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APPLICATION OF CHRONOAMPEROMETRY TO EVALUATION OF MEMBRANE POROSITY

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ABSTRACT

Conductance and electric permittivity of Epidian-5 epoxy resin membranes modified with benzene have been determined by the chronoamperometric method. In addition, membrane porosity was evaluated. The membrane porosity was found to undergo different changes in two benzene concentration ranges: in the 0–20% (wt) range the porosity decreases, in the 20–40% (wt) range it increases. The differences in porosity were found to be associated with structural differences of the membrane-induced benzene. Chronoamperometry was found to be an appropriate technique for the evaluation of membrane porosity. The proposed method allows for a convenient analysis of porosity variations in conditions matching the real conditions of membrane work.

INTRODUCTION

Studies of epoxy-resin-based membranes have drawn significant research interest in recent years. However, there exist severe drawbacks in the use of these materials. In particular, their permeability to metal ions is too low. However, their permeability to hydrogen ions is good [1–5]. Such membranes laminated with glass fibers are produced under the trade name of Selemion and are used in dialysis and electrodialysis processes to isolate acids and to separate salt and acid mixtures, e.g., H_2SO_4 + $MeSO_4$ [1, 2]. Among major advantages of such membranes is their relatively easy fabrication and their high mechanical resistance. The poor reproducibility of their performance constitutes, however, a significant drawback.

Studies of diluent (xylene, dibutyl phthalate, tetrachloroethylene) effect on the structure and properties of epoxy resins [6, 7] showed that small amounts of the diluent, 4–11% (wt), induce an increase in the degree of resin crosslinking relative to the undiluted resin, while a decrease in the degree of resin crosslinking was observed at higher diluent concentrations, causing in turn an increase in the volume of voids in the polymer. The results of those studies suggested that it was possible to obtain increased-porosity membranes by adding suitable amount of diluent to the epoxy resin.

The main goal of this research was to obtain epoxy resin Epidian-5 (E-5) membranes and to evaluate the diluent effect on their porosity. Benzene was used as the diluent because of its good miscibility with the epoxy resin.

Porosity is an important parameter governing the transport properties of membranes [8]. It is characterized by the pore mean size, pore size distribution, number of pores per volume unit, and pore shape.

The porous structure of the membranes can be characterized by several methods [9–15]. Among them, the chronoamperometric method has been applied to evaluate the porosity since it can be applied in real membrane working conditions. In addition, it is rapid and unsophisticated. An aqueous solution of NaCl was used as the electrolyte because both ions are of comparable size and neutral toward the membrane. Evaluation of the applicability of chronoamperometry to membrane porosity characterization was also one of the purposes of this research.

EXPERIMENTAL

Preparation of Membranes

The membranes were obtained from the Epidian-5 epoxy resin produced in Sarzyna, Poland (Zakłady Chemiczne Sarzyna); triethylenetetramine was used as the hardener. Each time the resin and hardener mixture was deaerated in a vacuum dryer at 45°C and about 90 kPa pressure for 10–15 minutes in order to remove air bubbles. In the cases of benzene-modified membrane fabrication, benzene was added to the deaerated mixture and the resulting mixture was deaerated again in a benzene atmosphere. The deaeration conditions (temperature 45°C, pressure ~40 kPa, duration 5 minutes) were determined experimentally. The prepared mixtures were then placed between two glass plates coated with polyethylene foil. During hardening the plates were subjected for 24 hours to a constant 0.5 to 2.5 N/cm^2 load (depending on the amount of benzene in the resin). The membranes were then removed from the polyethylene foil.

The membrane thickness was measured with an A-52 ultrameter with ±3% accuracy; it was typically ~0.1 mm.

The formed membranes with added benzene were dried again at 45°C and about 90 kPa pressure to remove benzene from the pores. The removal of benzene was controlled by IR spectra (transmission scale) using the 3150–2950 cm^{-1} aromatic ring band as the probe. The band was considered to be the sum of benzene and epoxy resin aromatic ring absorptions; the intensity became constant after the benzene had been removed from the pores. The 3150–2600 cm^{-1} band intensity in the

IR spectra of the membranes with maximum benzene concentration, 40% (wt), became constant after 120 minutes deaeration in a vacuum dryer in the above given conditions (Spectrum 4, Fig. 1).

Studies of Membrane Morphology and Structure

Scanning electron microphotographs (SEM) of membrane cross sections were made using the electron scanning microscope JSM-51 (Jeol Japan).

The density of membranes was estimated by a flotation method in a benzene and carbon tetrachloride mixture [16, 17].

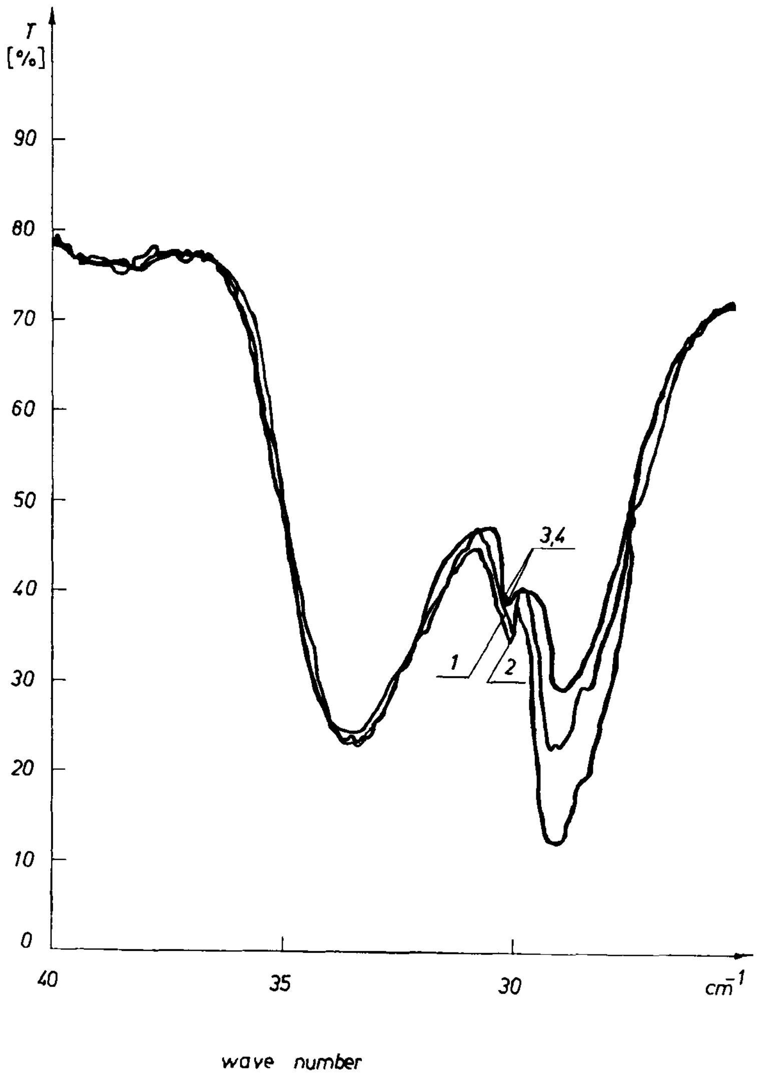


FIG. 1. IR spectra of the membrane with 40% (wt) benzene: (1) before deaeration, (2) after 15 minutes deaeration, (3) after 75 minutes deaeration, (4) after 120 minutes deaeration.

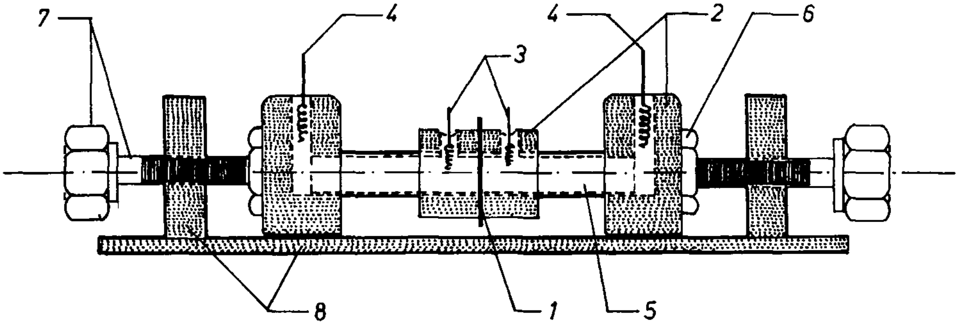


FIG. 2. The measuring vessel: (1) the membrane, (2) the Teflon containers supporting the membrane, (3) the silver–silver chloride electrodes, (4) platinum electrodes, (5) electrolyte-filled glass tube, (6) metal supports, (7) a screw, (8) a stand and a metal mount.

CHRONOAMPEROMETRIC MEASUREMENTS

The Measuring Apparatus

The measuring vessel used is presented in Fig. 2. The total volume of the two vessel chambers was 2.6 cm^3, the studied membrane surface area was 37.4 mm^2, and 0.1 M NaCl solution was the electrolyte. The measurements were carried out at 25°C.

The apparatus used in the studies is shown schematically in Fig. 3. It consisted of a four-electrode potentiostat based on operational amplifiers [18, 19]. The negative feedback potentiostat contained a differential system transmitting the potentials of no-current silver–silver chloride electrodes to the inverting input of the control amplifier. In addition, the potentiostat contained a solution resistance compensa-

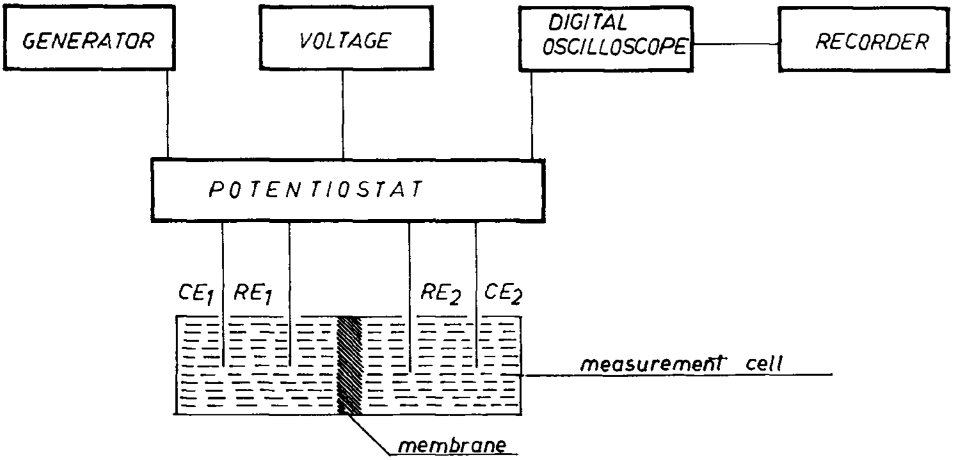


FIG. 3. The measuring apparatus diagram (the measuring vessel is filled with NaCl solution). RE_1, RE_2: the silver–silver chloride electrodes. CE_1, CE_2: the current electrodes.

tion circuit working in a positive feedback mode between the current–voltage output of the converter and the inverting input of the control amplifier. The current CE_1 and CE_2 electrodes were connected with the control amplifier output and directly to the inverting input of the current–voltage converter. The current passing through the vessel was measured as a voltage signal at the converter output. The potential difference between the measuring electrodes was fed through a high-resistance difference amplifier to the inverting input of the control amplifier. The circuit diagrams and the working principle of the four-electrode potentiostat used by us has been described in References 20 and 21. The voltage fed to the control amplifier of the potentiostat originated from a generator. It had a rectangular wave shape defined by the ΔE potential difference; the potential drops used ranged from 0.1 to 0.5 V. The electrolyte resistance was from 1.8 to 12.3 kΩ. Such values as the converter resistance (R_k), the time constant (τ), the frequency, and the potential drop were determined each time in order to optimize the measurements of membrane parameters. The time variations of the ΔE voltage applied to the membrane and of the I current are shown in Fig. 4. A digital-memory oscilloscope enabled us to show these characteristics on its screen. The time dependence of the current characterizing the membrane at constant ΔE was transmitted to the recorder which produced the Fig. 4 curves.

Equivalent Circuit of the Membrane

The equivalent circuit of the membrane used to interpret the experimental results is shown in Fig. 5. In electric measurements, the membranes were approxi-

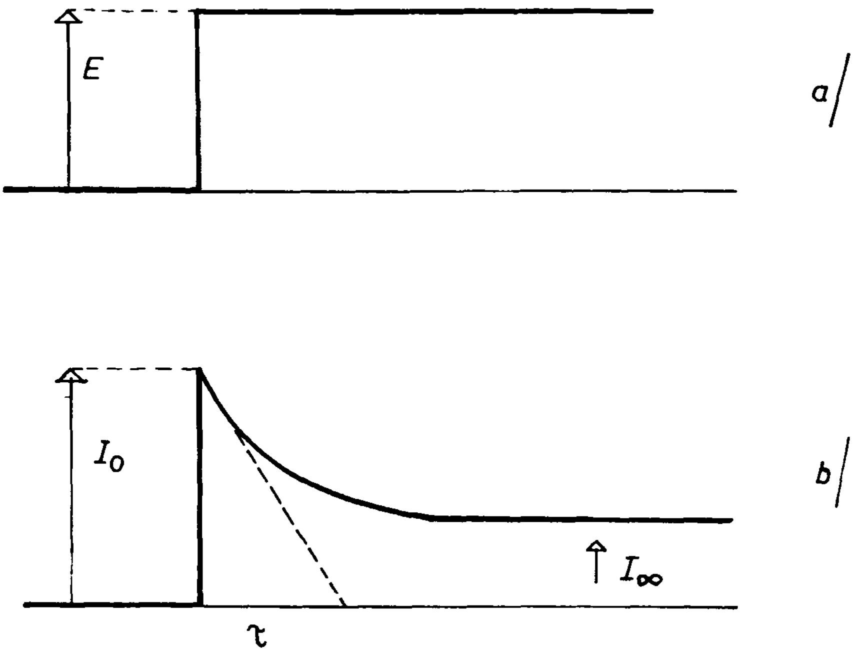


FIG. 4. The applied voltage signal (a) and the current response (b).

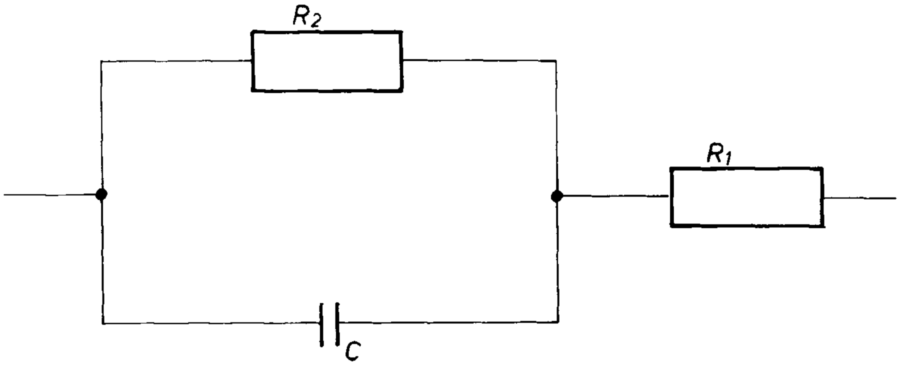


FIG. 5. The equivalent circuit of the membrane: R_1, the solution resistance; R_2, the membrane resistance; C, the membrane capacity.

mated by capacitors of capacitance C with a parallel resistance R_2. The presence of resistance R_2 is due to electrolyte conduction in the membrane pores. A R_1 resistance corresponding to the electrolyte resistance between the membrane and the indicator electrode tips is connected in series to the CR_2 system.

The capacitance C is determined by the membrane size and by the electric permittivity $\epsilon\epsilon_0$ of the hardened resin:

$$C = \epsilon\epsilon_0 S/d \tag{1}$$

where ϵ is the relative electric permittivity of the resin (relative to vacuum), ϵ_0 is the electric permittivity of the vacuum, S is the membrane surface area, and d is the membrane thickness. The R_2 resistance value is given by Ohm's second law: by the membrane size and by the specific conductance, κ, of the membrane with pores filled with the electrolyte solution:

$$R_2 = d/\kappa S \tag{2}$$

The principle of chronoamperometric determination of the accepted equivalent circuit elements is presented in Fig. 4. The current response to the voltage drop, E, applied to the system is presented in Fig. 4(b). The current I_0 at the moment of the application of voltage is given by the voltage drop and the resistance R_1 values:

$$I_0 = E/R_1 \tag{3}$$

The final current is

$$I_\infty = E/(R_1 + R_2) \tag{4}$$

The time constant, τ, is given by

$$\tau = R_1 C \tag{5}$$

Current-time characteristics were measured for membranes prepared from Epidian-5 with 0–40% (wt) benzene. The peak current depends to a great extent on the membrane capacity and on the current change frequency. Typical $I(t)$ characteristics of membranes containing 0 and 30% (wt) benzene are shown in Fig. 6. The

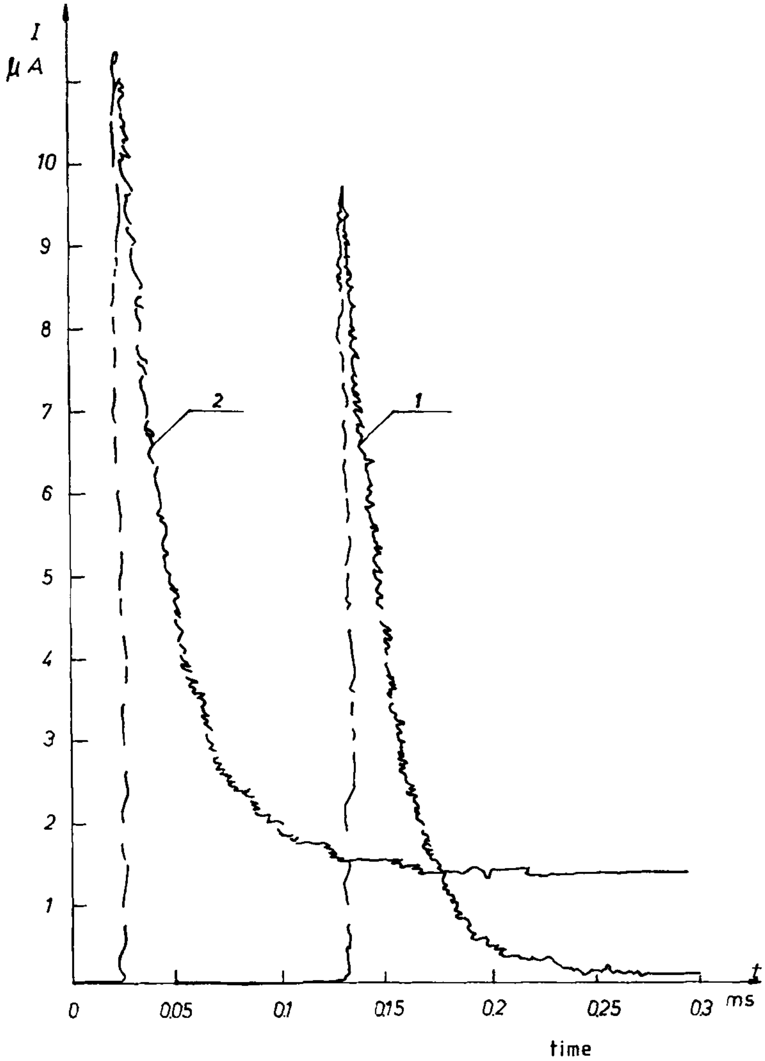


FIG. 6. The $I(t)$ characteristics of the membranes containing: (1) 0% (wt) benzene (ΔE = 0.5 V), (2) 30% (wt) benzene (ΔE = 0.119 V).

specific conductance and the coefficient of electric permittivity were determined from these characteristics.

RESULTS AND DISCUSSION

The Structure of Membranes

A representative picture of the porous membrane is shown in Fig. 7. Since the photograph was taken at an angle, the pores exhibit elliptic shape. Figures 8–10

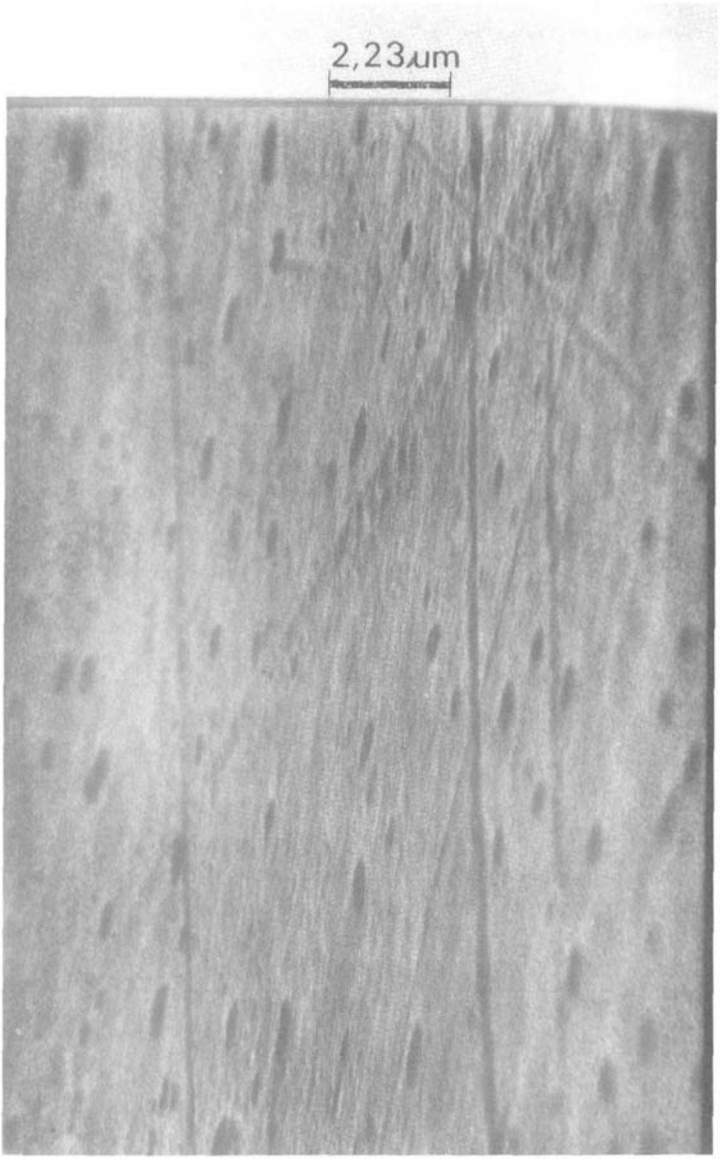


FIG. 7. A fragment of the porous membrane surface (magnification 9000 ×).

show the cross sections of membranes obtained from epoxy resins with various admixtures of benzene (magnifications of 300 × and 80 ×). In Fig. 11 a fragment of porous support is shown (magnification: 3000 ×). Density changes of tested membranes are shown in Fig. 12.

Analysis of Figs. 7–10 strongly indicates that the structure of membranes is not homogeneous. In membranes fabricated without benzene admixture, a thin

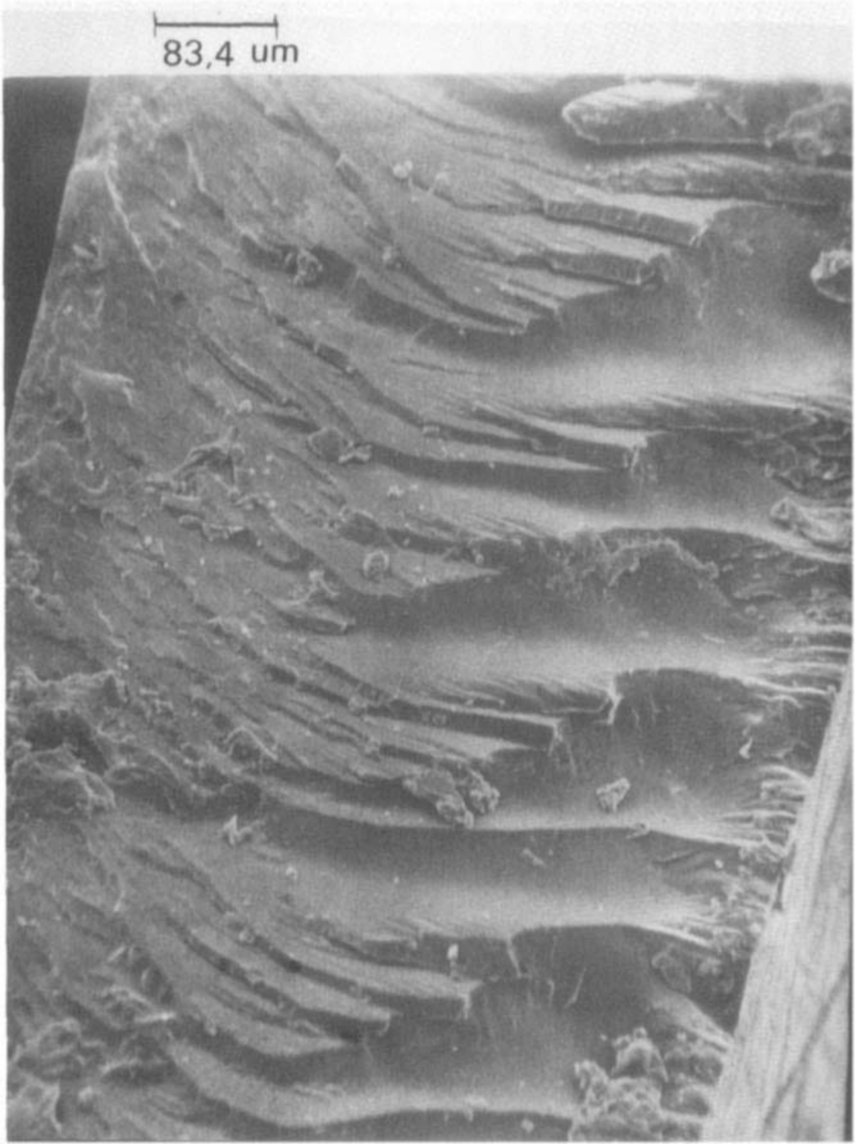


FIG. 8. SEM of the cross section of the epoxide resin membrane prepared without the addition of benzene (magnification 300 ×).

skin-type layer and a continuous nonporous layer can be distinguished. In membranes prepared with the use of benzene, a third, porous layer appears in addition to the skin layer and the continuous layer. The thickness of this additional layer increases with increasing benzene content. It is believed that the formation of layers is caused by sedimentation of resin aggregates created during the copolymerization reaction with the hardener. This reaction results in the effective removal of benzene,

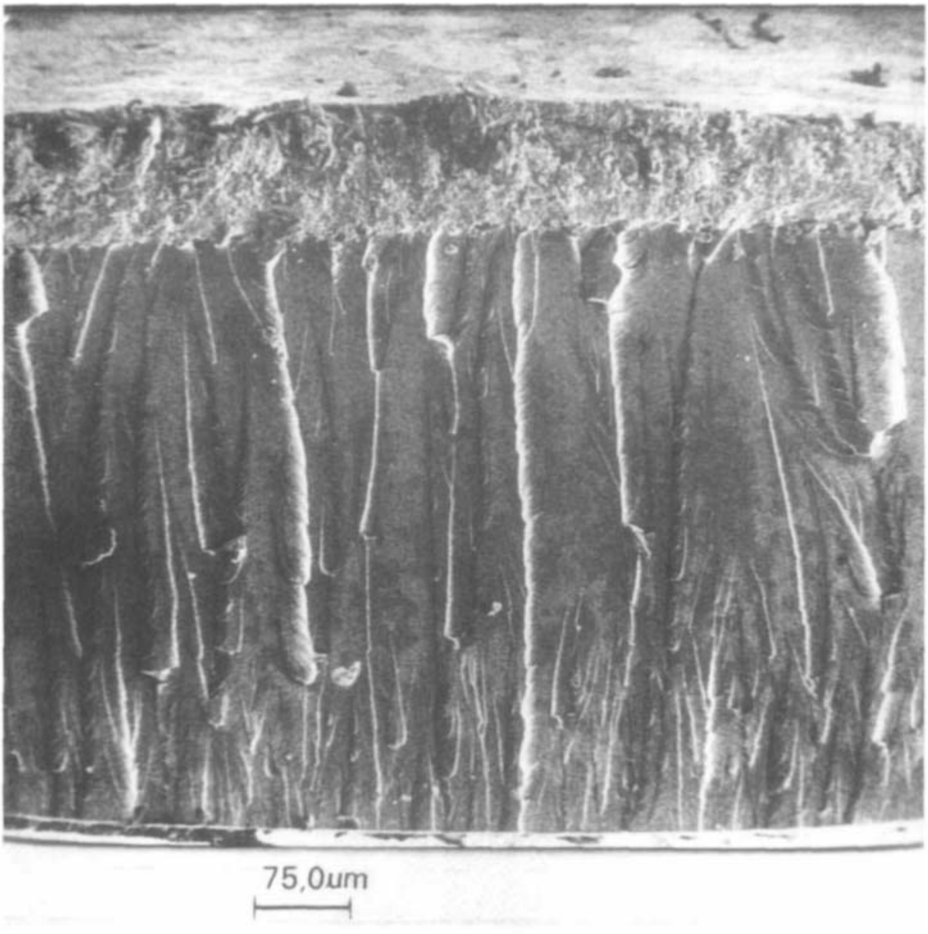


FIG. 9. SEM of the cross section of the epoxide resin membrane prepared with the addition of 15% (wt) benzene (magnification 80×).

which in turn leads to a continuous nonporous layer. The second porous layer is therefore benzene enriched.

In order to verify this hypothesis, we carried out several copolymerizations with varying benzene contents in a centrifuge with 150*g* acceleration. A typical centrifugation lasted 24 hours. The procedure led to the formation of two distinct layers. If no hardener was added to the mixture of the resin and benzene, no layer separation was observed.

Results of densitometric tests have shown that the density of membranes increases slightly in membranes formed with the addition of benzene from 0 to 20% (wt) and decreases in membranes with benzene addition from 30 to 40% (wt). This supports the view that the continuous glassy layer has the largest effect on the density of membranes.

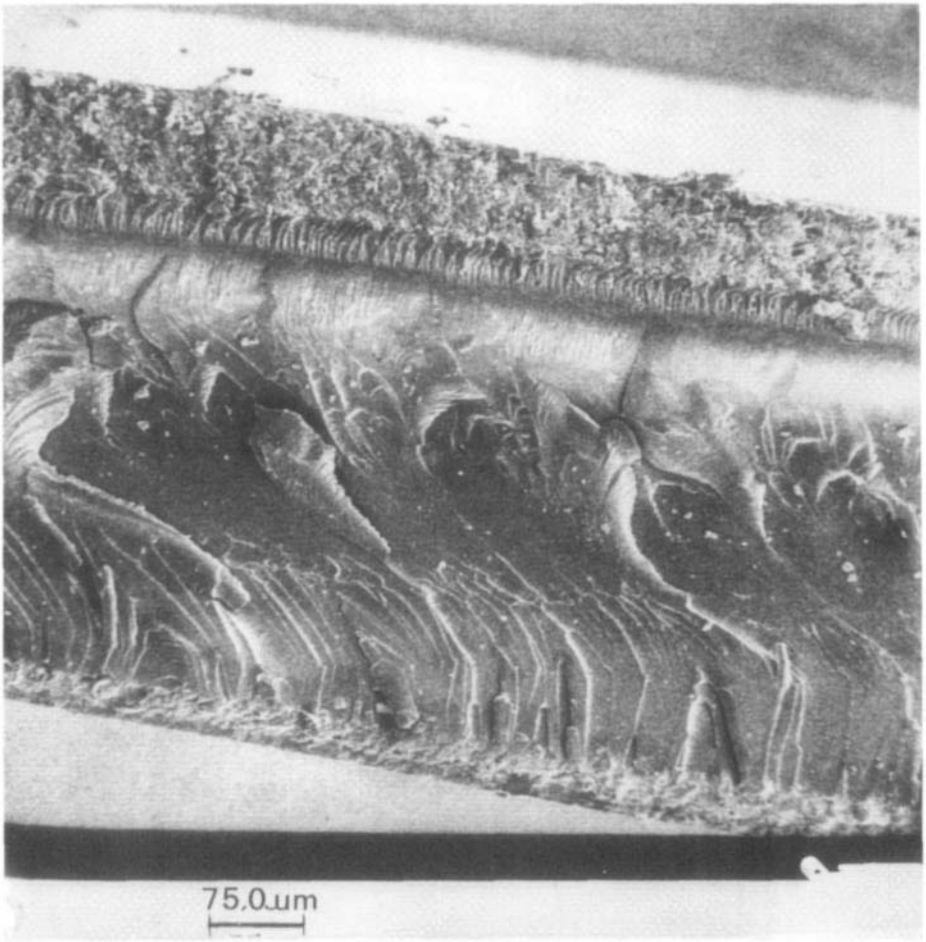


FIG. 10. SEM of cross section of epoxide resin membrane prepared with the addition of 30% (wt) benzene (magnification 80 ×).

Permeability of Membranes

The dependencies of specific conductance and relative electric permittivity of the membranes on the concentration of added benzene are presented in Figs. 13 and 14.

Analysis of the results (Figs. 13 and 14) shows that the variations in conductance and electric permittivity of the membranes are not monotonic in the whole range studied. Two variation ranges of the measured electric parameters could be observed as the benzene concentration was increased. Decreases in specific conductance and electric permittivity were found for all the membranes in the first range with 0–20% (wt) benzene. In the second range, 20 to 40% (wt) benzene, specific conductance and electric permittivity increased.

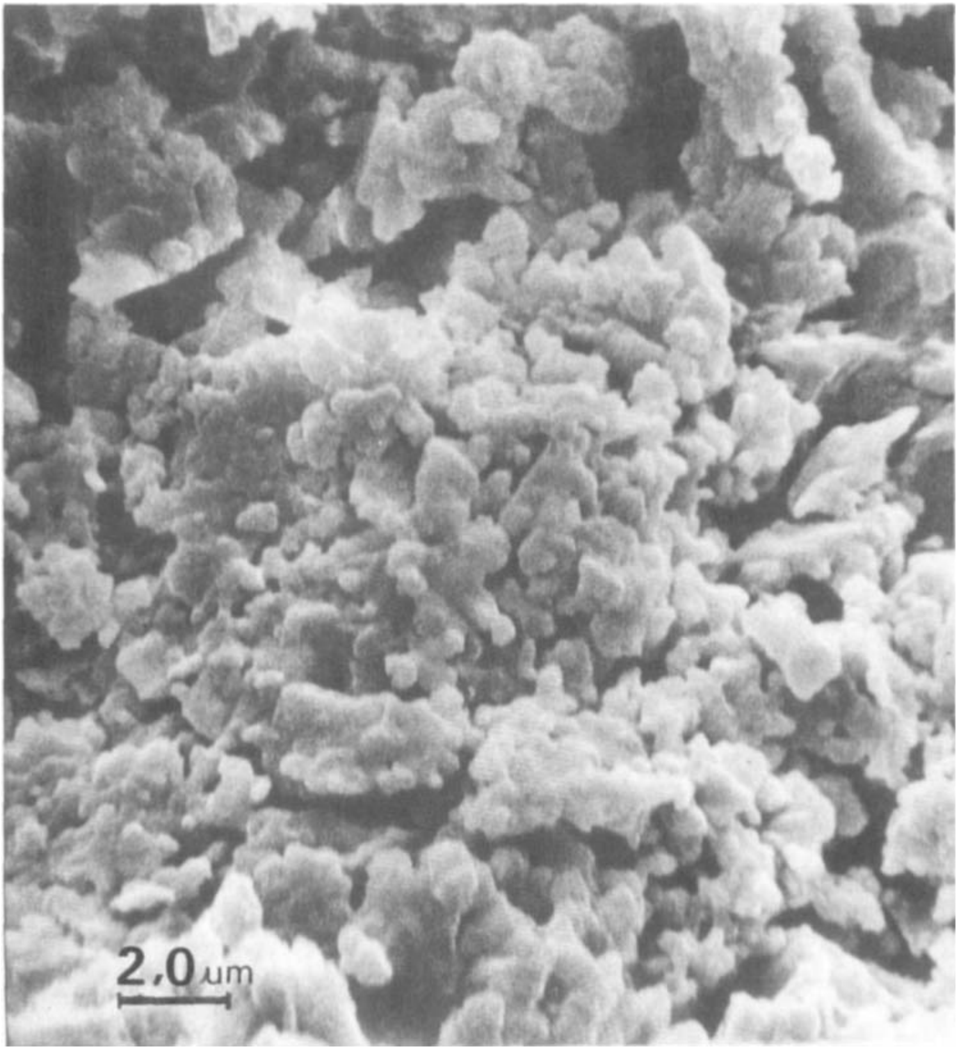


FIG. 11. A fragment of the porous support (magnification 3000×).

These changes in the measured parameters suggest that membrane porosity decreases upon the addition of 0–20% (wt) benzene and increases upon the addition of 20 to 40% (wt) benzene. It can be postulated that the variations of porosity are caused by membrane structural changes induced by the presence of benzene. This idea is strongly corroborated by densimetric studies of the membrane (Fig. 11). The addition of 0–20% (wt) benzene provokes an increase in membrane density whereas the densities of membranes formed with 20–40% (wt) benzene decrease. It is known from earlier studies [22, 23] that a small admixture of a small-molecule compound to the polymer brings about an increase in polymer chain packing; in the case of partly crystalline polymers it can even cause an increase in the degree of crystallinity [22, 23]. This phenomenon was explained by the increased mobility of macromolecule

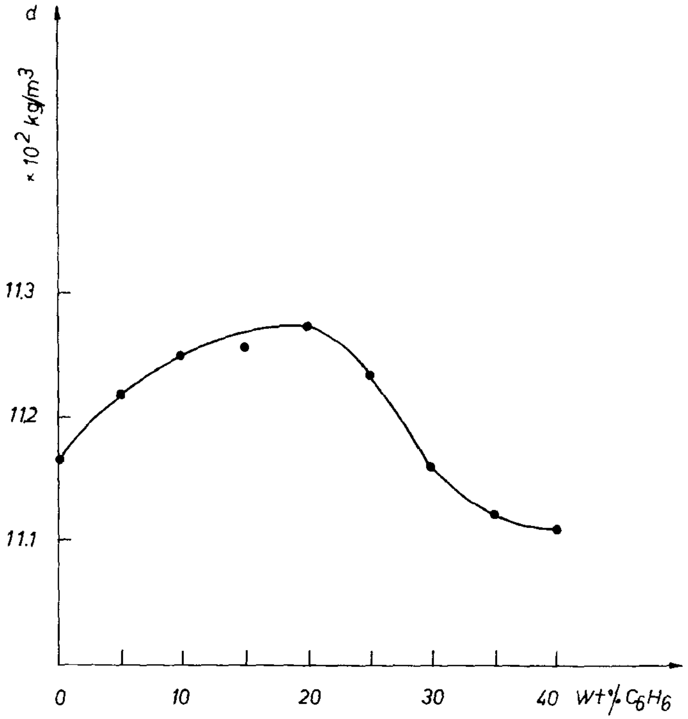


FIG. 12. Membrane density as a function of benzene concentration.

fragments not built into the crystal, resulting in enhanced polymer-polymer intermolecular bonding. If there are free polar groups in polymer chains and the small-molecule compound is also polar, then there are additional polymer-small-molecule compound interactions [24]. A further increase in the small-molecule compound concentration results in loosening of the structure because the amorphous parts of the macromolecule are then shifted away from each other, intermolecular bonds are broken, and layers of adsorbed small-molecule compounds are formed around the polymer chains.

Epoxy resins are amorphous polymers. They can be considered as polar polymers because they contain secondary OH groups in their chains. The dian resin structure can be schematically presented by the formula shown in Fig. 15. A fragment of the polyamine-hardened epoxy resin is shown in Fig. 16. Benzene, being nonpolar, is able to penetrate into free interchain interstices when added to the epoxy resin. At low benzene concentrations, 0–20% (wt), the mobility of macromolecule fragments probably increases and resin crosslinking is accompanied by hydrogen bond formation between free hydroxy groups of neighboring polymer chains not bonded to the network.

However, this does not imply that all the resin chains are hydrogen-bonded. The O···O distance must be about 2.8 Å if an O—H···O hydrogen bond is to be formed [25]. In cases where the epoxy resin chains are considerably shifted apart by

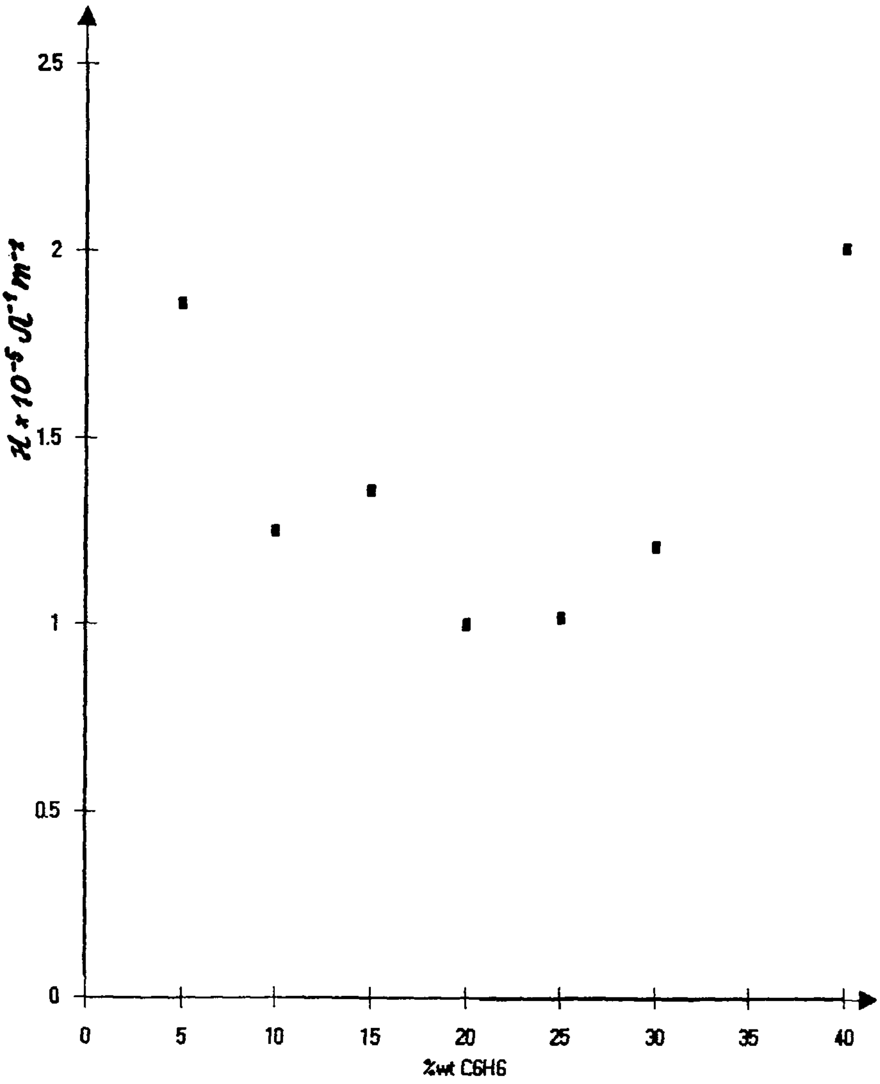


FIG. 13. The dependence of specific conductance of the membranes on added benzene concentration.

benzene molecules, the interchain distances are so great that neither a hydrogen-bonded network nor a network with the hardener molecules can be formed.

During membrane deaeration, benzene molecules are removed from the interstices, leaving space for a pore, while benzene molecules present between the network nodes and between hydrogen bonds remain within the membrane.

The porosity increase in membranes formed with 20 to 40% (wt) benzene is probably due to benzene molecule location predominantly in free interchain interstices. This causes an increase in interchain distances, and the number of hydrogen bonds does not increase. At higher benzene content, resin crosslinking is impossible.

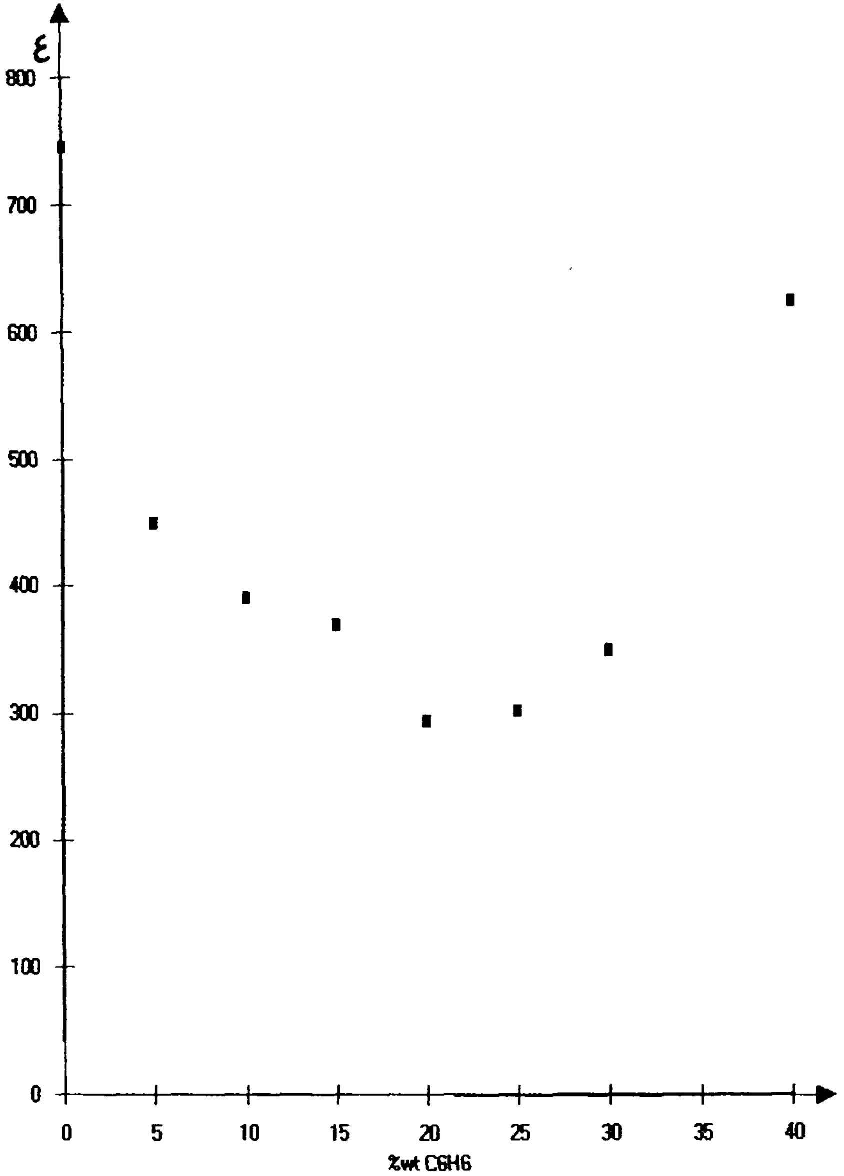
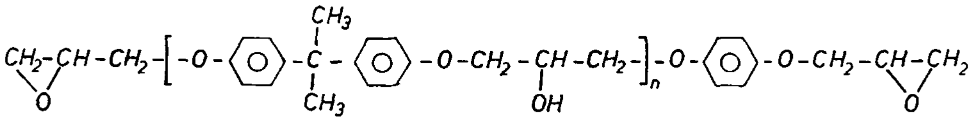


FIG. 14. The dependence of electric permittivity of the membranes on added benzene concentration.



$$CH_2(O)CH-CH_2-[-O-C_6H_4-C(CH_3)_2-C_6H_4-O-CH_2-CH(OH)-CH_2-]_n-O-C_6H_4-O-CH_2-CH(O)CH_2$$

FIG. 15. The dian resin structure.

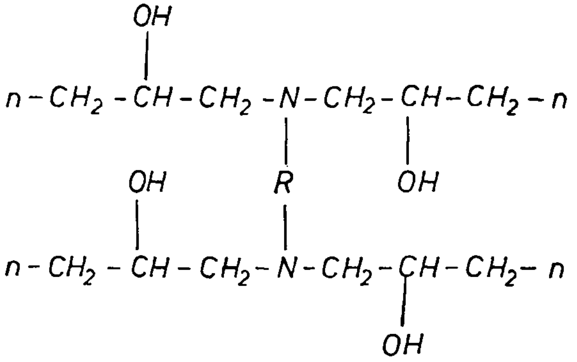


FIG. 16. The structure fragment of polyamine crosslinked resin.

The interpretation of porosity variations observed in this work is supported by Lee and Neville's result [7] that a dian resin containing a small amount of xylene [about 4% (wt)] and hardened with a tertiary amine is crosslinked to a higher degree than a resin with no diluent. They explained it by the increased mobility of functional groups in the diluted system. Similar conclusions were presented in Reference 6 on the grounds of a dibutyl phthalate and triethylenetetramine effect on the mechanical properties of the E-5 epoxy resin; the authors observed a maximum packing in the 7–11% (wt) small-molecule compound concentration range.

The packing maximum (permittivity and specific conductance minimum) observed in this work only for membranes obtained with 20% (wt) benzene added is probably due to the fact that the measured properties were different than in the above cited works. In this work the experimental permittivity and specific conductance values are affected by the presence of benzene enclosed by the network modes in the polymer and hydrogen bonds. The benzene occluded by the membrane weakens the bonds between the epoxy resin chains, and the packing increase process occurs at higher benzene concentrations.

The electric permittivity values obtained in this work are high relative to those of water. Therefore, we carried out independent permittivity measurements by measuring the capacity of a cylindrical vessel filled with the polymer swollen in water. The results are comparable with those from the chronoamperometric method.

CONCLUSIONS

To summarize, the results obtained in the course of our research allows us to draw the following conclusion: the admixture of benzene up to 20 wt% results in an increase of the resin crosslinking density. This, in turn, leads to a smaller free volume and a lower porosity of the system.

A further increase in benzene content (from 20 to 40 wt%) results in a significant increase of membrane porosity. This observation can be rationalized by assuming an increase of interchain distances due to benzene penetration into the interchain volume occurring during the formation of the membrane.

The chronoamperometric method can be successfully applied to membrane porosity studies. Further studies are required to estimate the applicability of two-component resins to the preparation of semipermeable resins. In particular, other modifiers and electrolytes must be tested.

ACKNOWLEDGMENT

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