

Filler Effects on the Structure and Properties of Semipermeable Polyethylene Membranes

INTRODUCTION

Microfiltration membranes based on hydrophilic polymers have excellent performance for the sterilization of aqueous solutions. However, these membranes very often change their structure in strong acidic and alkaline media and during the filtration of organic solvents. Polyolefin membranes are stable in such media. The phase inversion method of Loeb and Sourirajan is not applicable to preparation of polyolefin membranes due to their limited solubility. The method of mechanically induced porous structure in polymeric film is very suitable for that purpose. This method was proposed for the first time by Drioli and co-workers.¹ Later on Smatok et al.² prepared microporous polypropylene membranes by cold stretching in adsorption-active media. A method for the preparation of polypropylene membranes by thermomechanical deformation also is described in the literature.³ A polymeric composition consisting of polypropylene, a filler, and dibutylphthalate was extruded in the form of a sheet. After successive extraction of dibutylphthalate and the filler, the film was subjected to thermal deformation. The behavior of filled crystalline polymers subjected to thermal deformation has been extensively studied in the literature. In the present work we have made an attempt to study the influence of the filler in the polymeric composition on the porous structure and pore-size distribution during the preparation of membranes by thermomechanical deformation.

EXPERIMENTAL

Preparation of Membranes from High Density Polyethylene (HDPE)

A polymeric composition consisting of hdPE (Bulen V-01, melt index 3.1, g/10 min), a filler SiO₂ (Vulcasil KS-404), and oil (OK-1, petroleum fraction 340–500°C), respectively 25–35, 15–25 and 50 parts by weight was prepared by an extruder. A film with a thickness of 0.4 mm was prepared from the compression-molded composition. The oil was extracted with tetrachloroethylene at room temperature. The film was dried and subjected to thermomechanical deformation in a thermal chamber especially constructed for that purpose.⁴ Some of the films were treated with an alcoholic solution of NaOH for the extraction of SiO₂ before subjecting the Films to deformation.

Determination of the Membranes Structure, Porosity, and Permeability

The porosity β of the membranes is calculated from the following relation:

$$\beta = 1 - \rho_a / \rho_T$$

where ρ_a and ρ_T are respectively the apparent and true density of the membranes. ρ_a is defined as the mass per unit geometrical volume and ρ_T is determined experimentally with a pycnometer filled with butanol. Flux with respect to ethanol was determined with a laboratory cell "Sartorius" with a fluid volume of 200 cm³, membrane area 12,56 cm², and operated pressure 0.1 MPa. The structure of the membranes was observed by scanning electron microscopy (SEM). Pore-size distribution was registered by a Coulter porometer.

RESULTS AND DISCUSSION

The presence of filler in the polymeric composition leads to an increase in the number of superstressed zones and causes breaking of the interatomic bonds in the polymeric molecules

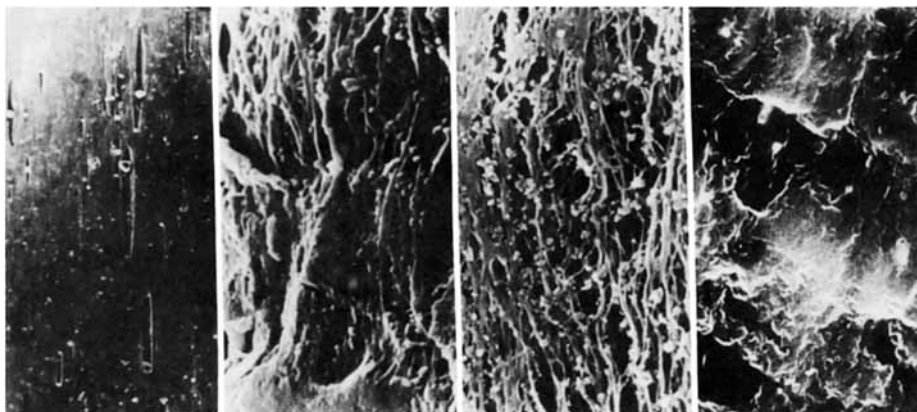


Fig. 1. Scanning electron micrographs of different parts of the polymeric film (hdPE : filler—1 : 1) subjected to thermomechanical deformation (draw ratio 6 and temperature of deformation $T=80^{\circ}\text{C}$): (a) formation of crazes in the neighborhood of the filler particles; (b) gradual formation of porous structure during the deformation process; (c) final porous structure; (d) a structure of the polymeric film subjected to deformation as in the above cases after extraction of the filler (residual filler contents 3%). Magnification 1000 \times .

during the deformation process. The stress has an unequal distribution throughout the polymer film. Although the basic mass of the film experiences a stress equal to the external loading, there exist some regions where the stresses are several times greater. Such superstressed regions are observed at the filler-polymer interfaces.⁵ The conclusion cited by Solomko et al. in the above

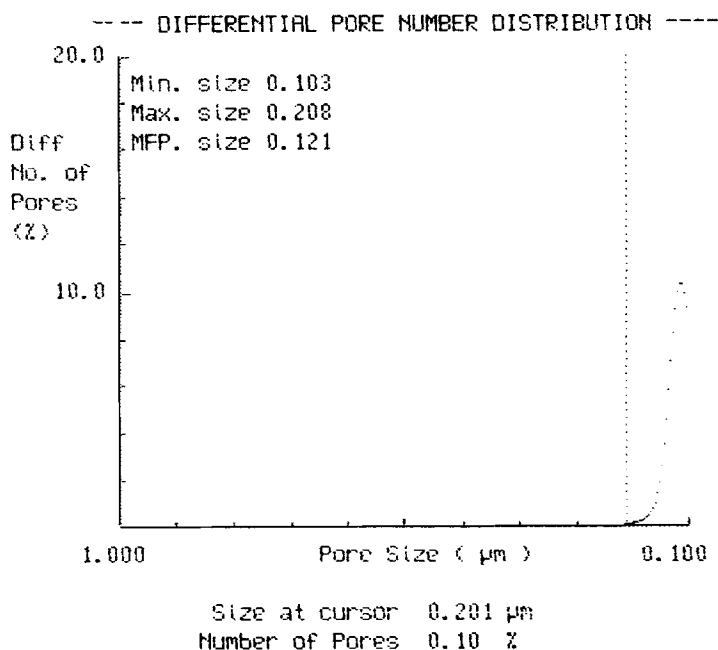


Fig. 2. Pore-size distribution of the membrane prepared under the condition described in Figure 1(c).

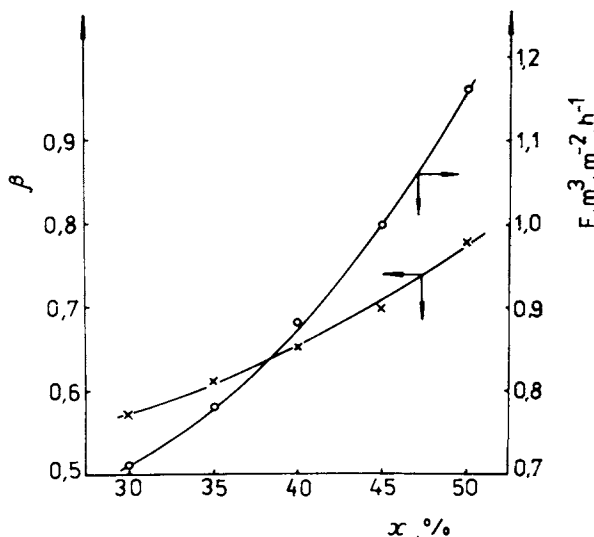


Fig. 3. The porosity β and ethanol flux F as a function of the filler contents x in the composition (draw ratio 6 and temperature of deformation 80°C).

literature is confirmed also by an experiment. Figure 1(a) shows very clearly the formation of crazes in the neighborhood of the filler particles during the monoaxial thermal deformation of the polymeric film. Figure 1(b) shows the gradual formation of porous structure. At one end of the figure, where the jaw of the apparatus held the film, the film is not deformed significantly and porous structure is not formed. Figure 1(c) shows the final porous structure of the membrane. The filler particles are situated mostly in the interfibrillar spaces. In Figure 1(d), porous structure is almost absent. In spite of the residual filler (about 3 wt %), this film deformed under the same conditions doesn't show visible porous structure.

The pore-size distribution of the membrane of Figure 1(c) is represented in Figure 2. The results show a satisfactory narrow pore-size distribution, which ensures good selectibility of the membrane in a microfiltration process.

The porosity β and the flux F as a function of filler content is represented in Figure 3. The filler particles provide steric hindrance to the mobility and orientation of the macromolecules during the deformation process, as a result of which crazes are formed in the neighborhood of the filler particles. The growth of the crazes with an increase in the draw ratio leads to decrease in the density of the film due to the porous structure formed. The porosity has a directly proportional relationship with the flux through the membranes. An increase in the filler contents leads to an increase in the number of superstressed zones during the deformation process and, as a result, the porosity and flux increase.

It may be concluded that, within the range of variation of the filler contents and the conditions of thermal deformation chosen in our experiment, the porosity increases proportionally with the filler contents. Most probably, besides its content, the nature, shapes, and sizes of the filler also play a vital role in the formation of porous structure of the membranes, which will be an object of our next investigation.

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Received November 16, 1989

Accepted January 31, 1990

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