Response of Filled Polyethylene Membranes to the Changes in the Environmental Conditions

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SYNOPSIS

The environmentally sensitive properties of polyethylene membranes filled with SiO_2 have been studied. The porous characteristics of the membranes is investigated with the aqueous solutions of pH 1–8 and aqueous electrolyte solutions with concentrations of 10^{-5}–10^{-1} mol/L. The experimental results are explained by the concept of coagulation-swelling behavior of the filler under different environmental conditions. The relaxation of membrane resistance with a change in pH is also studied.

INTRODUCTION

The role of membranes in technological processes continuously increases. Now membranes cover a variety of the fields of applications. The major field of application of the polymeric membranes is the filtration process. The basic requirement to the membranes applicable in the filtration process is their stability to the changes in environmental conditions (e.g., change in pH, ionic strength of the medium, composition of the permeating fluid, etc.). Such an ability is of utmost importance to carry out effectively filtration process on an industrial scale. In recent years, much attention has been paid to the development of environmentally sensitive membranes. These membranes can mimic biological membranes and are the potential candidates in the controlled-release drug delivery devices.[1-3]

Most of the polymeric environmentally sensitive membranes reported in the past act on the principle of chemical valves. Such membranes usually are based on acrylic or methacrylic acid-grafted polymers. The conformation of the grafted polymer changes depending on the environmental conditions, and thus the pores expand or contract resulting in a variable permeability.[4,5] In this work we have studied the permeability of highly filled polyethylene membranes depending on the changes in environmental conditions. The variable permeability of this type of membrane lies on a completely different principle. It is caused by the variable membrane resistance to the permeating fluid. Depending on the nature and composition of the permeating fluid, a redistribution of the filler particles (SiO_2) in the membrane matrix takes place and thus causes different contact surface between the permeating fluid and the filler particles resulting in different membrane resistances.

THEORETICAL

Flux through a membrane in the pressure-driven process obeys the following relationship:

$$J = \frac{\Delta P}{R\mu} \qquad (1)$$

where J is the flux (m^3/m^2 s), ΔP is the transmembrane pressure difference (Pa), μ is the viscosity (Pa·s) and R is the membrane resistance (m^{-1}).

To eliminate the influence of the fluid viscosity, a porosity parameter $\beta = J\mu$ may be introduced. For an environmentally stable membrane, the membrane resistance is constant. Therefore, at ΔP = constant, the porosity parameter remains constant.

The membrane resistance is a function of size, shape, and tortuosity of the pores. The variable resistance of the membranes in the present investigation is due to the redistribution of the silica particles in the membrane matrix depending on the change in the environmental conditions. The concept of coagulation-swelling of silica may be used to interpret the variable membrane resistances. Coagulation of colloidal silica is a result of the interaction of van der Waals forces acting between two particles at the moment of contact. There exist two factors tending to prevent the coagulation of colloidal silica[6]:

1. Hydration of colloid surfaces by the formation of water layer connected to the surface groups $-Si-OH$ by hydrogen bonds.
2. Electrical repulsive forces due to the negative charges generated on the particle surfaces at a pH value higher than 3.5.

On the other hand, the presence of electrolytes in the solution enhances the coagulation. Allen et al.[7] observed that the cation of the coagulating agent takes part in ion exchange with the proton of the silanol groups. The authors assumed that due to the adsorption of cations on the silica surface, the number of silanol groups capable of forming hydrogen bonds with water decreases and the colloid surface becomes dehydrated. Such a hydrophobization of the colloid surface leads to the coagulation of the particles. Regulating the pH and electrolyte concentration in the solution, the coagulation-swelling properties of silica may be regulated. The probable influence of the coagulation-swelling process of silica in the membrane matrix resulting in variable membrane resistances is illustrated schematically in Figure 1 (for simplicity of the scheme, the polymer particles are not shown in the figure). At about pH = 2, the filler particles are almost uncharged. Although the filler particles in contact with the permeating water are hydrated (indicated by a second perimeter around the filler particles), they are in a very compact state resulting in a very small contact surface between the permeating fluid and the pore wall, and thus low membrane resistance [Fig. 1(b)]. Figure 1(a) shows that at pH = 2 in the presence of an electrolyte, the filler particles are not only uncharged but also in a dehydrated form due to the osmotic effect. Thus the pore size in Figure 1(a) is larger than that in Figure 1(b). At pH = 5, the surface of the filler particles are charged negatively. The charged particles experiences a force of repulsion
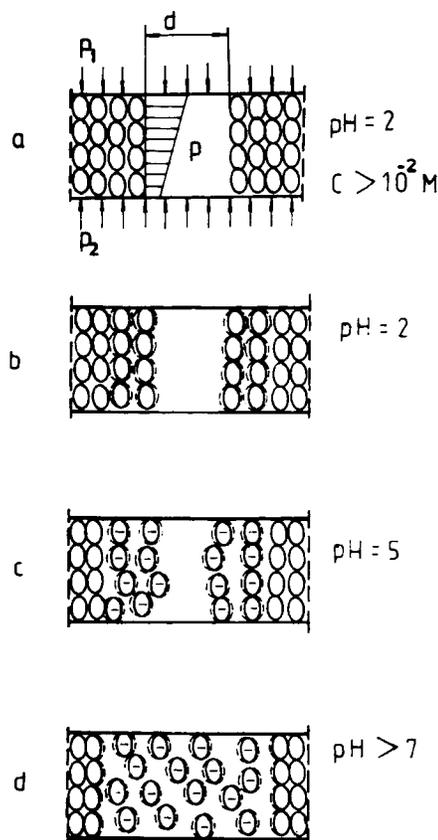
Figure 1 A schematic representation of the distribution of filler particles in the membrane matrix depending on the nature and composition of the permeating fluid. (a) pH = 2 and electrolyte concentration $C > 10^{-2}M$; (b) pH = 2; (c) pH = 5; and (d) pH = 7.

from other charged particles and at the same time, the permeating fluid exert a pressure on the particles when passing through the membrane. Under a certain condition, all the forces acting on the particles are in equilibrium. But the filler particles are much more dispersed at pH = 5 as compared with those at pH = 2. Therefore, the contact surface between the permeating fluid and the filler particles increases leading to higher membrane resistance [Fig. 1(c)]. In the same way, at pH = 7, the filler particles are much more dispersed than those at pH = 5, and corresponding membrane resistance is higher due to the higher contact surface and tortuosity of the chanel [Fig. 1(d)]. Thus with an increase in pH, the membrane resistance increases.

Equation for Relaxation Phenomenon of Membrane Resistance

Let the pH of the permeating fluid be increased with unity at time $t = 0$. The value of membrane resis-

tance $R(t)$ increases rapidly just after the pH change and then increases gradually up to a stationary state. Here, we consider the deviation of resistance at time t from the value at the stationary state $R(\infty)$. $R(\infty)$ corresponds to the state at which the forces of repulsion and those exerted by the permeating fluid balance each other:

$$\Delta R(t) = R(\infty) - R(t) \qquad (2)$$

The rate of variation of the deviation $\Delta R(t)$ with time is considered to be proportional to the magnitude of deviation

$$\frac{dR}{dt} = \frac{\Delta R(t)}{\tau} \qquad (3)$$

where τ is the time constant of the relaxation. From Eqs. (2) and (3), we obtain

$$\Delta R(t) = k \exp\left(\frac{-t}{\tau}\right) \qquad (4)$$

where preexponential factor k is equal to $R(\infty) - R(0)$.

The value of τ is obtained from the slope of the curve $\ln[R(\infty) - R(t)]$ versus t. Such a method for the investigation of the relaxation of grafted polymeric membrane under pressure gradient was reported by other authors during the measurement of streaming potential.[8,9]

EXPERIMENTAL

A polymeric composition consisting of high-density polyethylene (Bulen V-01, melt index 3.1 g/10 min), filler (Vulcasil KS-404, Degussa, Germany) and oil OK-1 (petroleum fraction 340–500°C, Neftochim, Bulgaria) in a weight ratio 2 : 5 : 8 was prepared with the help of an extruder. Flat sheets with a thickness of 0.7 mm were prepared from the compression-molded composition. Oil was extracted from the sheets with tetrachloroethylene. The films were dried and then subjected to thermomechanical deformation to form the porous structure. Details about the preparation procedure are described in Refs. 10 and 11.

The pH of the investigated solution was maintained by adding HCl or NaOH. The inorganic salts were used as received without further purification.

Flux through the membranes was determined with a laboratory cell with a membrane area of 12.56 cm^2 and at a transmembrane pressure 0.1 MPa.

RESULTS AND DISCUSSION

The porosity parameter β (defined as flux multiplied by viscosity) of the filled membranes as a function of the pH of the permeating water is represented in Figure 2. As it was expected, the concentration of the negative charges on the filler surfaces was negligible in the pH range 1–3, and they were in the form of large aggregates resulting in very low membrane resistance and correspondingly high porosity parameter. Within the pH range 3–5, gradual decrease in porosity parameter is in good agreement with the fact that at a pH > 3.5, the filler surfaces become partially negatively charged[6] leading to more dispersion throughout the membrane matrix and hence higher resistance and lower porosity parameter. A sharp decrease of porosity parameter is observed in the pH range 5–8. This phenomenon may be explained by the fact that at pH > 6, most of the silanol groups on the surface are charged negatively. It should be noted that within the pH range 1–5, the porosity parameter is reversible. At pH = 7, within the period of experiment (about 2.5 h), the porosity
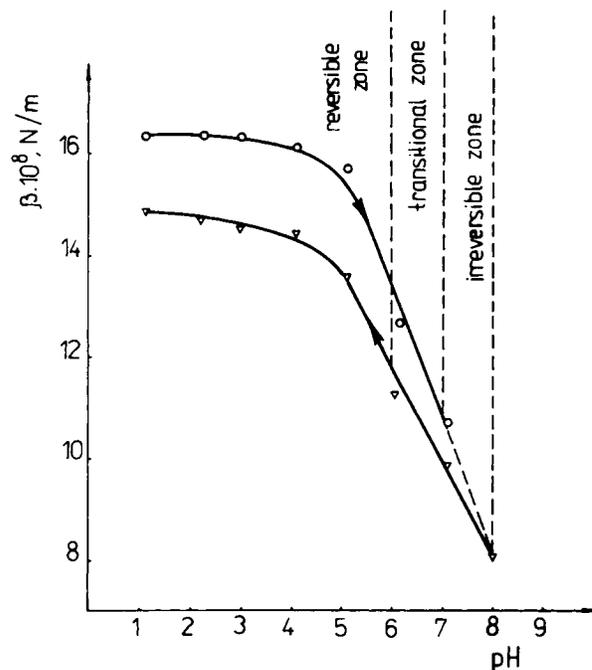
Figure 2 Porosity parameter β of the filled polyethylene membrane as a function of pH of the permeating fluid.

parameter was reversible. But an independent experiment for 8 h at pH = 7 showed that the porosity parameter lowers slightly from the stable value obtained at the experiment for 2.5 h. At pH = 8, porosity parameter decreases continuously. The value of porosity parameter at pH = 8 in Figure 2 was registered at t = 70 min. This value is connected with that of the porosity parameter at pH = 7 with discrete line, as the latter was a continuously decreasing function of time. All other values of β were registered after the stabilization of flux. The continuously decreasing value of β at pH = 8 may be explained with the assumption that a process of destruction of the —Si—O—Si— bonds starts in the alkaline medium. Thus along with the increase in the charge concentration on the filler surfaces, the large particles are fractioned into small ones resulting in higher contact surface and lower flux. Most probably due to the fraction of the large colloidal particles, the initial values are not recovered in the reverse course. Another possible cause for the irreversibility is that the distribution of the filler particles is not completely repeatable in the reverse course. It may be assumed from Figure 1 that the distribution of the filler particles at a change of pH from 7 to 2 is not necessarily the same as in Figure 1(b) within a short interval of time. Observing the relationship porosity parameter versus pH, the pH range is divided into three zones as pH = 1-6, 6-7, and > 7, respectively, as reversible zone, transitional zone, and irreversible zone.

The membrane resistance R as a function of operational time t is represented in Figure 3(a). The value of membrane resistance was calculated by Eq. (1). The pH 5-6 corresponds to the change of R with time at the change of pH from 5 to 6. The value at equilibrium corresponds to the porosity parameter in Figure 2. At the change of pH from 7 to 8, the membrane resistance monotonously increases and no equilibrium value was attained within the duration of investigation. The relaxation times at pH 5-6 and 6-7 were determined from the slope of the curves $\ln[R(\infty) - R(t)]$ versus t [Fig. 3(b)] and were found to be 15 and 26 min, respectively. At the change of pH from 4 to 5, the stabilization of the flux occurred within 10 min, and it was impossible to determine the relaxation time. Most probably the relaxation time depends on the initial membrane porosity, filler concentration, applied pressure gradients, etc. Therefore, the determined relaxation times should be considered a qualitative measure of increasing tendency of relaxation time with the increase in pH value.
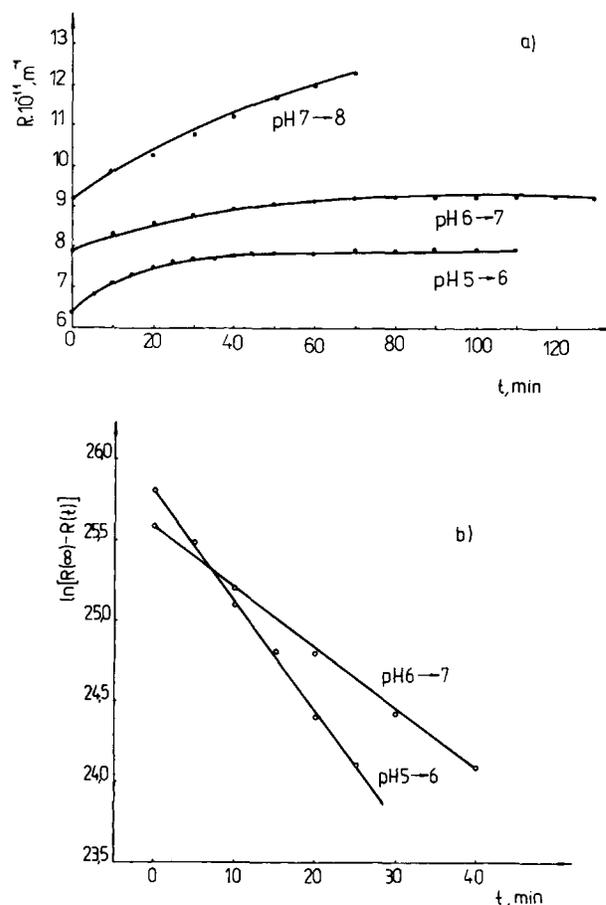
Figure 3   (a) Membrane resistance R as a function of operational time t. (b) $\ln[R(\infty) - R(t)]$ vs. t plot. The corresponding data are taken from Figure 3(a).

The influence of electrolyte concentration on the porosity parameter at constant pH is represented in Figure 4(a). The membranes were pretreated at pH = 8 for 1 h and then investigated. The electrolytes were chosen arbitrarily. The only criterion for the selection was a set of cations with different valence. The electrolytes under investigation were KCl, $CuSO_4$, $CaCl_2$, and $Cr(NO_3)_3$. As seen from the figure, the porosity parameter increases with an increase in the electrolyte concentrations. The effect of the electrolyte solutions follows the order KCl < $CuSO_4$ < $CaCl_2$. The coagulation process of colloidal silica under the action of electrolytes is explained in details by Iler.[6] The electrokinetic potential decreases as the electrolytes are added to the silica sol. At a certain moment, the charges on the silica surface reach a certain value that the van der Waals forces predominate over the electrolytic repulsion to form the aggregates.[12] Another mecha-

nism of coagulation is the formation of coordination bridge between the colloidal particles under the action of coagulating agents. Irrespective of the mechanism of coagulation, the effect for the membrane is the improvement of porosity parameter.

Figure 4(b) shows the influence of Cr^{3+} concentrations on the porosity parameters without adjustment of pH. Cr^{3+} ions form different complexes with OH^- ions in water, and the pH of the solution gradually decreases with the increase in the Cr^{3+} concentrations.[13] The effect of Cr^{3+} is a very interesting phenomenon. The pH of the solution under investigation varies from 4.8 to 2.7. The monotonously increasing character of the porosity parameter with the increase in Cr^{3+} concentration apparently is in disagreement with the porosity parameter versus pH relationship described in Figure 2. The latter shows

Figure 5   Improvement in porosity parameter $\Delta\beta$ (defined as $\Delta\beta = \beta_{lgc=-1} - \beta_{lgc=-5}$) as a function of pH.

Figure 4   (a) Porosity parameter β of the filled polyethylene membrane as a function of electrolyte concentration C of the permeating fluid at pH = 6. (b) Porosity parameter β of the filled polyethylene membrane as a function of Cr^{3+} concentration C of the permeating fluid without adjustment of pH.

that within the pH range 1.2–4, the porosity parameter is almost constant due to the negligible amount of charges on the filler surface. Dumont et al.[14] described that the colloidal silica is a very complex system and exhibits very high stability even at the point of zero surface charge. Depasse et al.[15] reported that the presence of mono-water layer between the surfaces of colloidal silica (with size < 25 nm) is sufficient enough to screen the dispersion forces and thus to prevent aggregation. Harding[16] also found that at pH = 2, under the action of very low concentration of electrolytes, the colloidal silica (with a size < 50 nm) does not coagulate due to the presence of the hydrated layer. Therefore the positive effect of $Cr(NO_3)_3$ probably should be attributed not only to the lowering of pH but also to the osmotic effect. At the same solute concentration, the osmotic pressure follows the order $Cr(NO_3)_3 > CaCl_2 > KCl$. Thus with the increase in $Cr(NO_3)_3$ concentration, the hydrated layer on the filler surface is destroyed leading to larger aggregates. Therefore, the degree of aggregation and corresponding porosity parameter at pH = 2 in the absence of inorganic salts cannot be considered as the maximum possible values. At lower pH, the osmotic effect of the solution is an important factor to determine the porosity parameter.

The improvement of porosity parameter for a change of electrolyte concentration from 10^{-5} to 10^{-1} mol/l as a function of pH is represented in Figure 5. It is obvious from the figure that the improvement is much more pronounced at the higher values of pH. This phenomenon may be explained by the fact that at lower pH the improvement is attributed only

to the osmotic effect destroying the hydrated layer of the filler surface. But at high pH, the improvement is due to the osmotic effect and lowering of the electrokinetic potential of the filler surface as well.

CONCLUSION

On the basis of the performed experiment, it may be concluded that polyethylene membrane filled with SiO_2 changes its porous characteristics depending on the composition of the solution permeating through it. It was found that with an increase in the pH of the solution, the porosity parameter decreases. Within the pH range 1–6, the porosity parameter was found to be changeable reversibly. At a constant pH, with an increase in the salt concentration in the permeating fluid, the porosity parameter increases. This effect was more pronounced at higher values of pH. Polyvalent cations were found to be more effective than univalent one.

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