

Gas Permeability of Deformed Polyethylene Films

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Synopsis

Low-density polyethylene films strained up to 35% exhibit an initial increase of diffusivity and permeability which soon reach a maximum and subsequently drop to steadily decreasing values below those of the unstrained starting material. The sorption steadily increases and seems to approach a plateau. The maximum and the subsequent decrease are probably caused by significant, recoverable plastic deformation which seems to depress the tortuosity factor but not the free volume, as one concludes from the opposite trend of diffusion and sorption. Permanently deformed drawn or rolled films on the strain range from 0.5 through 3.0 exhibit a continuous decrease of diffusivity and permeability with an almost constant reduction of sorption. This postulates a decrease in free volume and a steadily decreasing tortuosity factor as a consequence of the gradually increasing fraction of the new, practically impermeable fibrous structure.

INTRODUCTION

Gas permeability P of strained polymer films reflects the changes of specific volume and morphology of the sample which undergoes deformation under tensile stress. It has been shown that the gas and vapor permeabilities of elastically strained crystalline polymers (e.g., polyethylene and polypropylene) increase from that of unstrained film as the strain increases.¹ The change of permeability P is linear with low strain ϵ . At higher ϵ (between 0.005 and 0.02) the permeability of polyethylene quickly reaches a plateau value. The increase of permeability was postulated as being caused by a change of diffusion constant D based upon the increase by elastic strain of the free volume of a compressible solid with a Poisson ratio smaller than 0.5. In this postulation the solubility constant S was assumed to remain practically constant.

On the other hand, plastically deformed crystalline polymers show a drastic reduction of permeability, diffusion, and sorption,²⁻⁹ particularly at high draw ratios. Polyolefin films stretched to above 500% exhibit a substantial decrease of permeability for organic liquids² and vapors.³ Nylon 66 fibers show a steadily decreasing diffusion of dyes with increasing draw ratio.⁴ Particularly drastic effects were observed with highly drawn linear polyethylene films⁶⁻⁸ where the sorption dropped to one sixth, the diffusion constant to less than 1%, and the permeability to less than one thousandths of the values of the starting material. Such a drastic effect is character-

istic for drawing at low temperature where the sample cannot relax after drawing.⁸ Indeed, calorimetric,^{10,11} density,¹² and infrared¹³ measurements have shown that the chain conformation, heat content, and chain packing in the amorphous regions in such a sample substantially deviate from equilibrium values of supercooled melt. Annealing at a temperature higher than that of drawing, exposure to a swelling liquid, or drawing at a higher temperature yields a more relaxed amorphous component^{10,11} with smaller, if any, reduction of S , D , and P .^{6,8}

The reduction of transport coefficients is much higher than one would expect from the minor change of crystallinity and hence cannot be explained by the decrease of amorphous component or tortuosity factor of the original spherulitic structure. Hence, it is morphologic changes that consequently affect the transport properties of the amorphous regions.^{6,8,10} Drawing destroys the original spherulitic or microspherulitic structure and creates the new highly oriented fiber structure¹⁴ with substantial deviation from thermodynamic equilibrium of the amorphous component in the layer between consecutive crystal lamellae.¹⁰ So drastically is the number of sorption sites and still more the mobility of sorbent reduced that the microfibrils, the basic element of the fiber structure, can be considered as almost completely impermeable⁷ as compared to the microspherulitic matrix.

Most measurements of the effect of drawing on permeability were performed at rather high draw ratios where almost all the sample is already transformed into fibrous structure. It seems important, however, to investigate lower draw ratios and, particularly, the transition from elastic to plastic deformation, where the original spherulitic structure is still preserved and very little, if any, new fiber structure is present.

In the experiments performed in this laboratory some years ago, the strain was induced by the pressure difference between the permeant gas side and the vacuum side of an unsupported circular film; i.e., the film deformed into a spherical shell shaped with increased surface area and decreased thickness. The changes in area, thickness, and strain of the sample were estimated by assuming that the film deformed into a perfect spherical shape. Under the experimental conditions used, the deformation of film and the transport of the permeant gas occurred simultaneously, and, consequently, the estimate of diffusion constant D by time lag method could not be utilized to obtain D of the deformed film. Therefore, the change of D as a function of strain and the expected constancy of S under the strain could not be checked experimentally.

With a recently developed instrument,¹⁵ it became possible to measure directly the changes of P and D ; consequently, $S = P/D$ of unidirectionally strained films. The deformation of the sample is achieved outside of the permeability measuring instrument so that the direct measurements of thickness and strain of the film are feasible. Utilizing this technique, the effects of both elastic and plastic deformation of low-density polyethylene film on its gas permeability, sorption, and diffusion were examined in this study as a function of deformation.

EXPERIMENTAL

The sample used was low-density polyethylene film ($\rho = 0.92 \text{ g/cm}^3$), courtesy of Koppers Company, Inc., thickness approximately $4 \times 10^{-4} \text{ cm}$. The gas permeability was measured at 25°C by an IRD Permeability Meter GPM-200, Incentive Research and Development AB, Sweden. The details of the instrument and measurements have been reported before.¹⁵

The permeability of elastically deformed film was measured by using a specially designed stretchable sample holder. The movable end of the stretchable sample holder is fixed to a bolt which has a 0.5-mm pitch. By turning a nut, a film can be stretched to a known deformation ratio. After a sample was stretched to a predetermined draw ratio, the membrane thickness was measured by a micrometer, and the sample holder was inserted into the permeability meter. This process was repeated for further stretching of the sample and reversed for measurement at decreasing strain.

The plastically deformed samples were prepared by (1) drawing and (2) rolling. The film was drawn at 60°C in a table model Instron tensile testing instrument at a strain rate of $10\%/ \text{min}$. After stretching, the film was cooled to room temperature and kept with fixed ends for 30 min before removal from the clamps. The drawn samples were kept at least 24 hr at room temperature before the determination of the strain ϵ was made from ink marks printed on the film before stretching.

The rolled films were prepared by repeated rolling at room temperature in a calendar with 5-cm-diameter rolls, both rotating at the same speed. A maximum draw ratio λ of about 3 was achieved by this method. Attempts to increase λ by continued rolling yielded cracked films which could not be used for permeability measurement. Some shrinking was observed even at room temperature after the rolling. Therefore, the draw ratio of the sample was determined 24 hr after the rolling. The permeability measurement of plastically deformed films was done by using the standard sample holder of the IRD instrument.

With all samples, the permeation transient for CO_2 was measured. The asymptotic value yields P , the time lag the diffusion constant D . The ratio P/D is the equilibrium sorption S .

RESULTS AND DISCUSSION

Small Deformation

Results obtained in this study confirmed the general trend of the permeability increase observed in the previous study; i.e., the nearly linear increase of P at low ϵ below 0.01 or 0.02, with a plateau at higher ϵ between 0.06 and 0.10. However, at higher strain the analysis of the change of permeability and diffusion constant revealed some aspects that could not be observed formerly. A typical change of P , D , and $S = P/D$ for CO_2 is shown in Figure 1 with plots of $\Delta P/P_0$, $\Delta D/D_0$, and $\Delta S/S_0$ versus ϵ . Here, ΔP , ΔD , and ΔS are the changes of permeability, diffusion, and solubility, respectively; P_0 , D_0 , and S_0 are the values of unstrained film.

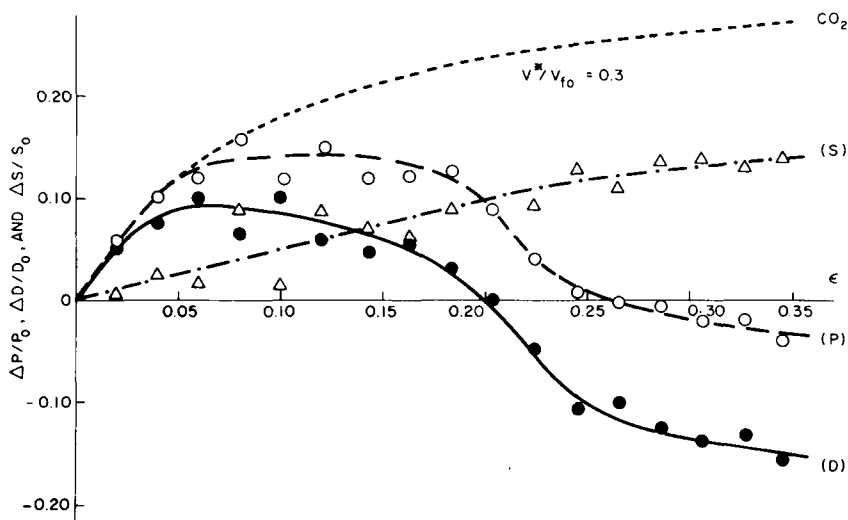


Fig. 1. Relative changes of permeability, $\Delta P/P_0$, diffusion constant, $\Delta D/D_0$, and sorption, $\Delta S/S_0$, of low-density polyethylene film as function of unidirectional strain $\epsilon = \Delta l/l_0$. The broken line represents the change of diffusion constant as calculated from eq. (7) with $V^*/V_{f_0} = 0.3$.

In the very low ϵ range, $\Delta P/P_0$ is nearly identical with $\Delta D/D_0$ as postulated in the previous study.¹ Between 2% and 3% strain, however, the difference between $\Delta P/P_0$ and $\Delta D/D_0$ becomes observable. It is quite appreciable when both $\Delta P/P_0$ and $\Delta D/D_0$ reach plateau values. As $\Delta P/P_0$ and $\Delta D/D_0$ diverge, the values of $\Delta S/S_0$ start to increase and continue to increase while $\Delta P/P_0$ and $\Delta D/D_0$ decrease from the plateau across zero to negative values. At higher strain, the negative values $\Delta P/P_0$ and $\Delta D/D_0$ increase at a gradually decreasing rate. In the whole range up to $\epsilon = 0.35$, the permeability curve is above the diffusion curve. Hence, the sorption data $\Delta S/S_0$ is positive. It is safe to assume that from $\epsilon = 0$ on, the $\Delta S/S_0$ values are proportional to the strain in the initial range. The gradually decreasing slope seems to indicate the existence of a plateau value at about $\epsilon = 0.30$.

The most striking new result shown in Figure 1 is the existence of a maximum, the subsequent decrease and negative values of ΔP and ΔD , and the steady increase of ΔS which seems to level off gradually at sufficiently high strain. Since the values of $\Delta P/P_0$ for plastically deformed crystalline polymers are negative, the existence of the maximum is anticipated. However, it is a rather striking fact that the maximum occurs at relatively low strain where the unrecoverable plastic component of the strain is not yet very conspicuous.

The change of S with strain is a convincing argument that the observed changes of permeability in the elastic range are not caused exclusively by the change of diffusion. One has indeed to consider explicitly the change of sorption if one wishes to describe properly the change of transport proper-

ties of drastically strained crystalline polymers. This requirement becomes even more stringent at higher strains when ΔD and ΔP reach a plateau and finally drop to negative values. In the range close to the sign change of ΔD and ΔP , the relative influence of ΔS is maximum. At higher strain, however, ΔS approaches saturation and changes less with strain than ΔD and ΔP so that its role in transport properties becomes less important.

The rapid saturation and still more the subsequent decrease and sign reversal of ΔP and ΔD with increasing strain are sure indications of a new strain effect, not only completely different from that of the perfectly elastic deformation but also from that of the purely plastic deformation. The gross effect in this region is reversible. Namely, after $\Delta P/P_0$ reached the negative value, the value reversed to the positive side as the stress was released and the film contracted. In this sense, the deformation is more elastic than plastic. Consequently, the maximum seems to be associated with the onset of an easily recoverable plastic deformation. This transient region will be discussed below in the theoretical consideration section.

Stress Relaxation and Strain Recovery

The combined effect of elastic and plastic deformation is still more pronounced if one measures permeability, diffusion, and sorption at constant strain during stress relaxation or after load release. Figure 2 shows the data obtained with a sample stretched by 20% and held at this strain for many hours, and Figure 3 shows a sample stretched by 6.11% and then released. In both cases, the extrapolated initial values $\Delta P/P_0$, $\Delta D/D_0$, and $\Delta S/S_0$ differ slightly from the data in Figure 1. They are all positive and rapidly decrease approaching plateau values, which as a rule are not zero. Hence, the transport properties do not return to the values of the undeformed sample. This is not surprising because in the former case the strain remains 20%, and in the latter case the unloaded sample does not return to the unstretched length as a consequence of a finite unrecoverable plastic deformation.

The slow reduction of ΔP and ΔD with almost constant ΔS during relaxation at constant strain seems to be caused by slow conversion of elastic-

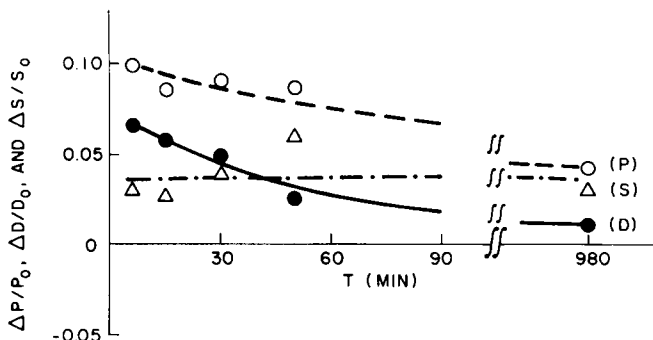


Fig. 2. Relaxation of $\Delta P/P_0$, $\Delta D/D_0$, and $\Delta S/S_0$ for the film with 20% strain.

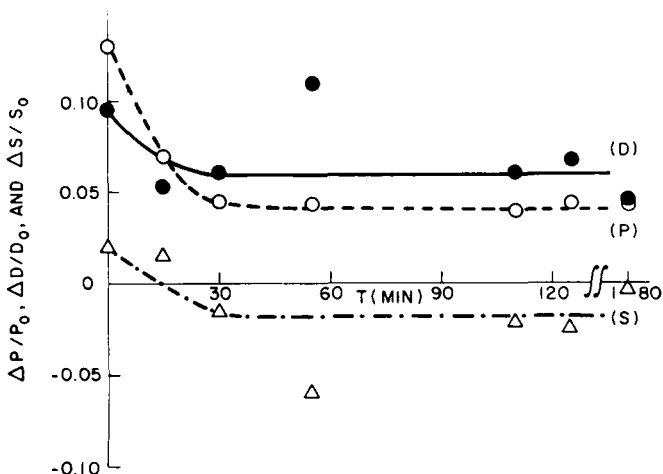


Fig. 3. Recovery of $\Delta P/P_0$, $\Delta D/D_0$, and $\Delta S/S_0$ for the film strained to 6.1% and immediately released.

into-plastic deformation as a consequence of submicroscopic flow of the material of the film.⁷ The flow involves crystal lamella slip and rotation, which are the main modes of deformation of a crystalline polymer at small strain. One cannot exclude some chain tilt and slip within the lamellae which, as well known, become more prominent at larger plastic deformation with neck formation.

In contrast to elastic deformation, the plastic deformation does not increase the specific volume of the amorphous component of the sample. It may even cause some reduction. Hence, the conversion from elastic into plastic deformation may reduce the free volume of the stretched sample and consequently decrease the transport properties. But the constancy of ΔS imposes some severe restriction on such an explanation. In spite of stress relaxation, the amorphous material of the sample where the sorption occurs must remain practically unchanged with the same free volume as in the just-strained sample. The drop in diffusion constant must have other causes, as will be discussed later.

It should be noted that the permeability of strained film under investigation is dependent not only on the strain but also on the stress which relaxes for long periods of time after straining. Consequently, the effect is highly dependent on the time scale of the experiment. The data shown in Figure 1 were taken approximately 15 min after stretching. After a longer time, the results would have been slightly different as can be seen from the data shown in Figure 2. A minimum of approximately 15 min is necessary for the measurement of thickness and for degassing of sample before gas permeability can be measured. By the same token, the values of $\Delta P/P_0$, $\Delta D/D_0$, and $\Delta S/S_0$ at a fixed strain would be different, depending on whether the strain was obtained in a single step or by steps with certain

time intervals between consecutive stretchings, such as was the case in the Figure 1 experiment.

In the case shown in Figure 3, the residual change of permeability after the load is removed depends on the unrecovered fraction of the strain the sample experienced under the applied load. The transition from the values under load to the final plateau is relatively rapid because the sample could immediately recover almost all of the elastic strain. The eventual recovery of the plastic deformation requires a much longer time than the period of our experiment so that its effect on transport properties is not yet observable in the data reported. But it is significant that the sorption change ΔS drops to very small negative values which seem to be slightly beyond the error limits of the experiment. This would mean that the amorphous component returns almost completely to the state of the original material before straining or even becomes slightly compressed as a consequence of some not yet recovered plastic deformation during straining.

Drawn and Rolled Samples

The prue effect of permanent plastic deformation on transport properties can be best observed on completely relaxed drawn and rolled films with no elastic strain involved. The results of $\Delta P/P_0$, $\Delta D/D_0$, and $\Delta S/S_0$ for drawn films at relatively low draw ratios ($\lambda = 1 + \epsilon$) are shown in Figure 4. The results for rolled films are shown in Figure 5. The effect of plastic strain on transport properties is similar in drawn and rolled film, although a more pronounced effect is seen in rolled films. This is probably a consequence of the compressive action of rolling which closes all microvoids that may have been present in the original material or may have been formed during plastic deformation. In both cases, P and D are steadily decreasing with increasing draw ratio. In the very limited range of plastic deformation investigated, the small change of S and hence a nearly parallel change of P and D with plastic deformation is very similar to the trend observed in the higher range of elastic deformation of polyethylene

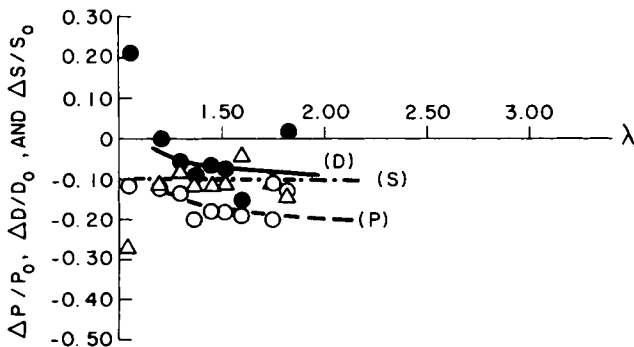


Fig. 4. Relative changes of permeability, $\Delta P/P_0$, diffusion constant, $\Delta D/D_0$, and sorption $\Delta S/S_0$ of a low-density polyethylene film as functions of the permanent deformation achieved by drawing at room temperature.

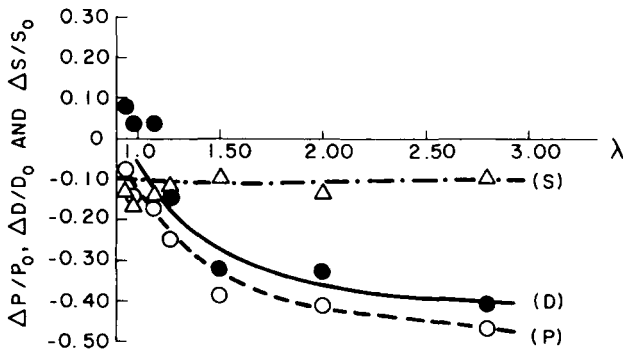


Fig. 5. Relative changes of permeability, $\Delta P/P_0$, diffusion constant, $\Delta D/D_0$, and sorption, $\Delta S/S_0$, of low-density polyethylene film as functions of the permeant deformation achieved by rolling at room temperature.

(above $\epsilon = 30\%$), although P and D in the former case decrease and in the latter case increase with strain. But the most important difference is that the magnitude of P and D changes. In the elastic case, the $\Delta P/P_0$ curves are always above the $\Delta D/D_0$ curves, while in the plastically deformed material, either drawn or rolled, they are below the curves. This means a decrease of sorption ($\Delta S < 0$) in the latter and an increase ($\Delta S > 0$) in the former case.

THEORETICAL CONSIDERATIONS

The overall permeability of semicrystalline polymer films to gases can be generally described by^{16,17}

$$P = X_a \tau D_a S_a \quad (1)$$

$$S = X_a S_a \quad (2)$$

$$D = \tau D_a \quad (3)$$

where X_a is the volume fraction of amorphous phase, τ ($0 < \tau < 1$) is the tortuosity factor that describes the tortuous nature of diffusion passage due to dispersed impermeable crystalline phase, D_a is the diffusion constant, and S_a is the solubility constant of amorphous phase. The permeability of strained film may be interpreted by the effect of strain on these terms e.g., in elastically deformed samples, it is quite reasonable to consider that X_a and τ are not significantly altered. Consequently, in this case the change of P can be attributed solely to the change in D_a and S_a , caused by the change of free volume of the elastically strained material. In plastic deformation, the crystal lamellae are deformed, translated, and rotated. Eventually, the spherulitic material is transformed into fibrous structure with completely different transport properties of the amorphous component. It is indeed almost impermeable to the solvent.⁷ The amorphous component in the fibrous material is almost completely inactivated. Hence, the fraction X_a of the amorphous component still active in the transport and the

tortuosity may change quite appreciably in addition to the free volume dependent changes of S_a and D_a of the remaining spherulitic material.

The unique role of the amorphous component in the transport properties of the crystalline polymers taken into account by eqs. (1)–(3) is still more accentuated by the fact that the amorphous material is intrinsically connected with, and inseparable from, the crystal lamellae. Most of the dimensional changes occur in it while the crystals remain practically undeformed. Therefore, the average strain ϵ_a is about $1/X_a$ times larger than ϵ of the sample and has to be substituted for ϵ in the theoretical expressions of the next two sections.

Elastic Deformation

The changes of P , D , and S caused by elastic deformation are expected to be completely reversible because they are a straightforward consequence of the reversible change of specific volume V under unidirectional strain (ϵ) or planar tensile strain ($\Delta A/A \sim 2\epsilon$), respectively. If the Poisson ratio μ is smaller than 0.5 (which is the case with most crystalline polymers but not with rubber), the change ΔV is positive with positive ϵ or ΔA , thus increasing the free volume V_f , i.e., the fractional free volume $f_0 = V_{f0}/V_0$, by its full value $\Delta V/V_0$:

$$V_f/V_0 = V_{f0}/V_0 + \Delta V/V_0 \quad (4)$$

$$f = f_0 + (1 - 2\mu)\epsilon.$$

For the discussion that follows, it is advisable to introduce a parameter β

$$\beta = (1 - 2\mu)\epsilon/f_0 \quad \text{uniaxial strain} \quad (5)$$

$$\beta = (1 - 2\mu)\Delta A/A_0 f_0 \quad \text{planar strain}$$

so that the fractional free volume of the elastically strained membrane reads

$$f = f_0 (1 + \beta). \quad (6)$$

The parameter β , positive for extension and negative for compression, merely measures the relative free volume change of the strained polymer.

The *diffusion constant* depends on the free volume by the exponential term $\exp(-V^*/V_{f0})$, where the coefficient V^* is proportional to the product of the cross section of the diffusant molecule and the jump length in the Eyring's activation energy model of diffusion.¹⁸⁻²¹ The exponential term increases with increasing free volume, thus yielding for the diffusion constant

$$\begin{aligned} D_\beta &= A \exp(-V^*/V_{f0}) = A \exp[-V^*/V_{f0} (1 + \beta)] \\ &= D_0 \exp[\beta V^*/V_{f0} (1 + \beta)]. \end{aligned} \quad (7)$$

The increase eventually slows down as $\exp(-V^*/V_{f0})$ approaches unity, i.e., as $(1 - 2\mu)\epsilon$ becomes large compared to f_0 . In Figure 6, the theoretic-

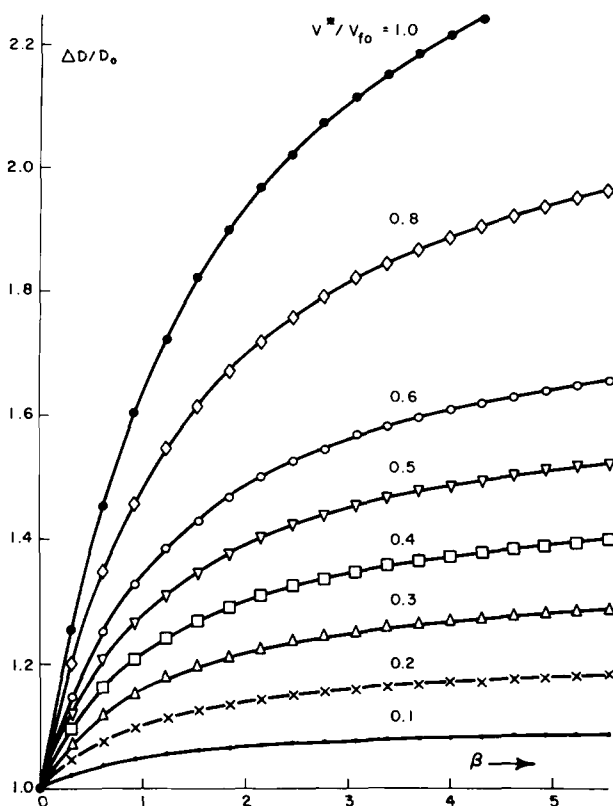


Fig. 6. Changes of diffusion constant $\Delta D/D_0$, according to eq. (7) as function of β for different values of the parameter V^*/V_{f_0} .

cally expected increase of diffusion constant $\Delta D/D_0$ is plotted as a function of some values of V^*/V_{f_0} between 0.1 and 1. Since $1 - 2\mu \sim 0.1$, one expects on the basis of a free volume model a substantial deviation from a linear increase of diffusivity with strain at $\epsilon = 0.25$ and a leveling off at a much larger strain value, between 1.50 and 3.00. Much more drastic is the reduction of diffusivity with compression. It drops to zero at $\beta = -1$ because at that value the free volume of the polymer has dropped to zero.

The sorption in the strained polymer was formerly treated as swelling of a rubber in a stress field.²² The result adapted¹ for water sorption in polyethylene with 50% of amorphous component,

$$S_\beta/S_0 \approx 1 + 0.015 A/A_0 \sim 1 + 0.03\epsilon \quad (8)$$

yields an unobservably small change $\Delta S/S_0 \sim 0.01$ at the highest strain $\epsilon = 0.35$ of Figure 1 in contrast with the observed value of about 0.13. Moreover, the effect on swelling according to this treatment is independent of the specific volume change of the polymer, thus demanding the same increase of sorption in a crystalline polymer and a rubber. This is in striking

contrast with experimental data of Barrie and Platt²³ showing no observable changes for the solubility of hydrocarbons in stretched rubber up to the point where crystallization began, i.e., up to several hundred per cent extension. Equation (8) would demand in such a case a measurable sorption increase of about 10%.

A much better approach is based on the change of free volume of the strained polymer.²⁴ One starts with the well-known equation for the change of chemical potential of sorbate in a gas or liquid (subscript 1) mixture with a polymer (subscript 2),²⁵

$$\mu_1 - \mu_1^0 = RT [\chi_1 v_2^2 + (1 - 1/x)v_2 + \ln(1 - v_2)] \quad (9)$$

where v is volume fraction and $x = V_2/V_1$, the ratio of molecular volume of polymer and sorbate. According to Hildebrand,²⁶ this expression can be derived from the free volume contributions of the components if the fractional free volume is the same for both. If, however, the fractional free volume of the polymer increases as shown in eq. (6), the fractional volume v_2 in the entropy terms of eq. (9) (but not in the energy term $\chi_1 v_2^2$) has to be replaced by

$$v_{2\epsilon} = v_2(1 + \beta)/(1 + \beta v_2) = 1 - v_{1\epsilon}. \quad (10)$$

The dependence of the chemical potential on $\ln v_1$ for $\beta = 0, 1, 2, 3$, and 4 and $\chi_1 = 3$ can be seen in Figure 7.

The low activity $a_1 = p/p_T$ of permanent gases at room temperature can be taken into account in Figure 7 by shifting the horizontal zero line to the ordinate $\ln a_1$. This yields a smaller equilibrium value v_1 at smaller values of $p < p_T$. In eq. (9), one has to subtract $RT \ln a_1$, so that the equilibrium condition for the chemical potential reads

$$\mu_{1\epsilon a} - \mu_{1a}^0 = RT[\chi_1 v_2^2 + v_{2\epsilon} + \ln(1 - v_{2\epsilon}) - \ln a_1] = 0. \quad (11)$$

The relationship between p and v_1 hence turns out to be

$$\ln v_1 = \ln p(1 + v_2\beta)/p_T - \chi_1 v_2^2 - v_2(1 + \beta)/(1 + v_2\beta). \quad (12)$$

Since v_1 is so small that for all practical purposes v_2 equals 1, one derives

$$v_1 = p(1 + \beta)/p_T \exp(1 + \chi_1) = (S_\beta p \rho_2/\rho_1)(1 + S_\beta p \rho_2/\rho_1). \quad (13)$$

Here ρ_1 is the density of the sorbent in the sorbent state and ρ_2 that of the polymer. The sorption in the strained state thus reads

$$S_\beta = \frac{\rho_1 v_1}{p \rho_2 (1 - v_1)} \approx (1 + \beta) \rho_1/\rho_2 p_T \exp(1 + \chi_1) = (1 + \beta)S_0 \quad (14)$$

$$\Delta S/S_0 = S_\beta/S_0 - 1 = \beta.$$

The relative increase of sorption from S_0 of the unstrained to S_β of the strained film is proportional to the ratio of the relative increase of specific volume of the sample divided by the initial fractional free volume. At higher sorption S_0 in the unstrained state and high β , the nonlinear terms

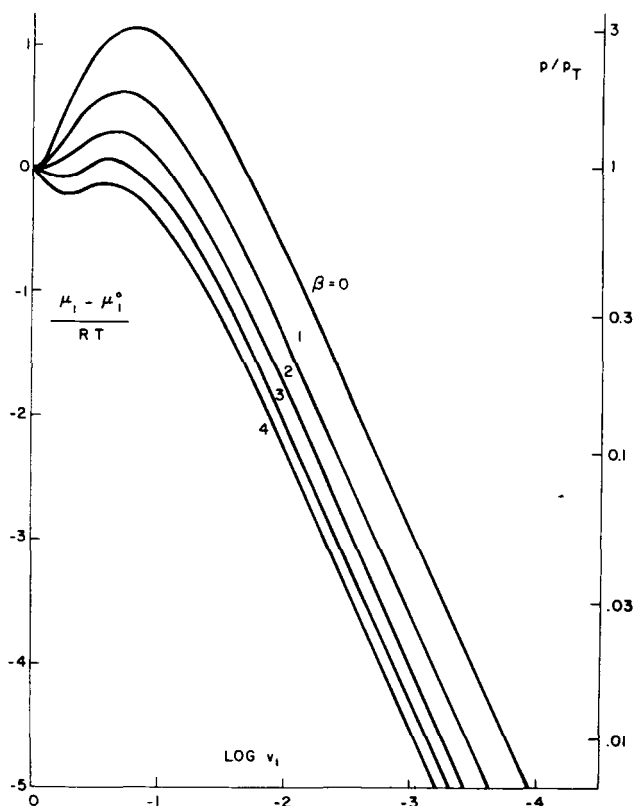


Fig. 7. Chemical potential change of the sorbate in mixing according to eq. (9) with $v_{2\epsilon}$ as function of $\log v_1$ for $\beta = 0, 1, 2, 3,$ and $4,$ and $\chi_1 = 3.$ The right-side ordinate locates the abscissa line for different activities $a_1 = \ln p/p_T$ according to eq. (11).

neglected in this derivation yield a nonlinear dependence of S on $\beta,$ but neither a saturation value nor a maximum with subsequent drop.

The initial linear increase of ΔS with ϵ in Figure 1 can be described as

$$\Delta S/S_0 = \epsilon/2 = (1 - 2\mu)\epsilon/f_0 \quad (15)$$

yielding

$$1 - 2\mu = f_0/2 = 0.01 - 0.04 \quad (16)$$

which is below the estimate $1 - 2\mu = 0.1.$ The deviations from linearity of $\Delta S/S_0$ and higher ϵ can be easily attributed to the incipient plastic deformation.

If the volume fraction of amorphous phase and tortuosity do not change with strain, one obtains for the permeability of the strained material

$$P_\beta = (1 + \beta) \exp[\beta V^*/V_{f_0} (1 + \beta)] \cdot P_0 \quad (17)$$

as the product of $D_\beta,$ eq (7), and $S_\beta,$ eq. (14). It increases faster with β than with D_β and $S_\beta.$ The nonlinear terms in D_β and S_β cause a nonlinear

dependence of P_β on β . But in no case one can derive a maximum with subsequent drop. In a purely elastic deformation yielding an increase of specific volume with strain, the diffusion constant, sorption, and permeability increase steadily or approach a limit (D_∞) with increasing strain. Any deviation from such a behavior must be caused by some other mechanism. According to eq. (1), the main causes are a reduction of amorphous fraction X_a or a decrease of tortuosity factor τ .

Plastic Deformation

At sufficiently high strain, above a few hundred per cent, the permanent plastic deformation drastically reduces the transport properties of the crystalline film. A more detailed consideration of morphology of plastic deformation¹⁴ has shown that at sufficiently high draw ratio, the originally unoriented more or less spherulitic material is completely transformed into fibrous structure. The basic element of this new morphology is the microfibril composed of alternating crystal blocks and amorphous layers bridged by a great many taut tie molecules. They impart to the microfibril the high longitudinal elastic modulus and tensile strength. But their high degree of alignment also reduces the specific volume and hence the fractional free volume of the amorphous component. As a consequence, the sorption and the diffusion constant of low molecular weight permeants drop so drastically that, in the first approximation in the study of transport phenomena of samples with incomplete transformation into fibrous structure, the microfibrils can be considered as an impermeable element of the material.⁷

In such a case, the new, nearly impermeable fibrous structure is imbedded in a matrix of more or less deformed original material. With progressive transformation, the fraction of the spherulitic matrix steadily decreases. The transport of the diffusant will occur primarily through this matrix and will avoid the fibrils. This means an increase in transport path, which causes a reduction in the tortuosity τ , a reduction in transport active volume per volume element X_a , and a probable change in true diffusivity through the deformed matrix D_a .

From small-angle x-ray studies of the initial stages of permanent plastic deformation,²⁷ one knows that in this range the packing of parallel lamellae is quite conspicuously affected. Lamellae parallel to the strain are compressed and those perpendicular to it are partially separated. The amorphous component is oriented particularly by the alignment of tie molecules as a consequence of lamella slip and incipient fracture.²⁸ Among all these effects, the alignment of chains in the amorphous component increases the density of the material through which the transport takes place. It hence reduces S_a and D_a . The lamella slip and rotation interfere with the continuity of amorphous passages, thus lengthening the path the diffusing molecule has to travel and decreasing the tortuosity factor.

The experimental data of Figures 4 and 5 with negative ΔP and ΔD above $\epsilon = 0.20$ require quite a substantial effect of chain alignment and tortuosity over the majority of the sample for overcompensating the increase of

permeability in those sections where the lamellae are partially separated under tension.

As soon as during drawing the stress at any place in the matrix reaches the yield stress, the spherulitic structure starts to be transformed into bundles of parallel microfibrils of the new fibrous structure. The resulting decrease of the deformed matrix reduces X_a , and hence the apparent sorption S , even if S_a remains constant. This effect gradually increases with the draw ratio up to the total exhaustion of spherulitic material. Together with the steady increase of the almost impermeable fibrous material, it reduces the tortuosity factor. In terms of the material transport by diffusion, this means a relatively rapid initial decrease of D_a to a limiting value as a consequence of matrix deformation up to the yield strain. It also means a much more gradual decrease of D and P over a wider range of λ , caused by increased tortuosity (smaller τ) and decreasing X_a , which is in good agreement with the experimental data in Figures 4 and 5. At still larger λ , not investigated in this paper, the microfibrils prevail to such an extent that no coherent path through the matrix between the opposite surfaces of the film is available. The transport properties drop drastically because now the transport has to go through the much more impermeable microfibrils which could formerly be avoided.¹⁹ The strain range of our experiments is far below this critical range. The transformation to fibrous structure in low-density polyethylene is neither completed nor much prevalent at $\lambda = 3$; consequently, the tortuosity factor τ would not drop close to zero.

Intermediate Range

The observations of deformed films as shown in Figure 1 can be to some extent explained as a combination of elastic and plastic deformation which occurs already at very low strains. The former increases the free volume and therefore enhances D_a , S_a , and P as actually observed at very low strains. The plastic deformation appears at larger strains in the early stages before any microfibril formation. It may cause some reduction in free volume and some change in crystal/amorphous arrangement as already mentioned above in the discussion of permanent plastic deformation. The reduction of free volume reduces D_a and S_a , the changes in crystal-amorphous arrangement reduce the tortuosity factor and hence D without affecting S . The combined effect of both types of deformation thus explains in a straightforward manner the initial increase, the maximum, and the subsequent drop of D to negative values. But the steady increase of S with strain contrasting with the decrease of S in drawn samples demands some modification in this model. One has to assume that the plastic deformation that is still recoverable, if one waits long enough, affects the transport properties differently than the permanent plastic deformation of drawn and rolled samples. One can indeed explain qualitatively the curves in Figure 1 by assuming that the recoverable plastic deformation very slightly increases the free volume but significantly reduces the tortuosity factor so that S increases and D decreases in spite of an increase of D_a . Such a large effect in

tortuosity factor is imaginable with larger shearing distortion of amorphous layers between the lamellae which does not result in any volume changes, with partial shear deformation of lamellae themselves, and with rotation of stacks of lamellae which interrupt the coherence of amorphous layers through which the diffusion proceeds.

In the explanation of D and P as functions of increasing strain, one has to pay more attention than anticipated to the apparent increase of S . The free volume concept yields a simultaneous increase of D and S in the case of extension (elastic tension) and a decrease in the case of volume compression which seems to occur in plastic deformation. The tortuosity factor, however, affects only D and not S . One could conclude that the experimental data demand a free volume increase also during recoverable plastic deformation (intermediate range), yielding an increase of S and D with strain, coupled with such a large decrease of the tortuosity factor that it overcompensates the increase of D as a consequence of the free volume increase, thus yielding the observed decrease of D with increasing fraction of plastic strain.

CONCLUSIONS

The transport properties of low-density polyethylene film under strain and after drawing or rolling demonstrate the basic difference between elastic and plastic deformation. In elastic deformation, the sorption, diffusion, and permeability increase with strain. Such an effect can be explained by the increase of the fractional free volume as a consequence of the increase of specific volume of the film under tensile strain. The parameter $\beta = (1 - 2\mu)\epsilon/f_0$ describing the situation is the ratio between the increase of specific volume and the fractional free volume of the unstrained material. The diffusion constant first increases linearly with ϵ and later approaches a saturation value which rapidly increases with the volume of the diffusing molecule. The sorption, derived from the thermodynamic theory of mixing, also increases linearly with ϵ but does not show any conspicuous saturation effect.

The leveling off of diffusivity and permeability with increasing strain and the subsequent drop below the values of unstrained material can be interpreted as a consequence of the recoverable plastic strain. The continuing increase in sorption excludes the interpretation in terms of reduced fractional free volume which would yield a simultaneous decrease of sorption and diffusion. The decrease of diffusion can be achieved only by the reduction of the tortuosity factor, i.e., by an increase of the average path the diffusing molecule has to travel. Such an increase may be caused within the spherulitic matrix by lamella rotation, sliding, and fracture which may block existing passages through the amorphous component. Such deformation is to some extent recoverable after stress removal.

The permanently deformed drawn or rolled fibers show a steadily decreasing diffusivity and permeability but a nearly constant decrease of

sorption. The last effect, which is in sharp contrast with the above-mentioned situation of recoverably strained films, means that the permanently deformed spherulitic matrix has also suffered some unrecoverable specific volume reduction which reduces sorption and diffusion. The main effect, however, is the steady increase of the fibrous fraction which gradually reduces the tortuosity factor to almost zero.

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