P[1 - \exp(-E_2 t/\eta_2)]/E_2 \tag{7b}$$

$$\epsilon_3 = -\Delta P t/\eta_3 \tag{7c}$$

where $\Delta P$ is the applied pressure, and $t$, the operational period.

For eqs. (7a)–(7c), we have

$$E_1 = -\Delta P/\epsilon_1$$

$$\epsilon_{2,\infty} = -\Delta P/E_2 \tag{8a}$$

or

$$E_2 = -\Delta P/\epsilon_{2,\infty} \tag{8b}$$

where $\epsilon_{2,\infty}$ is the viscoelastic deformation for the time $t \to \infty$.

Let $b = -\Delta P/\eta_3$ = slope of the linear portion of the curve $\epsilon = f(t)$; then,

$$\eta_3 = -\Delta P/b \tag{8c}$$

Now, for $0 < t < t_{2,\infty}$ (where $t_{2,\infty}$ indicates the minimum time necessary for the complete development of viscoelastic deformation):

$$\epsilon_2 = \epsilon - \epsilon_1 - \epsilon_3$$

or

$$\epsilon_2 = \epsilon + \Delta P/E_1 + \Delta Pt/\eta_3 \qquad (9)$$

From eqs. (7b) and (8b), we have

$$\epsilon_{2,\infty} - \epsilon_2 = \exp(-E_2t/\eta_2) \qquad (9a)$$

or

$$\ln(\epsilon_{2,\infty} - \epsilon_2) = -E_2t/\eta_2 \qquad (9b)$$

The value of the ratio $-E_2/\eta_2$ may be obtained from the slope of the curve $\ln(\epsilon_{2,\infty} - \epsilon_2)$ vs. $t$, from where $\eta_2$ may be calculated.

Thus, all the parameters of the proposed model may be calculated. If no plastic deformation is observed, the third term in eq. (7) vanishes and the remaining parameters are calculated by the same procedure from the data in Figure 4(a).

Some authors[7] propose the hysteresis area bounded by the curves flux vs. pressure as a measure for the mechanical stability of the polymeric membrane. The pressure is increased and decreased stepwise ($P_1, P_2, \ldots, P_{n-1}, P_n, \ldots, P_2, P_1$) and the corresponding flux is measured after a predetermined period of time. It may be easily shown from eq. (7) that depending on the chosen operational time the deformations will be different, resulting in different fluxes at the same pressure. If the membrane undergoes only elastic and viscoelastic deformations and the experimenter chooses a period of $t_3 > t_{2,\infty}$ [see Fig. 4(a)] for each flux measurement, then no hysteresis area will be observed [curve 1, Fig. 5(a)], because the time $t_3$ is sufficiently high for the complete development as well as for the recovery of the viscoelastic deformation during, respectively, the direct and reverse courses. However, if the experimenter chooses a period of $t_1 < t_{2,\infty}$ [see Fig. 4(a)] for each flux measurement, then a hysteresis area will be observed [curve 2, Fig. 5(a)], because the time $t_1$ is not sufficient for the complete development as well as the recovery of the viscoelastic deformation during, respectively, the direct and reverse courses.

Most fatal is the case when the membrane undergoes the three types of deformations. If the times for each experiment are chosen to be $t_1$, $t_3$, and $t_4$ as shown in Figure 4(b), then the corresponding flux vs. the pressure relationship will be described by curves 1, 2, and 3 [Fig. 5(b)] with the increasing order of bounded areas. This is because for the time $t_1 < t_{2,\infty}$ the membrane is not in a position to develop

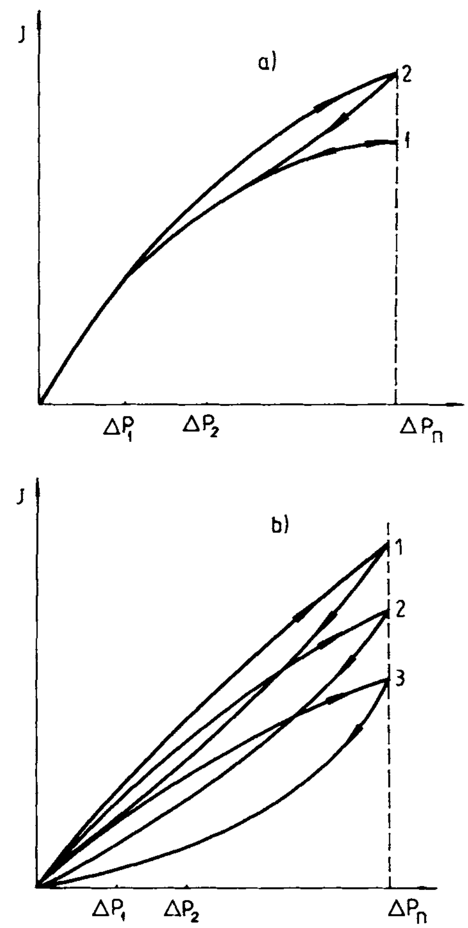


**Figure 5** Flux $J$ vs. pressure $\Delta P$ in direct and reverse courses: (a) a membrane with elastic and viscoelastic deformations only; (b) a membrane with elastic, viscoelastic, as well as plastic deformations. The meanings of 1, 2, and 3 are explained in the text.

equilibrium viscoelastic deformation in the direct course, and at the same time, the operational period is low enough to develop significant plastic deformation. For that reason, the hysteresis area bounded by the curves of flux vs. pressure is small. On the other hand, as the plastic deformation increases linearly with time, the higher the chosen operational time, the higher the hysteresis area. For that reason, the chosen operational periods $t_1 < t_3 < t_4$ correspond to the hysteresis areas in the same sequence. Thus, the same membrane, depending on the experimenter, will show different mechanical stability.

## CONCLUSION

On the basis of the above discussions, it may be concluded that the hysteresis area bounded by the curves of flux vs. pressure in the direct and reverse courses depends to a great extent on the chosen operational period and cannot be accepted as a true measure for the mechanical stability of the polymeric membranes operating in pressure-driven processes. It does not offer any insight into the membrane deformation process. It is mainly a measure for the plastic deformation only. On the other hand, the proposed mechanical model describes all types of deformations and its parameters are independent of the chosen operational period of investigation. The proposed method for the determination of the parameters of the model provides an opportunity to observe the changes in the membrane thicknesses. Therefore, it is much better to characterize the deformational behavior of a polymeric membrane by a mechanical model.

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