

On the Mechanism of the Formation of Porous Structure in Filled Polyethylene Film by Thermomechanical Deformation

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SYNOPSIS

The pore-formation mechanism in filled polyethylene film during the process of thermomechanical deformation has been studied. The film material consists of a high density polyethylene and SiO₂. The rate of deformation as well as the initial thickness of the polyethylene film play a vital role in the formation of the porous structure. With an increase in the deformation rate, the contribution of crazes in the film decreases. Keeping all the parameters constant, with the increase in the initial film thickness, the porosity of the membranes decreases. The mechanism of pore formation is observed by scanning electron microscopy. It is established that the formation of crazes in the deformation process starts from the zones with lower adhesion of the filler with polymer and in the course of the process propagates throughout the mass. The final pore-size distributions as well as the permeability data provide additional indirect evidence in favor of the observed mechanism.

INTRODUCTION

Most polymeric membranes are prepared by the Loeb-Sourirajan technique. The basic part of the method includes preparation of a polymer solution in some suitable solvent. The membranes prepared by this method are unstable in organic solvents. The membranes based on polyolefins are stable in such media. Exactly for that reason, the Loeb-Sourirajan technique is almost inapplicable for the preparation of membrane from polyolefins.

Drioli et al.¹ were the first to prepare membranes based on polystyrene and ABS terpolymer and to induce crazes in their dense films. Many authors describe methods for the preparation of membranes by deformation in adsorption active media² or by a multistep process of thermomechanical deformation.³ Solomko⁴ studied the process of formation of crazes in the filled crystalline polymers subjected to deformation and observed that the crazes are formed due to the generation of a high concentration of stresses at the polymer-filled interface. In our pre-

vious study,^{5,6} we reported that the presence of filler in the polymer film plays a vital role in the formation of a porous structure of the membrane during the process of thermomechanical deformation. It was established that with an increase in the filler content and degree of deformation, the porosity, and correspondingly the ethanol flux through the membrane, increases. Further investigation showed that besides the degree of deformation, the initial thickness of the samples and the rate of deformation also influence the process of formation of porous structure in the membrane. In the present paper, we have made an attempt to investigate the influence of the mentioned parameters on the formation of the porous structure of the membranes. It was found that during the process of thermomechanical deformation, highly defect zones were affected first and were converted to porous zones. Then gradually more and more low defect zones take part in the formation of porous structure and with the advancement of the deformation process, the boundary of the porous zones moves through the undefected zones. Finally the isolated porous zones are interconnected and cover the film thickness to form an open porous structure. These phenomena were observed by scanning electron microscopy. Porous characteristics as measured by a Coulter porometer and per-

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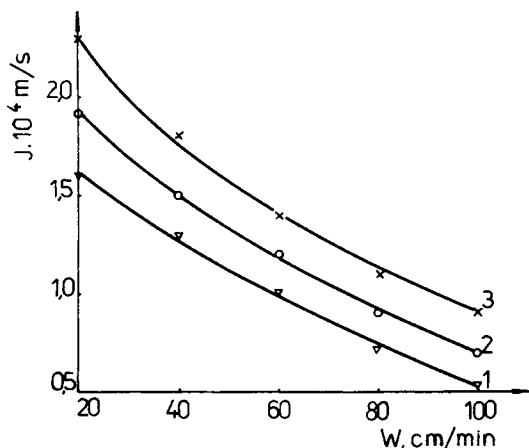


Figure 1 Ethanol flux J through polyethylene membrane as a function of the deformation rate w for the preparation of the membranes. Initial membrane thickness $l_0 = 0.8$ mm, temperature of deformation $T = 90^\circ\text{C}$, degree of deformation ϵ is (1) 400%, (2) 500%, (3) 600%.

meability data also provide indirect evidence as to the mechanism of formation of the porous structure.

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) in a weight ratio 2 : 5 : 8 was prepared with the help of an extruder. Films with a thickness of 0.4–1.2 mm were prepared from the compression-molded composition. Oil was extracted with tetrachloroethylene. The films were dried and then subjected to thermomechanical deformation in a thermal chamber especially constructed for that purpose.⁷ Films with a size of 8×3 cm² (different thicknesses) were placed between the jaws of the holders. The heating was performed only by hot air. The desired temperature (90°C) was attained after about 15 min. The temperature was maintained with an electronic thermoregulator. The samples were kept at that temperature for 5 min and then they were subjected to deformation at a desired rate. Then the chambers were cooled down to room temperature and the samples were taken out.

Ethanol flux through the membranes were determined with a laboratory cell (Sartorius type) with a membrane area of 12.56 cm² and at a pressure of 0.1 MPa. The mechanism of the formation of porous structure was observed by scanning electron mi-

croscopy. Pore-size distributions of the membranes were measured by a Coulter porometer.

RESULTS AND DISCUSSION

During mechanical loading most polymers show long, narrow bands—so-called crazes. They are localized plastic deformation zones in the polymer. Similar to microcracks, they are oriented orthogonally to the load direction. Unlike cracks, crazes are characterized by an interior structure of strong plastically deformed material (often fibrils), and the boundary to the relatively undeformed surrounding is rather sharp.⁸ When the crazes are interconnected and propagate through the whole thickness of the polymer film, they then form a network of porous structure in the film. The method of preparation of membranes by thermomechanical deformation is based on the formation of a network of porous structure by the crazes. The deformation process of the polymer film in our experiment is performed at a temperature less than the melting point of the filled polymer. The orientation of the macromolecules is accompanied by two parallel processes: forced elastic deformation with and without the development of crazes. Depending on the rate of deformation, one of the two processes mentioned predominates. The development of crazes is of the utmost importance for the formation of porous structure. When the crazes propagate through the whole thickness of the film before reaching the limiting value of forced elastic stress, the process of formation of crazes will predominate.⁹ Thus at a

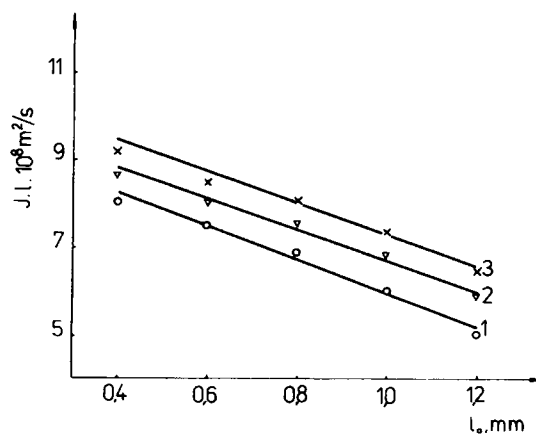


Figure 2 The parameter $J \cdot l$ (flux \times membrane thickness) as a function of the initial film thickness l_0 . Preparation conditions of the membranes: $T = 90^\circ\text{C}$, $w = 40$ cm/min, ϵ is (1) 400%, (2) 500%, (3) 600%.

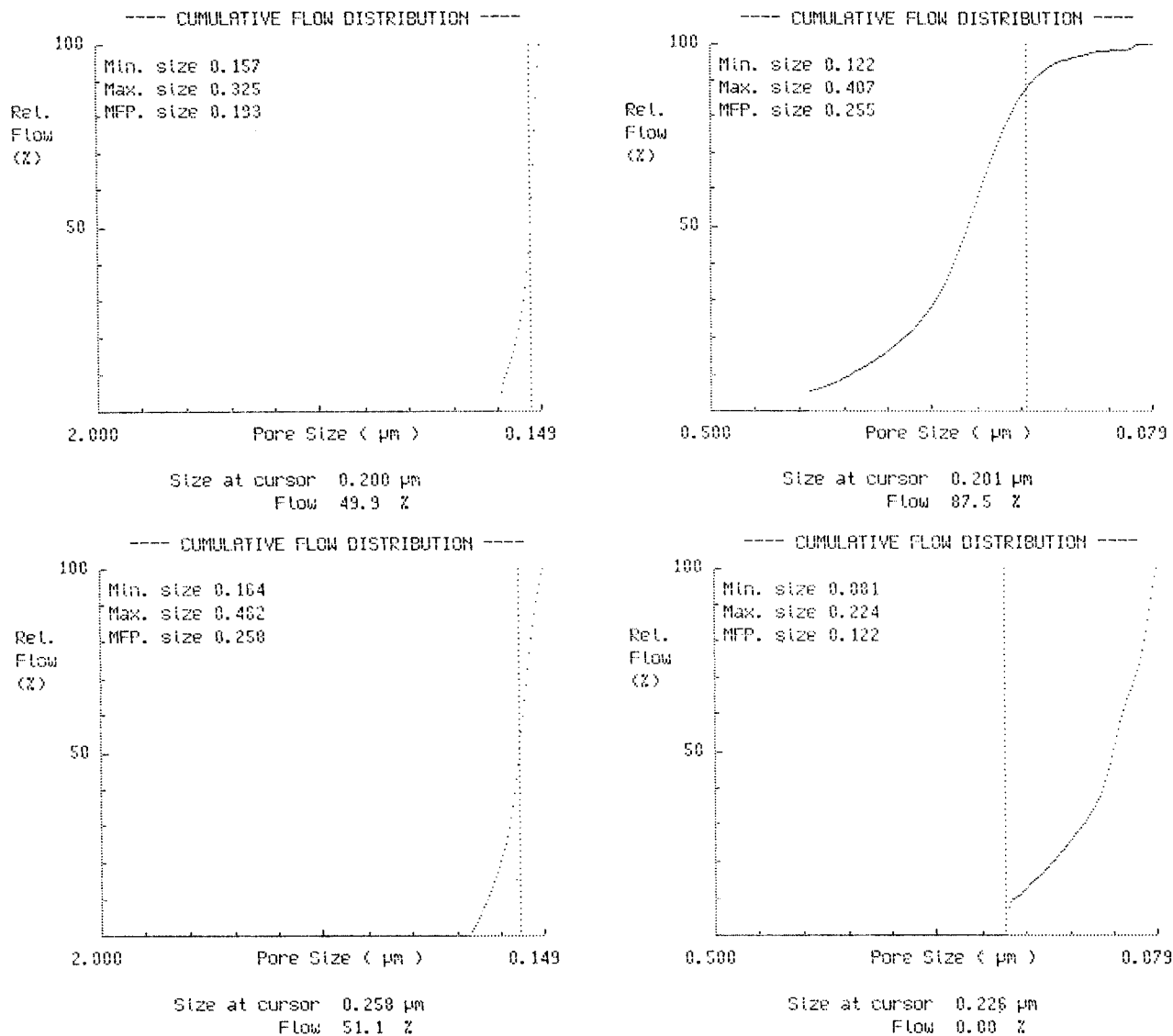


Figure 3 The pore-size distribution of the membranes prepared under the following conditions:

$l = 0.8 \text{ mm}$, $T = 90^\circ\text{C}$, $\epsilon = 600\%$; (a) $w = 20 \text{ cm/min}$. and (b) $w = 80 \text{ cm/min}$.
 $T = 90^\circ\text{C}$, $\epsilon = 400\%$, $w = 40 \text{ cm/min}$; (c) $l_0 = 0.4 \text{ mm}$ and (d) $l_0 = 0.8 \text{ mm}$.

lower deformation rate and smaller sample thickness, the deformation process occurs mostly by the development of crazes. At a higher deformation rate, the deformation process occurs by a mixed mechanism. The ethanol flux through the membranes as a function of the deformation rate for membrane preparation is represented in Figure 1. It is obvious from the figure that with an increase in the deformation rate, the flux through the membranes decreases. Therefore it may be concluded that with an increase in the deformation rate, the contribution of interconnected crazes to the deformation process decreases.

To demonstrate the influence of the initial thickness on the porous structure, the permeability of different membranes formed under the same conditions but with different initial thickness, is determined. According to Darcy's law, the flux $J(\text{m/s})$ of a fluid through a porous medium is directly proportional to the pressure gradient applied across the medium, and indirectly proportional to its viscosity. The law may be described by the following expression¹⁰:

$$J = \frac{K \Delta P}{\eta l}$$



Figure 4 Scanning electron micrographs of the films deformed under the following conditions: $l_0 = 1.0$ mm, $T = 90^\circ\text{C}$, $w = 20$ cm/min, ϵ is (a) 0%, (b) 100%, (c) 200%, (d) 450%.

where η is the viscosity of the permeating fluid ($\text{Pa}\cdot\text{s}$); ΔP is the pressure difference between the two surfaces of the membranes (Pa); l is the membrane thickness (m); and K is constant of Darcy (m^2).

The constant of Darcy is a function of the sizes,

shapes, and tortuosity of the pores. In our experiment, the viscosity of the permeating fluid (ethanol) was constant. But as the starting polymeric films were of different initial thicknesses, the final thicknesses were different for different membranes. Therefore, at constant pressure and fluid viscosity,

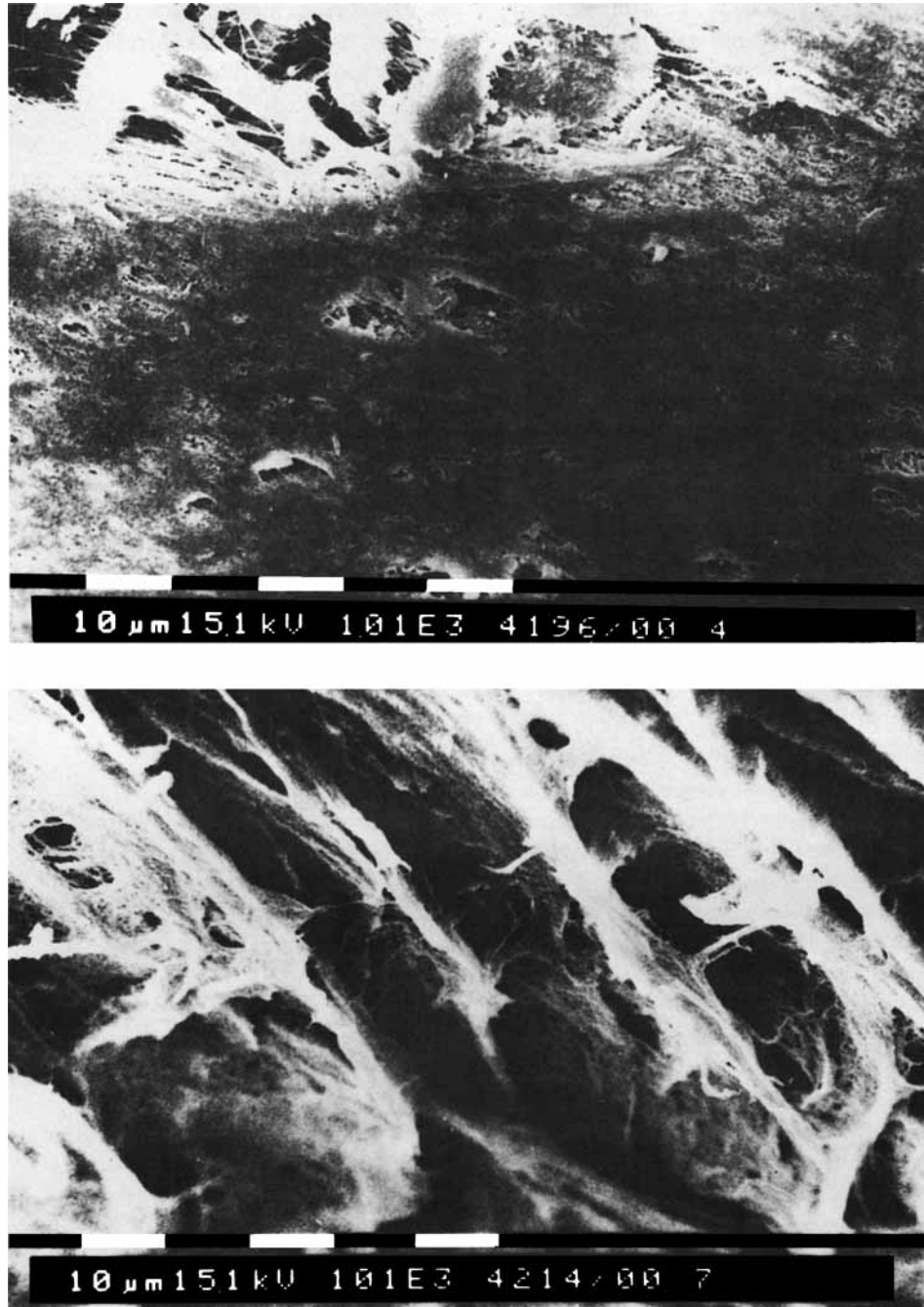


Figure 4 (continued from the previous page)

following Darcy's law, the parameter $J \cdot l$ (flux multiplied by the final thickness) was taken as a measure of the porous structure of the membranes.

It is seen from Figure 2 that with an increase in the initial film thickness, even under the same preparation conditions, the porosity parameter decreases.

The pore-size distribution of two membranes prepared under the same conditions except for de-

formation rate are represented in Figures 3(a) and 3(b). It is obvious from the figures that at lower deformation rate, the mean flow pore-size is larger than those formed at higher deformation rate. The relative contributions to the total flow of the pores with the sizes larger than $0.20 \mu\text{m}$ are 49.9 and 87.5% for the membranes prepared with higher and lower deformation rate, respectively. Thus the pore-size

distributions of the membranes prepared at different deformation rates correlate well with the permeability properties shown in Figure 1. The pore-size distributions of two membranes prepared under the same conditions but with different initial thicknesses are represented in Figure 3(c) and 3(d). It is obvious from the figures that at lower initial thickness, the mean flow pore-size is larger than that formed at higher initial thickness. The relative contributions to the total flow, of the pores with the sizes larger than $0.258 \mu\text{m}$ are 0 and 51.5% respectively for the membranes prepared with higher and lower initial thickness. The permeation properties in Figure 2 are in agreement with the porous characteristics.

The scanning electron micrographs of the polymeric films prepared by different degrees of deformation are represented in Figure 4. Figure 4(a) shows the cross-section of an undeformed film. As can be seen from the figure, there exist some defected zones in the polymeric matrix. These defects most probably appear as a result of the nonuniform distribution of the filler as well as low adhesion of the filler particles to the polymer. These defects become the centers of superstress during the process of thermomechanical deformation. Vacuoles are formed in the vicinity of the filler particles with loose adhesion to the polymeric matrix, and the formation of porous fibular structure is initiated [Figure 4(b)]. The whole cross-sectional area of the film in Figure 4(a) is smooth (except the defected zones). Unlike the film in Figure 4(a), that in Figure 4(b) shows that in the course of the deformation process, more and more low defect zones take part in the formation of porous structure, and that the boundary of the porous zones starts moving towards the undefected zones along the direction of deformation. As the deformation process proceeds, nonconnected porous zones are observed in almost the whole cross-sectional area [Fig. 4(c)]. Gradually the isolated porous zones are interconnected and experience further development to form the open porous structure of the polymeric film [Fig. 4(d)].

Observing the mechanism of formation of the porous structure, it may be assumed that for a polymeric film with lower initial thickness, the isolated porous zones are interconnected at a lower degree of deformation than would have happened in the case of a film with higher initial thickness. After the interconnection of the isolated porous zones, the fibular structure experiences further development

to form larger pores. Thus the results shown in Figures 2, 3(c), and 3(d) correlate well with the pore-formation mechanism.

CONCLUSION

On the basis of the experiments performed, it may be concluded that besides the degree and the temperature of deformation, the deformation rate and the initial film thickness also play a substantial role in the formation of the porous structure in the membranes. With an increase in the deformation rate and initial film thickness the porosity of the membrane decreases. The scanning electron micrographs of the polymeric films confirm that the formation of the porous structure starts from the defect zones and gradually the fibular porous structure penetrates into the undefected zones. When the isolated porous zones are interconnected, the film is considered to be a membrane with open porous structure.

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