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Mobility and solubility of antioxidants and oxygen in glassy polymers. III. Influence of deformation and orientation on oxygen permeability

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Abstract

The mobility of small molecules in a glassy polymer is largely determined by the amount of free volume present in the material. The amount of free volume can be altered by changing the physical state of the polymer. Plastic deformation under compression reduces this amount, whereas the application of a tensile stress increases it. Furthermore, orientation of a polymer introduces an anisotropy in the free volume. The change in free volume was monitored by oxygen permeation experiments. A clear correlation was found between the draw ratio, plastic deformation and stress on the one hand and oxygen permeability on the other. Since the mobility of oxygen is an important parameter for the stabilisation of a polymer against oxidation, the physical state of the polymer can have a significant influence on the service life of the product.

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1. Introduction

In two previous papers [1,2] we have addressed the relationship between the presence of free volume in a glassy polymer and the mobility and solubility of small molecules such as antioxidants and oxygen. It was shown that the diffusion coefficients of several antioxidants could be very well predicted from the free volume present in the polymer. This free volume depends on the nature of the polymer, but also on its physical state. Physical ageing in amorphous glassy polymers reduces the free volume and thus reduces the mobility of antioxidants and oxygen in a polymer. This is very important when the chemical stability of a polymer is concerned. Experimental work showed a direct relationship between the physical parameters solubility and mobility of the antioxidant, and the service life of a polymer product. Furthermore, the service life of a polymer product is affected by the concentration and transport of oxygen in the polymer. This means that polymers that are highly permeable to oxygen can show a lower stability against oxidation.

Generally at moderate temperatures, the permeability of oxygen is sufficient to reach almost the equilibrium solubility over the whole thickness [3]. This means that most of the alkyl radicals initiated during the ageing are transformed into peroxy radicals. Oxygen diffusion-limited effects occur when the oxygen consumption is comparable to the supply by diffusion. This can be the case during processing, when the oxygen concentration is low, but also in accelerated ageing experiments.

From the research on the efficiency of antioxidants it becomes clear that the mobility and solubility of the antioxidant as well as the permeability of oxygen in the polymer are very important parameters in polymer stabilisation. The magnitude of these parameters is governed by the polymer–antioxidant and polymer–oxygen interactions. The physical state of the polymer has an influence on the mobility and solubility of the antioxidant and/or oxygen. This physical state can be changed by e.g. ageing, rejuvenation, plastic deformation, orientation and stress. Most of these phenomena change the free volume in the polymer, which is responsible for changes in diffusion and

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possibly in solubility. Ito et al. [4] presented a clear correlation between the oxygen permeability and the free volume as obtained from positron annihilation measurements in a series of EVOH polymers.

In a previous paper [2], the influence of physical ageing and rejuvenation on the mobility of small molecules has been discussed. In the present paper, a study on the influence of orientation, plastic deformation and stress on the permeability of oxygen is presented.

2. Theory

The free volume present in an amorphous polymer is a very significant parameter determining the mobility of any additives present in the polymer. The diffusion coefficient of an additive is correlated to the free volume by a model developed by Vrentas et al. [1,2,5,6]. The free volume in a polymer can be changed by several pretreatments, such as plastic deformation, orientation and the application of a tensile stress. Changes in free volume due to these pretreatments will be modelled and incorporated in the model describing the diffusion coefficient. In this way, the significance of the physical state of the polymer will be elucidated in relation to the mobility of a stabiliser and oxygen.

2.1. Diffusion and free volume

The diffusion transport of small molecules in amorphous polymers is related to the frozen in ‘free volume’ [7,8]. According to this model, the transport is faster in more open matrices having a higher free volume. The diffusional step is possible by a rearrangement of a relatively large number of structural segments. This collective rearrangement is stimulated by the presence of free volume.

In the previous papers [1,2] the mobility of a series of phenolic antioxidants and oxygen was described based on the free volume model developed by Vrentas et al. The free volume theory is based on the assumption that molecular mobility is determined by the amount of empty space available for a diffusion jump. In the present paper, we only consider oxygen permeability. The solubility of oxygen in polycarbonate at a pressure of 8 atm is roughly 2 mg/ml [9]. For these low concentrations the self-diffusion coefficient can be written as [2]:

$$D_1 = D_0 \exp\left[-\frac{E}{RT}\right]\exp\left[-\frac{\gamma\xi\hat{V}_2^*}{\hat{V}_{\mathrm{FH2}}}\right] \qquad (1)$$

D_0 is a pre-exponential factor, E the critical energy that a molecule must possess to overcome the attractive force holding it to its neighbours, R the universal gas constant and T the temperature. γ is an overlap factor that is introduced because the same free volume is available to more than one molecule (this parameter should be between $\frac{1}{2}$ and 1). $\hat{V}_2^*$ is the specific critical hole-free volume of the polymer segment required for a diffusion jump. $\hat{V}_{\mathrm{FH2}}$ is the free volume present in the polymer. ξ is the ratio of the molar volume of the jumping unit of oxygen to that of the polymer ($= \hat{V}_1^* M_{1j}/\hat{V}_2^* M_{2j}$). M_{1j} and M_{2j} are the molecular weight of the jumping unit of oxygen and polymer, respectively. Since the oxygen permeability measurements are performed at room temperature, the $\exp(-E/RT)$ term can be incorporated in the prefactor, D_{01}. The permeability, P, is obtained by multiplying the mobility and the solubility:

$$P = S \times D_1 = P_{01}\exp\left[-\frac{\gamma\xi\hat{V}_2^*}{\hat{V}_{\mathrm{FH2}}}\right] \qquad (2)$$

In contrast to the strong dependence of the permeability of e.g. CO_2 on the concentration or pressure in glassy polymers [7,10], the permeability of oxygen is hardly pressure dependent. Chen et al. [9] presented a permeability between 1.8 and 2.0 Barrer (= 116–130 $\mathrm{cm^3\ mm\ atm^{-1}\ day^{-1}\ m^{-2}}$) in polycarbonate for pressures up to 9 atm, whereas Sada et al. [11] found a constant value for the oxygen permeability in PMMA for pressures to 30 atm. This means that the diffusion coefficient of oxygen in PMMA and PC is independent of the concentration for the oxygen pressures studied here.

The free volume of the polymer, $\hat{V}_{\mathrm{FH2}}$, depends on the physical state of the polymer: glassy or rubbery [1,2].

2.2. Deformation and free volume

2.2.1. Orientation

When a polymer is hot drawn, several changes can occur. The polymer chains will be oriented in the direction of the applied force. For a semi-crystalline polymer, this can cause an enhanced crystallisation and a reduction of the total amount of free volume. For an amorphous polymer, the amount of free volume increases upon drawing, due to the fact that the polymer was thermally rejuvenated when brought above the glass transition temperature. Furthermore, the polymer becomes anisotropic, which results in an anisotropy of the free volume. The voids in the polymer are elongated and the amount of free volume in the longitudinal direction will be more than in the transversal direction. Xia et al. [12] performed diffusion measurements of a photochromous dye in polycarbonate after elongation of the sample. At 100% elongation (a draw ratio of 2), the diffusion coefficient perpendicular to the draw direction decreases by a factor of one and a half, whereas the longitudinal diffusion coefficient increases by a factor of three. This was explained by a deformation of the free volume. The change in fractional free volume due to elongation above T_g, assuming affine deformation, along ($\Delta f_{\|}$) and perpendicular ($\Delta f_{\perp}$) to the draw direction is given by Xia et al. [12] as:

$$\Delta f_{\|} = \kappa_{\|} f^o (1 - \delta^{-1}) \qquad \Delta f_{\perp} = \kappa_{\perp} f^o (1 - \delta^{1/2}) \qquad (3)$$

f^0 is the fractional free volume before deformation and is equal to $\hat{V}_{\mathrm{FH2}}/\hat{V}^o$. δ is the draw ratio of the polymer ($=2$ for 100% elongation) and $\hat{V}^o$ the specific volume ($=1/$ density). The free volume of the polymer can now be given by:

$$\begin{aligned}\hat{V}_{\mathrm{FH2},\parallel} &= \hat{V}^o_{\mathrm{FH2}} + \Delta f_\parallel \hat{V}^o = \hat{V}^o_{\mathrm{FH2}}[1+\kappa_\parallel(1-\delta^{-1})] \\ \hat{V}_{\mathrm{FH2},\perp} &= \hat{V}^o_{\mathrm{FH2}} + \Delta f_\perp \hat{V}^o = \hat{V}^o_{\mathrm{FH2}}[1+\kappa_\perp(1-\delta^{1/2})]\end{aligned} \tag{4}$$

The parameters $\kappa_\parallel$ and $\kappa_\perp$ incorporate the number of chains and mean distance between two chains in the longitudinal and transverse direction, respectively. Since the oxygen permeability measurements are performed only perpendicular to the film and thus to the draw direction, only this case shall be discussed. Combining Eqs. (2) and (4) result in the following equation for the oxygen permeability of an oriented polymer in the direction perpendicular to the draw direction:

$$P_\delta = P_o \exp\left[\frac{\gamma\xi\hat{V}_2^*}{\hat{V}^o_{\mathrm{FH2}}} - \frac{\gamma\xi\hat{V}_2^*}{\hat{V}^o_{\mathrm{FH2}}[1+\kappa_\perp(1-\delta^{1/2})]}\right] \tag{5}$$

P_o is the permeability of the initial undrawn film.

Another approach for the change in diffusion coefficient upon deformation was given by Vertogen et al. [13]. Based on the theory of liquid crystals, the change in diffusion coefficient was thought to be due to the change in orientation of the rod-like segments. This approach was also used for e.g. the dielectric anisotropy in liquid crystalline polymers [14,15]. The relation for the permeability perpendicular to the draw direction can now be given by:

$$P_{\delta\perp} = S\left[D^*_\parallel \frac{1-P_2}{3} + D^*_\perp \frac{2+P_2}{3}\right] \tag{6}$$

S is the solubility of oxygen in the polymer and is assumed to be not dependent on the orientation. $D^*_\parallel$ and $D^*_\perp$ are the diffusion coefficients of the oxygen parallel and perpendicular to the polymer chains. P_2 is the order parameter, which can be written for affine deformation as a function of the draw ratio according to Kuhn and Grün [16]:

$$P_2 = \frac{2\delta^3+1}{2(\delta^3-1)} - \frac{3\delta^3}{2(\delta^3-1)^{3/2}}\arctan\left[(\delta^3-1)^{1/2}\right] \tag{7}$$

2.2.2. Tensile stress

Applying a tensile stress to a polymer will result in an elongation of the sample. The cross-area of the sample will decrease. The reduction of the dimensions of the cross section depends on the Poisson's ratio of the polymer, ν. This is the ratio of the lateral strain (ϵ_2 and ϵ_3) to the longitudinal extension (ϵ_1 in an uniaxial tensile test and is given by:

$$\nu = -\frac{\epsilon_2}{\epsilon_1} = -\frac{\epsilon_3}{\epsilon_1} \tag{8}$$

The relative volume reduction ($\Delta V/V$) due to the application of a tensile stress can be given by [17,18]:

$$\frac{\Delta V}{V} = (1-2\nu)\epsilon_1 \tag{9}$$

in case of a rubber material, which has a Poisson's ratio of approximately 0.5, the volume reduction is negligible and thus the change in free volume is also very minor. A glassy polymer has a Poisson's ratio below 0.5 (e.g. 0.39 for PC [17]). Therefore, the reduction in volume and consequently in free volume can be in the order of several ml/kg for a uniaxial loaded glassy polymer. The relation for the total free volume in the polymer under a tensile stress becomes:

$$\hat{V}_{\mathrm{FH2}} = \hat{V}^o_{\mathrm{FH2}} + \hat{V}^o(1-2\nu)\epsilon_1 \tag{10}$$

Combination of Eqs. (2) and (9) leads the following relation for the permeability of a stressed film:

$$P_\sigma = P_o \exp\left[\frac{\gamma\xi\hat{V}_2^*}{\hat{V}^o_{\mathrm{FH2}}} - \frac{\gamma\xi\hat{V}_2^*}{\hat{V}^o_{\mathrm{FH2}} + \hat{V}^o(1-2\nu)\epsilon_1}\right] \tag{11}$$

Ruan et al. [17] suggested that large strains increase the free volume and reverse or retard the physical ageing of the polymer. They found an increase in free volume using positron annihilation lifetime spectroscopy (PALS). The intensity of the signal, I_3, remained constant upon straining a polycarbonate sample to 7%, but the lifetime of the ortho-positronium, τ_3, increased from 2 to 2.05 ns, indicating that the size of the voids increases when a tensile stress is applied. They also found that the relative increase in the fractional free volume with strain, measured by PALS is substantially larger than the fractional increase in the bulk volume. Thus the increase in free volume is larger than that produced by an affine expansion of the holes. Xie et al. [19] showed that tensile deformation beyond the yield strain of polycarbonate resulted in a decrease in the PALS lifetime, τ_3, and also a decrease in the intensity, I_3. This is in agreement with the increased density and decreased free volume fraction of a polymer glass when stressed beyond the yield point.

Compression stresses result in an immediate decrease in both lifetime and intensity. The change in free volume upon straining polycarbonate to 3% is $+5$ ml/kg for tensile and -6 ml/kg for compression stress [19].

The change of the free volume upon stress not only has a direct influence on the mobility of the polymer molecules, it also alters the glass transition temperature of the material [20]. An estimation for the glass transition of a strained polymer ($T_{\mathrm{g},\sigma}$) is given in the following relation:

$$T_{\mathrm{g},\sigma} = \frac{T_{\mathrm{g}}}{1+\epsilon_1(1-2\nu)/f^o} \tag{12}$$

f^0 is the fractional free volume and is equal to $\hat{V}_{\mathrm{FH2}}/\hat{V}^o$. Therefore, the influence of a decrease in glass transition temperature must also be incorporated in the study of the mobility of small molecules in a polymer. In the case of polycarbonate for deformations just below the yield point, the glass transition temperature decreases to about 100 °C.

2.2.3. Plastic deformation

For mechanical rejuvenation, the polymer is plastically deformed under compression beyond its yield point, which results in more mobile polymer chains. However, it is found that upon plastic deformation, the density of the polymer increases [19,21,22]. This can be explained by a reduction in free volume. Stachurski [18] showed that straining polycarbonate above 4% resulted in an increase in Poisson's ratio above 0.5. This means that a strain of more than 4% reduces the volume of the polymer. This correlates with the increase in density upon plastic deformation [19,21,22]. It is therefore to be expected that the diffusion rate of small molecules in the polymer decreases upon plastic deformation

For the plastically deformed polymers the shift in free volume upon deformation can be calculated using the following equation under the assumption that the solubility hardly changes with ageing:

$$\frac{P_{\mathrm{def}}}{P_o} = \exp\left[\frac{\gamma\xi\hat{V}_2^*}{\hat{V}_{\mathrm{FH2}}^{o}} - \frac{\gamma\xi\hat{V}_2^*}{\hat{V}_{\mathrm{FH2}}^{\mathrm{def}}}\right] \tag{13}$$

P_o is the permeability of the undeformed polymer and P_{def} that of the polymer after deformation. The value of γ is assumed to be equal to 1.

3. Experiments

Six polymer materials were used for the experiments on antioxidant sorption and oxygen permeability. A selection of these polymers were mechanically or thermally rejuvenated, oriented and stressed, and the change in sorption behaviour was determined.

3.1. Materials

Polycarbonate: Additive free polycarbonate (Lexan 105) was received from General Electric Plastics. 20 wt% solutions were made by dissolving the appropriate amount in methylene chloride (Fluka). After 2 h stirring at room temperature a homogeneous solution was obtained. This solution was cast on a glass plate and after evaporation of the solvent polycarbonate films were obtained, having thicknesses between 55 and 65 μm. The films were dried at room temperature for at least two days, before further experiments were conducted (= PC_G).

Polycarbonate K1 film was produced by Kodak Eastman Chemicals. The 25 μm film was kept at room temperature for 31 years (PC_K).

Polystyrene: Polystyrene (N5000) was supplied by Shell. A film was cast from a 20 wt% solution in methylene chloride. After drying at room temperature the resulting film thickness ranged between 35 and 45 μm (PS_S). A Window film 6003 produced by DOW (25 μm) was kept at room temperature for 16 years (PS_D).

Polymethyl methacrylate: An additive free PMMA sample was supplied by Röhm and Haas. A film was cast from a 20 w% solution in methylene chloride. After drying at room temperature the resulting film thickness ranged between 35 and 45 μm (PMMA).

Polysulphone: Polysulphone film (25 μm), obtained from Union Carbide was kept at room temperature for 33 years (PSU).

Polyethylene: LDPE film (36 μm), obtained from ESSO was kept at room temperature for 30 years (LDPE).

Poly (ester-block-ether): The poly (ester–ether) block copolymer was received as a 25 μm film from DSM. The polyester phase is PBT (65%) and the polyether phase is polytetrahydrofuran (35%) (Pe*b*E).

3.2. Treatment

Thermal rejuvenation: Cast and/or aged samples were thermally rejuvenated. Thermal rejuvenation was performed by heating the polymer above the glass transition temperature for 2 h. This means 180 °C for polycarbonate and 130 °C for polystyrene. For polyethylene, the glass transition temperature is below storage temperature. This means that the free volume in this polymer is in equilibrium and will not change upon rejuvenation.

Plastic deformation: Plastic deformation or mechanical rejuvenation was achieved by rolling the polymer film between the rolls of a two-role mill. In this way the polymer was plastically deformed and the thickness reduction between 10 and 20% was obtained.

Orientation: Films of polycarbonate, polystyrene and polymethyl methacrylate were oriented by heating the material above its glass transition temperature and elongating the film. A maximum draw ratio of about three was obtained. The orientation was frozen in by quenching the film afterwards.

Stress: A tensile stress was applied to the polymer film during oxygen permeability measurements. The stress and the strain depends on the polymer used, but is always kept below the yield point.

3.3. Oxygen permeability measurements

The oxygen permeability was measured at room temperature using the setup depicted in Fig. 1. An oxygen pressure of 7 bar was applied to one side of the polymer film. The increase in pressure at the other side of the polymer film is monitored in time as can be seen in Fig. 2. From the slope of the pressure evolution in time the permeability can be calculated, according to $P = C\Delta p/\Delta t$. C is a constant in which the dimensions of the apparatus and oxygen pressure are accounted for. The permeability, P, is expressed in $\mathrm{cm}^3\ \mathrm{mm}\ \mathrm{atm}^{-1}\ \mathrm{day}^{-1}\ \mathrm{m}^{-2}$. The time t_{L} is the

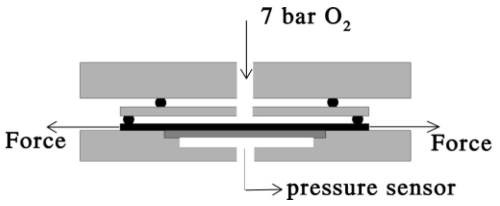

Fig. 1. Schematic representation of the oxygen permeability setup. An oxygen pressure of 7 bar is applied to one side of the polymer film and the pressure increase with time is monitored. A tensile force can be applied to the polymer film.

time lag, which can be used to estimate the diffusion coefficient. This time lag can be obtained from ordinary diffusion equations [23]: $t_L = d^2/6D_1$. Unfortunately, in most of the experiments performed, this time lag could not be accurately measured, since it was in the order of seconds. The dependence of the oxygen permeability on stress was obtained by applying a tensile force to the polymer film during the permeability measurement.

A list of all oxygen permeability experiments is given in Table 1.

4. Results and discussion

4.1. Modelling parameters

For modelling the diffusion coefficients of oxygen a number of parameters are needed. Most of the parameters for polycarbonate are given in the previous papers [1,2]. These are listed in Table 2. Parameters for other polymers studied in this paper are also listed in this table. The values for the free volume of unaged material at room temperature, $\hat{V}^{o}_{\mathrm{FH2}}$ (RT), were obtained from PALS measurements found in the literature [2,28,29]. The molar masses of the jumping units are also found in Ref. [1,27], except for PSU. This value is assumed equal to that of polycarbonate, because it contains the same bis-phenol group.

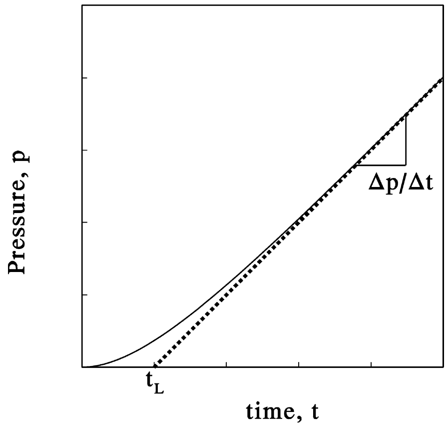

Fig. 2. Pressure evolution with time during the permeability experiments.

4.2. Plastic deformation

The results of the oxygen permeability measurements on various polymers are listed in Table 3. The influence of mechanical rejuvenation is clearly visible.

Plastic deformation (20% thickness reduction) of polycarbonate reduces the oxygen permeability from 55 to 38 $\mathrm{cm^3\ mm\ atm^{-1}\ day^{-1}\ m^{-2}}$. Antioxidant sorption experiments conducted as described in a previous paper [1] showed that the mobility of BHT decreases from 5.9×10^{-16} to $4.4 \times 10^{-16}\ \mathrm{m^2/s}$. Plastic deformation of PMMA (12% thickness reduction) also results in a decrease in both oxygen permeability (from 6.9 to 5.5 $\mathrm{cm^3\ mm\ atm^{-1}\ day^{-1}\ m^{-2}}$) and the antioxidant (BHT) mobility (from 34 to 27 ($\times 10^{-16}\ \mathrm{m^2/s}$)). Combining these results, Eq. (13) and Table 2 with the knowledge of an increase in density upon plastic deformation [19,21,22], it can be concluded that the free volume in polycarbonate is reduced with 0.003 ml/g for 10% thickness reduction and 0.005 ml/g for 20% thickness reduction. That in PMMA decreased with about 0.001 ml/g upon deformation. Positron annihilation measurements on plastically deformed polycarbonate showed a reduction in free volume of about 0.004 ml/g [30], which is consistent with the oxygen permeability measurements. Xie et al. [19] found a

Table 1
Oxygen permeability experiments on polymer samples

Polymer		Plastically deformed	Oriented	Stress applied
PC_G	Cast	O_2		O_2
PC_K	Aged for 31 years		O_2	O_2
PC_K	Thermally rejuvenated			O_2
PS_S	Cast		O_2	
PS_D	Aged for 16 years			O_2
PS_D	Thermally rejuvenated			O_2
PMMA	Cast	O_2	O_2	O_2
PSU	Aged for 33 years			O_2
LDPE	Aged for 30 years			O_2
LDPE	Thermally rejuvenated			O_2
Pe*b*E	As received			O_2

Table 2
Parameters needed for modelling the diffusion and solubility of antioxidants in polycarbonate

	O_2	PC	PMMA	PS	PSU	LDPE	PE*b*E
$\hat{V}_i^*$ (cm^3/g)	1.292 [24]	0.732 [25]	0.788 [25]	0.850[25]	0.691 [26]	0.948 [26]	0.838[a]
M_{ij} (g/mol)	32	195 [1]	188 [27]	164[27]	195[b]	42 [27]	72[a]
$\hat{V}^0_{FH2}(RT)$ (cm^3/g)		0.0583 [2]	0.0347 [2]	0.0506[2]	0.0496 [28]	0.0502 [29]	0.08[a]

[a] The specific critical hole-free volume needed for a diffusion jump and the molar mass of the jumping unit of Pe*b*E are the values for the soft polyether block only, since this is the amorphous part. The free volume is an estimation and not really essential in the following calculations.

[b] The molar mass of the jumping unit of polysulfone is assumed equal to that of polycarbonate.

Table 3
Change in oxygen permeability P ($cm^3\ mm\ atm^{-1}\ day^{-1}\ m^{-2}$) upon plastic deformation

Polymer	Cast		Mechanical rejuvenation		
	P	$\hat{V}^0_{FH2}(RT)$ (cm^3/g)	Thickness reduction (%)	P	$\hat{V}^{def}_{FH2}(RT)$ (cm^3/g)
PC_G	55 ± 4	0.0583	10	46 ± 5	0.0556
PC_G	55 ± 4	0.0583	20	38 ± 3	0.0529
PMMA	6.9 ± 1.5	0.0347	12	5.5 ± 1.3	0.0335

reduction of 0.0054 ml/g in free volume of polycarbonate at a compression strain of 8%. This strain is beyond the plastic deformation of the polymer.

4.3. Orientation

Orientation experiments have been performed on polycarbonate, polystyrene and poly methyl methacrylate. The polymers were stretched above T_g to an elongation of approximately three. In Fig. 3, the oxygen permeability in polycarbonate, polystyrene and polymethyl methacrylate is plotted versus the draw ratio.

The solid lines in Fig. 3 are least square fits using Eq. (5). These fits result in values for the deformation constant $\kappa_\perp$ of 0.052 for PC, 0.053 for PS and 0.055 for PMMA. From these measurements it appears that the orientation has a similar influence on the deformation of free volume for all three polymers.

The permeability measurements could also be fitted using the alternative approach based on the theory of liquid crystallinity. Combining Eqs. (6) and (7) resulted in an alternative fit of the measured points in Fig. 3. A least square fit was used and the fit results are given in Fig. 4.

The least square fits in this figure are equally good as the ones based on the free volume. From the fits it was possible to calculate the diffusion coefficients of oxygen parallel and perpendicular to the polymer chains. These values are listed in Table 4.

Table 4
Oxygen permeability ($cm^3\ mm\ atm^{-1}\ day^{-1}\ m^{-2}$) parallel and perpendicular to the polymer chains

	$P^*_\parallel = S \times D^*_\parallel$	$P^*_\perp = S \times D^*_\perp$	$P^*_\parallel / P^*_\perp$
Polystyrene	286	132	2.2
Polycarbonate	137	79.1	1.7
Polymethyl methacrylate	12.6	4.6	2.7

For the diffusion of BHT as determined according to the method described previously [1,2], the value for the diffusion coefficient perpendicular to the draw direction was found to change from 5.9 to 2.7 ($\times 10^{-16}$ m^2/s) for polycarbonate and from 34 to 13 ($\times 10^{-16}$ m^2/s) for PMMA. A simple conversion to changes in free volume is difficult to give for BHT diffusion, since the diffusion coefficients are concentration dependent as was described in the previous paper [1]. However, it can be stated that the mobility of the small antioxidant BHT decreases in the transverse direction upon orientation of a glassy polymer.

4.4. Tensile stress

The last physical parameter to be varied was the

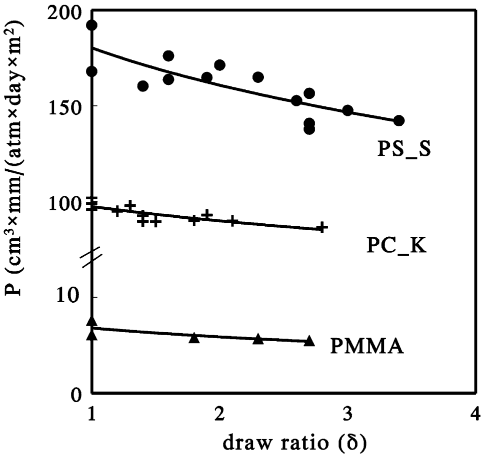

Fig. 3. Oxygen permeability versus draw ratio for polystyrene and polycarbonate and polymethyl methacrylate. The solid lines are least square fits to the data according to Eq. (5).

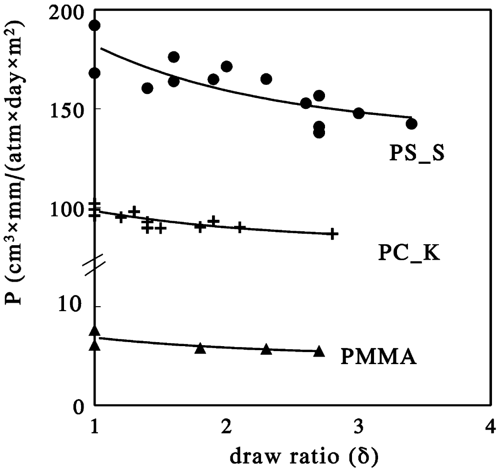

Fig. 4. Oxygen permeability versus draw ratio for polystyrene and polycarbonate and polymethyl methacrylate. The solid lines are least square fits to the data according to Eqs. (6) and (7).

application of a tensile stress. The polymer films submitted to this experiment are listed in Table 5. First mechanical stress–strain measurements have been performed. From these measurements, the Young's modulus and linear region for which $\sigma = \epsilon E$ is valid, was determined. The values for the initial free volume, $\hat{V}^{o}_{FH2}$, are derived from previous permeability measurements and from Ref. [2]. The values for the theoretical Poisson's ratios are also found in Refs. [17,26]. The permeability curves versus stress for the polymers are depicted in Figs. 5–10.

The plots for polycarbonate are shown in Fig. 5. The difference between cast additive free (PC_G), commercial aged (PC_K) and commercial rejuvenated (PC_K(rejuv)) are clearly visible.

The solid lines in Fig. 5 are fitted according to Eq. (11) and a linear relation between stress and strain is assumed. The value of γ is assumed to be 1 and the other fit parameters are listed in Table 5. The dotted lines are correction for the non-linear behaviour, as can be seen in the previous paper [2]. Using the fit parameters from Table 5, the Poisson's ratio of the polymer can be obtained. The resulting values are listed in Table 5. There appears to be a very good agreement between the fitted values and the experimental ones.

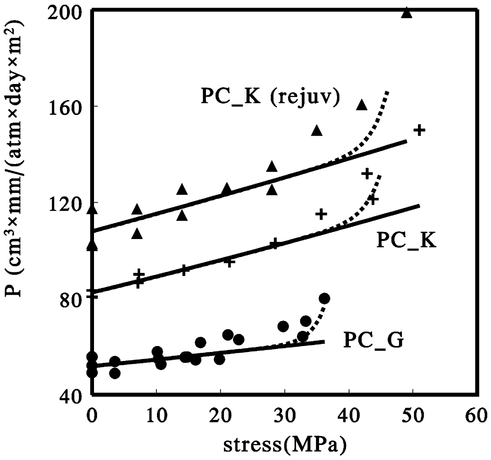

Fig. 5. Oxygen permeability versus draw ratio for polycarbonate. The solid lines are least square fits to the data according to Eq. (11).

This data processing has been done for the other polymers as well. All the glassy polymers follow a more or less linear relationship between stress and oxygen permeability as predicted from Eq. (11), as shown by the solid lines in the figures. The calculated Poisson's ratios are all in the order of 0.4, and in very good agreement with literature values.

However, the correlation between oxygen permeability and stress for the rubbery polymers is not as good as for the glassy polymers. Especially the results of the poly(ester–ether) blockcopolymer are scattered. The solid lines are least square fits and they result in a Poisson's ratio of about 0.5 for both rubbery polymers. This is in agreement with the fact that volume changes in rubbery polymers are very small when they are stressed. The result of oxygen permeability versus stress of the rejuvenated LDPE film were identical as the aged LDPE film, indicating no change in free volume upon ageing of this polymer.

As was mentioned previously in this paper, Ruan et al. [17] found that the relative increase in the free volume with strain for polycarbonate, measured with PALS was markedly larger than the fractional increase in bulk volume. Since the oxygen permeability measurements in our study are very well predicted with changes in bulk volume and

Table 5
Young's modulus, initial free volume, etc. for the permeability versus stress plot

Polymer	E (GPa)	$\hat{V}^{o}_{FH2}$ (ml/g) [2]	$\xi\hat{V}^{*}_{2}$ [2]	P_0 (cm^3 mm atm^{-1} day^{-1} m^{-2})	ν_{exp}	ν_{lit} [17,26]	Linear region (MPa)
PC_G	2.28	0.0583	0.212	55	0.39	0.39	0–20
PC_K	2.29	0.0550	0.212	82	0.35	0.39	0–28
PC_K (rejuv)	1.79	0.0583	0.212	102	0.38	0.39	0–25
PS_D	3.16	0.0466	0.252	96	0.38	0.38	0–45
PS_D (rejuv)	2.69	0.0506	0.252	148	0.40	0.38	0–30
PMMA	2.62	0.0347	0.220	6.9	0.40	0.40	0–20
PSU	2.15	0.0439	0.212	50	0.41	0.42	0–30
LDPE	0.26	±0.05	0.984	132	0.495	>0.49	0–4
Pe*b*E	0.02	±0.08	0.574	404	0.498	>0.49	0–4

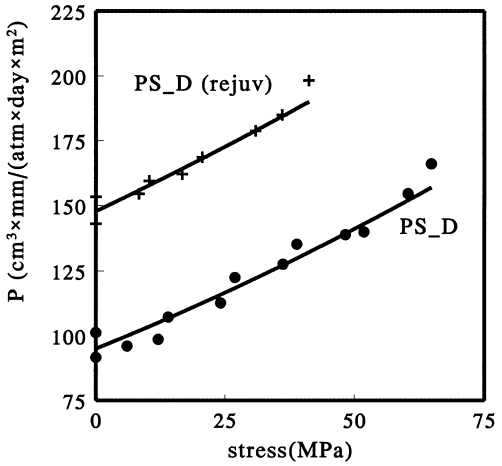

Fig. 6. Oxygen permeability versus draw ratio for polystyrene. The solid lines are least square fits to the data according to Eq. (11).

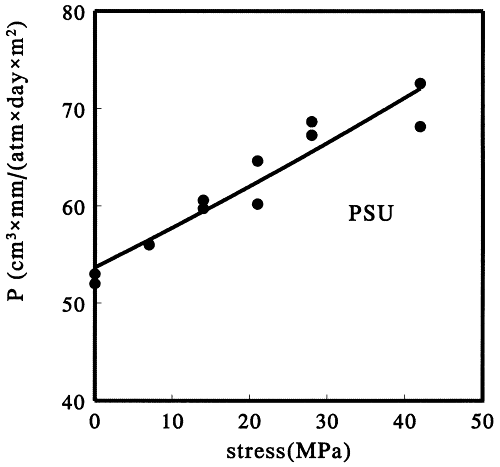

Fig. 8. Oxygen permeability versus draw ratio for polysulphone. The solid line is a least square fit to the data according to Eq. (11).

oxygen permeability is largely governed by the free volume in the polymer, caution is advised with the results presented by Ruan.

4.5. Lifetime predictions

The service life of a polymer product depends on several parameters. Important are the presence of oxygen and antioxidants at the oxidation site. In the previous paper [1], it was shown that the protection time of an antioxidant changes with temperature, since the parameters mobility and solubility are temperature dependent. The present study clearly showed that the physical state of the polymer has a significant influence on the mobility of oxygen and antioxidants. Since the protection time against oxidation is a function of the mobility of antioxidants, it can be concluded that the physical state also influences the protection time of an antioxidant against oxidation. Plastic deformation and orientation decrease the free volume and thus the mobility of oxygen and antioxidants. A decreased mobility of the antioxidant has a positive influence on the oxidation stability, whereas a decreased permeability of oxygen reduces the availability of oxygen to alkyl radicals present in an oxidising polymer. In contrast, the application of stress increases mobility and subsequently reduces the service life.

5. Conclusions

The mobility of small molecules in a glassy polymer is largely determined by the amount of free volume present in the material. In the previous paper [1] it was shown that the change in diffusion coefficient with temperature could be explained very well by the change in free volume. In the present paper, a study is presented about the effect of deformation of a polymer on the free volume. This deformation included orientation by hot drawing, plastic deformation and the application of a mechanical stress. It was shown that free volume and oxygen permeability are closely correlated. Therefore, oxygen permeability measurements were conducted in order to evaluate the

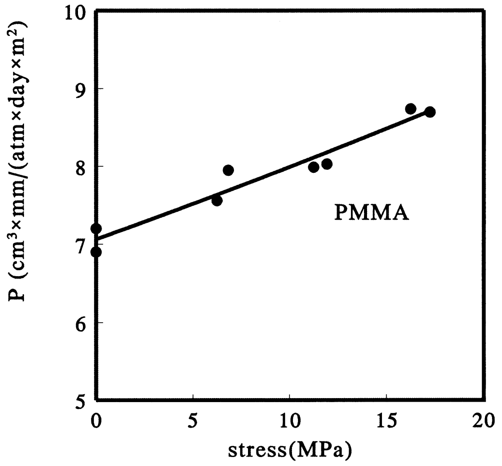

Fig. 7. Oxygen permeability versus draw ratio for polymethyl methacrylate. The solid line is a least square fit to the data according to Eq. (11).

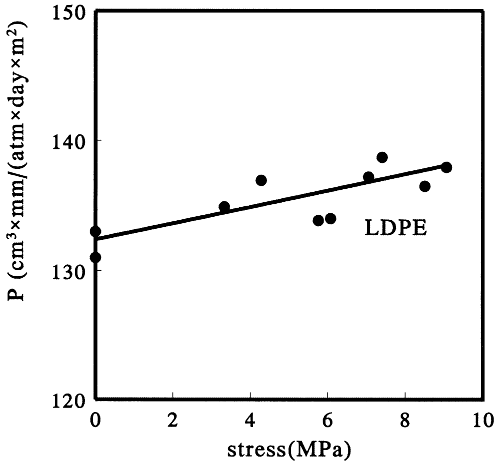

Fig. 9. Oxygen permeability versus draw ratio for polyethylene. The solid line is a least square fit to the data according to Eq. (11).

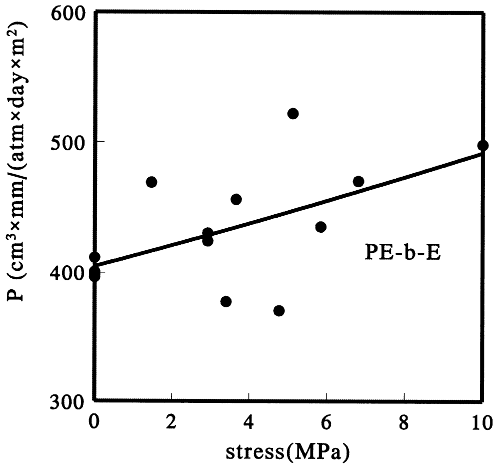

Fig. 10. Oxygen permeability versus draw ratio for poly(ester–ether) block copolymer. The solid line is a least square fit to the data according to Eq. (11).

influence of a pretreatment of a polymer. Some antioxidant sorption measurements were performed as well and they corroborated the results found for the oxygen permeability experiments. The following conclusions can be drawn:

- Plastic deformation or mechanical 'rejuvenation' of a polymer result in a decrease of oxygen permeability. This is consistent with a decrease in free volume [30] and an increase in density [21] as was found by other researchers.
- Orientation of a glassy polymer above the glass transition temperature and quenching the material afterwards changes the oxygen permeability in the transverse and longitudinal direction. Permeability measurements in the transverse direction showed a decrease in permeability with increasing draw ratio. The experiments for polycarbonate, polystyrene and polymethyl methacrylate could be very well fitted assuming affine deformation of the free volume. The value for the deformation constant was found to be comparable for the polymers PC, PS and PMMA. This means that the free volume deforms in the same way upon affine deformation for these three polymers.
- The application of a tensile stress to a polymer film results in an increase in oxygen permeability. This change can be predicted by the increase in bulk volume upon straining, which depends on the Poisson's ratio of the polymer material. A Poisson's ratio of 0.5 for rubbery polymers predicts a constant bulk and therefore no change in free volume and permeability volume upon straining. This was found for polyethylene and a poly(ester–ether) block copolymer. The Poisson's ratio obtained from the permeability experiments for the glassy polymers PC, PS, PMMA and PSU were all around 0.4. This value is in good agreement with literature values.

With respect to the service life of polymer products under thermal stress, it is concluded from the results presented that the lifetime can depend on the pretreatment and service conditions of the product. Since plastic deformation and orientation decrease the free volume and thus the mobility of oxygen and antioxidants, the service life can increase. This is because of the reduced availability of oxygen at the oxidation site and a reduced migration of antioxidant to the environment. Polymers under a low mechanical stress show an enhanced mobility of the small mobile components resulting in an increasing oxidation rate.

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