polymer review

A review of small molecule diffusion in polyolefins

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(Received 16 April 1991; revised 5 July 1991; accepted 27 October 1991)

The transport of small molecules in polyolefins is a subject of both technical and commercial importance. It is technically important because the factors, such as morphology and molecular interactions, that control diffusion are not well determined. Also, the existing theory of diffusion, based on macroscopic parameters, is difficult to interpret in terms of the interactions occurring between the polymer matrix and the diffusants. It is commercially important because the use of polyolefins in applications such as wire coatings, barrier layers and structures is extremely widespread. Failure of such applications can impact the lifetime of large amounts of capital investment. Examples such as wire and cable, landfill liners and automotive components all have expected lifetimes. Previous research indicates that loss of stabilizers may be the major factor in failures and that previous estimates of the loss mechanisms have been inaccurate due to a lack of basic knowledge about the transport properties of polyolefins. This review attempts to cover the previous work on transport in polyolefins and to correlate the results where possible.

(Keywords: polyolefin; diffusion; transport)

INTRODUCTION

This review covers the physical causes of thermal oxidation in polyolefin materials. Physical mechanisms are distinguished from chemical mechanisms of oxidation in which a particular reaction and/or reaction product sequence is the principal focus of study. Chemical mechanisms have been studied by many researchers[1–4]. Physical mechanisms tend to be phenomena that separate the antioxidant materials from the polymer. Physical mechanisms are often based on diffusion, which is dependent on many parameters including solubility, morphology, orientation, thermal processing history, crystallinity and degree of crystallization, solvent extraction, annealing, crystal growth, antioxidant vapour pressure, permeability and morphological structures in the amorphous regions. *Figure 1* shows schematically the effects of these physical processes on transport in polyolefins. Physical changes in a polyolefin's formulation due to its environment have been recognized recently as a prime reason for polymer failure[5,6]. Although the actual failure is due to thermal oxidation, it is the loss of the antioxidants that precipitated the oxidation, not a failure of the antioxidants. There are a number of useful reviews related to oxidative failure of polyolefins[7–11]. Some data on diffusion and solubility of diffusants in polyolefins has been collected, e.g. diffusion constants[12], and solubility parameters[13].

Since most polyolefins are semicrystalline materials, they have a range of behaviour that can be traced to their multiphase structure. Typical polyolefin formulations include polypropylene (PP), low density polyethylene (LDPE) (a randomly branched structure), high density polyethylene (HDPE) (primarily linear chains with few branches and high crystallinity), crosslinked low density polyethylene (CLPE), and linear low density polyethylene (LLDPE) (longer chains with small branches). The variations in morphology due to these chain structure differences contribute to the wide range of physical properties in polyolefins and are a key to their extensive use[14]. Usually they have glass transition temperatures (T_gs) well below room temperature and, as a result, the amorphous regions are rubbery in nature. However, the crystalline domains, which tend to be in the form of small platelets (lamellae) are nearly impermeable to small molecules due to the dense packing of the polymer chains. This mixture of rigid crystallites in a rubbery matrix gives the polyolefins their toughness. Since antioxidant molecules are generally confined to the amorphous regions they will be influenced by changes in crystalline content that occur during annealing. (Fortunately, oxygen molecules are also excluded from the crystalline regions.)

The process of crystallization will tend to exclude defects, such as branches, from the crystalline regions, concentrating them in the amorphous regions. Since tertiary bonded carbons are much more reactive towards oxidation than secondary bonded carbons, it is desirable for the antioxidants to be concentrated in the amorphous region. One concept requiring study is the need for thermal antioxidants to have mobility in order to reach reaction sites. It should be noted that carbon black is an effective thermal antioxidant, and since it has a particle size on the order of 200–300 μm it does not diffuse.

Transport, or diffusion, is a function of structure of both the polymer and the diffusant. This includes both local chemical structure and longer range order, described as morphology. Temperature, solubility,

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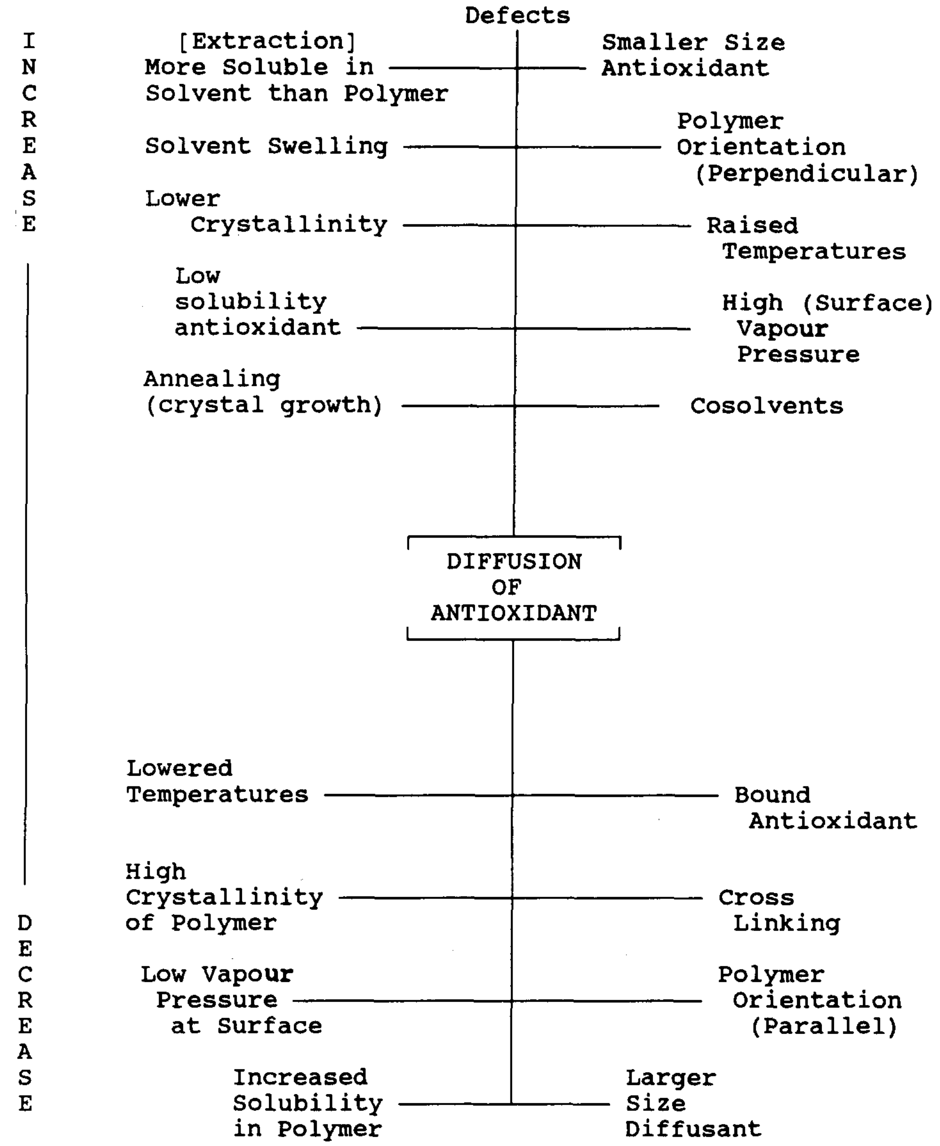


Figure 1 Physical processes that modify antioxidant diffusion. The effects on diffusion rate of a wide variety of modifications to a polyolefin–antioxidant system are shown. The rate increases and decreases are not to scale, but have been shown as indications of the direction of change only

reactivity, orientation and composition modify the transport process. If processing induces orientation, the crystalline lamellae will be aligned, and what was previously a tortuous diffusion path is now aligned, with channels from which rapid depletion can occur. The diffusion can be thought of as classical Fickian, similar to that which occurs in rubbery materials, but with a pathlength variable that is dependent on the morphology. However, there is the strong possibility that regimes exist where other forms of diffusion dominate. This is a consequence of the semicrystalline structure present in polyolefins. Because there are two distinct materials present there is the possibility that a time-dependent behaviour could manifest itself and dominate the diffusion process. A similar situation can occur in glassy polymers, where a time-dependent deformation is induced by the solvation process, giving rise to a dramatic change in the diffusion rate. This question has not been explored for the polyolefins.

The morphology issue is still far from resolved. Many diffusion studies of polyethylene are contradictory, because questions of crystallinity, branch content, processing adhesives and processing history have not been completely described. The study of orientation effects on clean, defined samples may even have problems due to anisotropy in the diffusion rate as a function of measurement relative to the orientation direction(s). Clearly, improvements are needed in defining the samples used.

General conclusions can be summarized. Transport in polyolefins is complicated by many variables. Increasing the crystallinity without introducing defects will tend to reduce the diffusion rates and the equilibrium solubility of small molecules in polyolefins. Branch content is related to oxidation rates, all other factors being equal. Orientation of semicrystalline polyolefins and thermal processing can lead to contradictory results due to a lack of understanding of the morphologies being formed. Increasing molecular size, or rigidity, of the diffusant will decrease the diffusion rates. Increasing the surface-to-volume ratio increases the loss of diffusants if they can volatilize or transfer to a liquid at the surface. Temperature tends to increase diffusion rates, but there is a delicate thermodynamic balance related to phase transformations available to the diffusants. Our understanding of diffusion and solubility needs significant improvement to be useful for quantitative prediction.

DIFFUSION MODELS RELEVANT TO POLYOLEFINS

Current knowledge of the mechanism of diffusion is often empirical, at best. This phenomenological approach tends to impose constraints, from observations of bulk behaviour, on the diffusion models. For example, surface concentration phenomena (which modify boundary conditions and the resulting solutions to the diffusion equation), polymer swelling and crack behaviour, kinetics, and molecular interaction through Flory–Huggins χ parameters, have been incorporated into diffusion models without a detailed knowledge of the underlying chemistry and physics of the molecular interactions. The result is a plethora of models that give results applicable primarily to specific cases. It is also known that the diffusion behaviour is very sensitive to the molecular species involved. This suggests that diffusion studies could be used to study molecular interactions if our understanding of the diffusion process can be improved.

In semicrystalline polymers, diffusion is thought to be confined to the amorphous regions, where the diffusion is primarily classical Fickian in a rubbery matrix[15]. The degree of crystallinity and the morphological organization will have a large impact on the overall diffusion behaviour. This contrasts with glassy polymers where observations of a sharp boundary to the penetrant front are well documented[16–20]. Diffusion with a sharp boundary that also moves with a constant velocity is referred to as Case II diffusion[17,18,20–22]. In both cases, a solvent's ability to diffuse in a polymer can be drastically modified by trace amounts of other molecules[16,22–24]. Additionally, there is evidence that surface concentrations are not simple continuations of adjacent bulk concentrations[20,25–28]. Various forms of 'anomalous' diffusion have been noted[20,25,27,29,30]. Often this refers to deviations from a simple diffusion model in which the Fickian solution shows a linear mass sorption increase relative to $t^{1/2}$ (t = time). The existence of pores, or cracks, has been suggested[22,25,31–34]. In glassy polymers, relaxation phenomena are also occurring, which modify diffusion and are in turn modified by the penetrant concentration[22,26,28,35]. In some cases this is incorporated in models by introducing a concentration dependent diffusion coefficient[36,37]. Another approach has been to incorporate the polymer's mechanical response to the osmotic pressure due to the solvent at the diffusion front[38–41]. At present, no model has been completely successful in predicting all the observations of diffusion[42].

In Case II diffusion the stress between the glassy core and the solvent swollen surface can control the dimensional behaviour of the swelling[17,18]. In extreme cases the pressure differences established by the diffusing material are enough to cause fracture[21,22] and/or stress-induced orientation[43,44]. A related phenomenon occurs under conditions of applied stress, in that crack behaviour and failure times are influenced by solvent concentration[24,25]. However, above the T_g and in the melt, diffusion is usually well behaved compared to that in the glassy state[46–61].

Techniques to follow diffusion include the optical detection of chemical labels[16–18,27,62], mass labels detected using Rutherford backscattering (RBS)[20,28,35], radioactive labels[63–66], Raman microprobe on sections[19], rotating-polarizer ellipsometer[67], laser interferometry to follow thickness changes[68], capillary column inverse gas chromatography[60], weighing[23,27,29,31,32,34,36,46,47,49,50,57,59,61,69–71], mechanical measurement of thickness changes as a function of swelling[17,18,44], birefringence[36,44], n.m.r.[36], u.v. adsorption[36], and the optical density of thin layers[58]. An alternative approach has been to measure steady state transport across a polymer membrane, thereby extracting diffusion constants[48]; one such method relies on the permeation of argon gas through thin films[31].

In order to have a basis for comparison in the following sections it is useful to give a clear set of definitions of what is meant by diffusion. Most models of diffusion start with Fick's second law:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (1)$$

where C is the concentration of the diffusing material, x is the space coordinate normal to the surface and D is the diffusion coefficient (L^2t^{-1}: L = length, t = time). This equation can be modified to incorporate diffusion constants that depend on concentration, inhomogeneous media, and a host of boundary conditions which can assume many forms. In many cases these modifications result in complicated solutions, even for relatively simple models. Further, these empirical models have not been fully successful in modelling experiments using glassy polymers. Although such empirical approaches are essentially ways to incorporate fitting parameters, they do allow some testing of the effects of glassy polymer relaxation processes in diffusion models. A discussion of these approaches is given by Windle[72]. Multiphase materials, such as many of the polyolefins, have not been fully investigated with regard to their diffusion behaviour *versus* morphology. It is helpful, and common, to formalize the experimental diffusion observations according to the following definitions.

Case I diffusion – or Fickian diffusion occurs when the rate of diffusion is much less than the relaxation rate of the polymer. For diffusion into a semi-infinite medium from an infinite solvent source, mass sorption is proportional to $t^{1/2}$ (initial medium concentration is zero and surface concentration is constant). However, for a semi-infinite planar sheet in an infinite solvent source, the $t^{1/2}$ relation holds only at short times, at best[73].

Case II diffusion – diffusion is very rapid compared to the polymer relaxation process. Frequently a sharp solvent front which propagates into the polymer at a constant velocity is associated with Case II diffusion. The resulting mass sorption is then directly proportional to time[21]. It has been assumed that the solvent front demarcates a rubbery shell from a glassy core, and if the mechanical properties of the two states are sufficiently different fracture can occur in the glassy core.

Case III diffusion – non-Fickian, or anomalous diffusion occurs when the diffusion and relaxation rates are similar. Basically all cases that cannot be modelled by Cases I and II are collected as Case III. As an indicator for anomalous diffusion, some descriptions suggest mass sorption is related to time raised to a power between

0.5 and 1.0. Exceptions occur, such as at short times, when this is not a reliable indicator because of the sensitivity of the diffusion equation solutions to boundary and initial conditions.

Fickian diffusion and Case II diffusion models are the extremes of diffusion behaviour. Fickian behaviour is based on a random walk without interactions while Case II has very strong interactions and a moving interface. It should be noted that often the Boltzmann transformation of Fick's second law is cited as evidence that the concentration profile, or gradient, is proportional to $x/2t^{1/2}$ without noting the limited conditions of applicability[72]. Specifically, C must be a function of $x/2t^{1/2}$ only and the boundary conditons must also be functions of $x/2t^{1/2}$ only[73]. The Boltzmann transformation is mainly a technique for changing a partial differential equation into an ordinary differential equation.

For Fickian diffusion, a calculation model has been developed, based on a symmetric structure, for a free-standing film immersed at $t = 0$ in an infinite solution. These results are applicable to having only one face in contact with the liquid phase and an impermeable barrier at the centre of the film (noting the reduction in the thickness). This is equivalent to the free film because there is no net mass transport through the plane at the centre of the free film. The boundary conditions for sorption are[73]:

$$C = C(1), \text{ for } x < -L \text{ and } x > L$$

$$C = C(0) = 0 \text{ for } t = 0, \text{ for } -L \leqslant x \leqslant L$$

where $C(1)$ is the bulk concentration outside the film, $C(0)$ is the initial concentration inside the film. The general solution for this system is:

$$\frac{[C - C(0)]}{[C(1) - C(0)]} = \frac{C}{C(1)} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}(-1)^n \frac{e^{-(2n+1)^2\pi^2 Dt/4L^2}}{(2n+1)} \times \cos\left(\frac{(2n+1)\pi x}{2L}\right) \qquad (2)$$

Mass transport, or sorption, *versus* time is derived from the concentration profile by integrating C from $-L$ to L giving:

$$\frac{M}{2LC(1)} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{e^{-(2n+1)^2\pi^2 Dt/4L^2}}{(2n+1)^2} \qquad (3)$$

where $2LC(1) = M_\infty$, the saturation of sorbed material after infinite time. For the case of desorption the initial conditions are:

$$C = C(1) = 0, \text{ for } x < -L \text{ and } x > L$$

$$C = C(0) \text{ for } t = 0, \text{ for } -L \leqslant x \leqslant L$$

The solution for the concentration gradient (equation (2)) can be rewritten for desorption as:

$$\frac{C}{C(0)} = \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{e^{-(2n+1)^2\pi^2 Dt/4L^2}}{(2n+1)}\cos\left[\frac{(2n+1)\pi x}{2L}\right] \qquad (4)$$

and the corresponding mass desorption is:

$$\frac{M}{2LC(0)} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{e^{-(2n+1)^2\pi^2 Dt/4L^2}}{(2n+1)^2} \qquad (5)$$

where in this case $M_\infty = 2LC(0)$, the initial concentration in the film. These are the solutions for sorption and desorption corresponding to Fickian behaviour. Calculated sorption concentration profiles are shown in *Figure 2*. The corresponding mass sorption curve is shown in *Figure 3*. Similarly the calculated desorption concentration profiles are shown in *Figure 4* while *Figure 5* shows the mass desorption curve.

Figure 2 shows a set of concentration profile curves that plot normalized concentration (concentration/solution concentration) *versus* normalized penetration depth (depth/total thickness). The family of curves are plots done at different values of time (scaled by D/L^2). These curves correspond to concentration profiles that would be obtained for a plane sheet in contact with solvent on one side, or half way through a plane sheet dipped in solvent, if diffusion follows Fick's second law. The normalized mass sorption curves in *Figure 3* are the result of integrating the family of curves in *Figure 2*. The mass

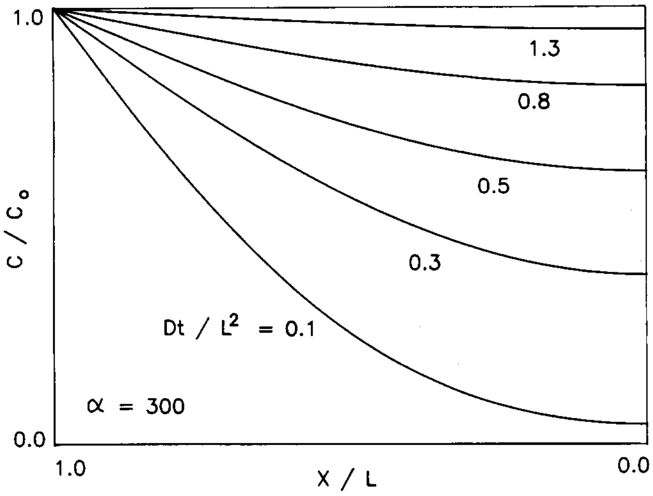


Figure 2 Calculated sorption concentration profiles based on classical Fickian diffusion from equation (2). This is representative of concentration profiles for the standard problem of diffusion in a slab of finite thickness but of infinite extent, with an external source, with no dependence of D on concentration. The concentration is normalized to $C(1)$, the initial concentration external to film, and the interface plane in contact with the solution is at 1.0 while the distance is normalized to the thickness of the slab. Time has also been scaled by D/L^2 for ease of calculation. In the figure C_0 is identical to $C(1)$ in equation (2) the bulk concentration

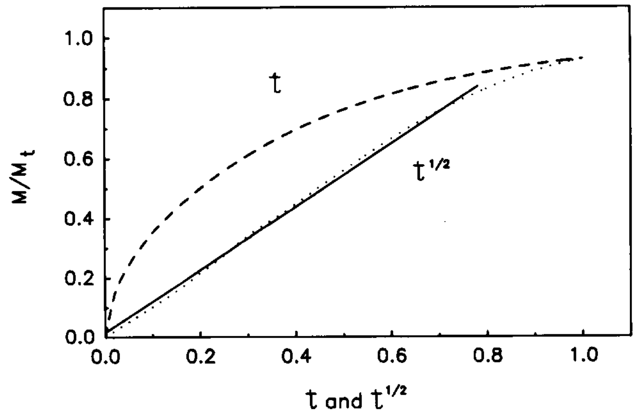


Figure 3 Mass sorption curves calculated for the diffusion problem. Normalized mass is plotted *versus* scaled time. Plot of the mass sorption results are shown *versus* both time (t) and $t^{1/2}$

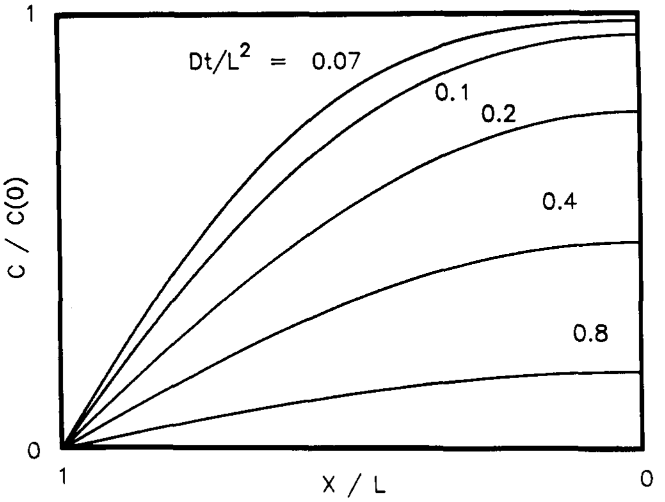


Figure 4 Calculated desorption concentration profiles from the solution in the text to Fick's second law. This is representative of concentration profiles for the standard problem of diffusion from a slab of finite thickness but of infinite extent to an infinite external media with no dependence of D on concentration. The concentration is normalized to $C(0)$, the initial concentration in the film, and the surface of the plane in contact with the solution is at 1.0 while the distance is normalized to the thickness of the slab. Time has also been scaled by D/L^2 for ease of calculation

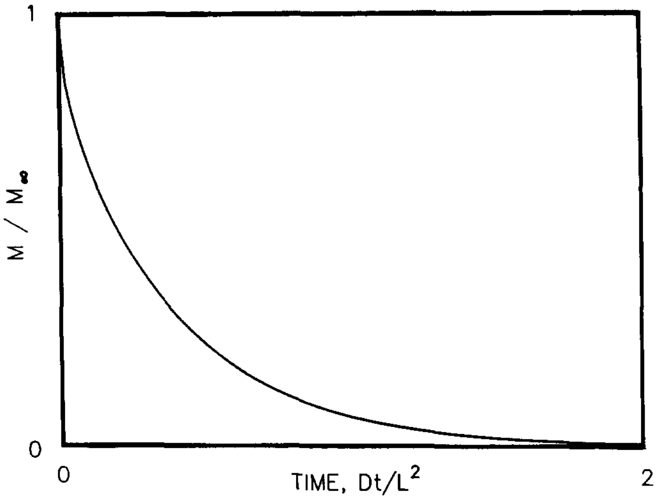


Figure 5 Mass desorption curves calculated for the diffusion problem. Normalized mass is plotted *versus* scaled time. Plot of the mass sorption results are shown *versus* time only

sorption is also plotted *versus* the same scaled time as used in *Figure 2*. Plotting the mass sorption *versus* time was done for ease of comparison with the experimental data, frequently linear in time. When the mass sorption is plotted *versus* $(Dt/L^2)^{1/2}$ the curve is approximately linear up to $(Dt/L^2)^{1/2} = 0.75$ as expected for Fickian diffusion. This is also shown in *Figure 3*.

A number of studies have indicated that diffusion in polyolefins deviates from classical Fickian through a concentration-dependent diffusion coefficient[74,75]. Further, they have specified that D depends on C exponentially[74,75]. It should be noted that this is thought to be valid at low concentrations where Henry's law is valid[75]. (Henry's law states that the vapour partial pressure of solute i, above an ideally dilute solution, is proportional to the mole fraction of i in the solution.) This behaviour can be related to the 'free volume' theories of diffusion discussed below. We have calculated the effect of this on the concentration gradients and mass sorption curves. These are plotted in *Figures 6* and *7*.

Physical evidence of surface effects on diffusion have been detected[20,26–28,65] and a surface interaction is very plausible as part of the explanation of anomalous diffusion. However, a problem with this approach is determining what the surface effect is and how to model it. Further, it cannot be used to model the observations that have been grouped under Case II behaviour.

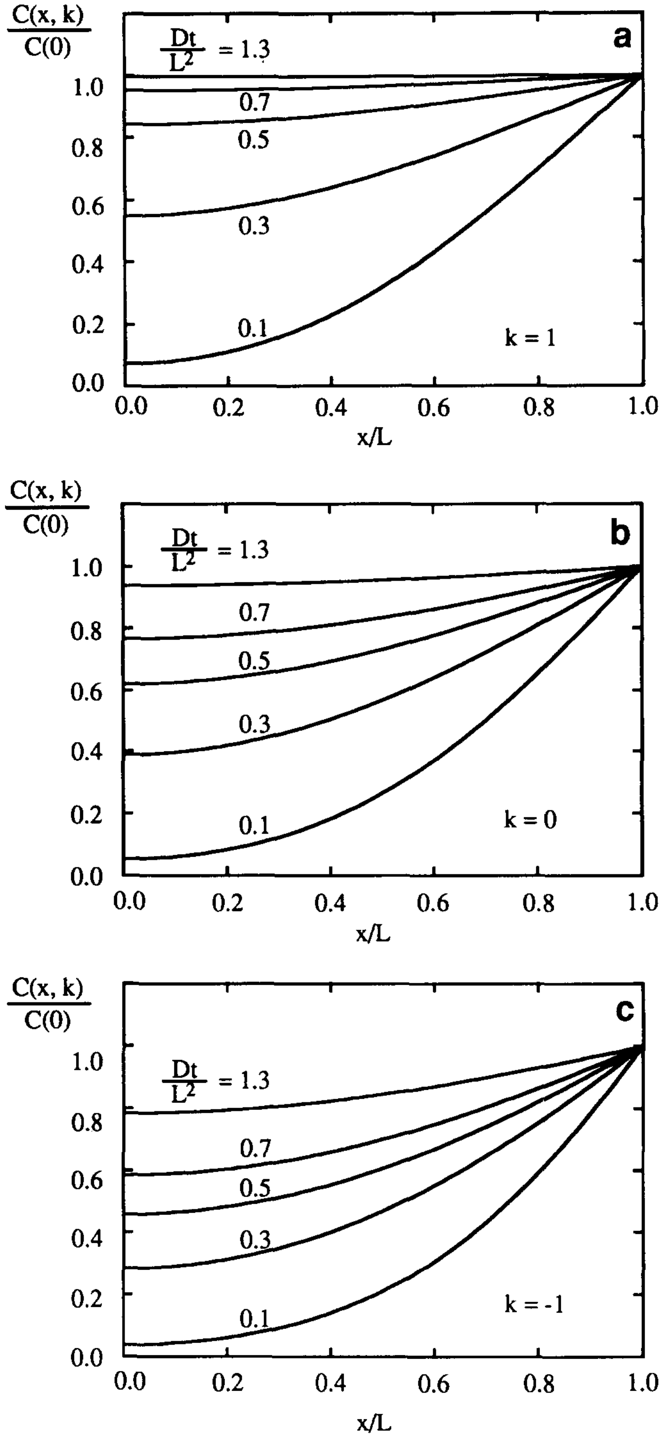


Figure 6 Calculated concentration profiles for sorption where the diffusion coefficient is an exponential function of the concentration $[D = D_0 \exp(kC)]$. Parameters as for *Figure 2*. (a) $k = 1$, curves show an enhancement of the diffusion rate; (b) $k = 0$, curves correspond to *Figure 2*; (c) $k = -1$, curves show a reduction in the diffusion rate. In these figures $C(0)$ is the bulk concentration

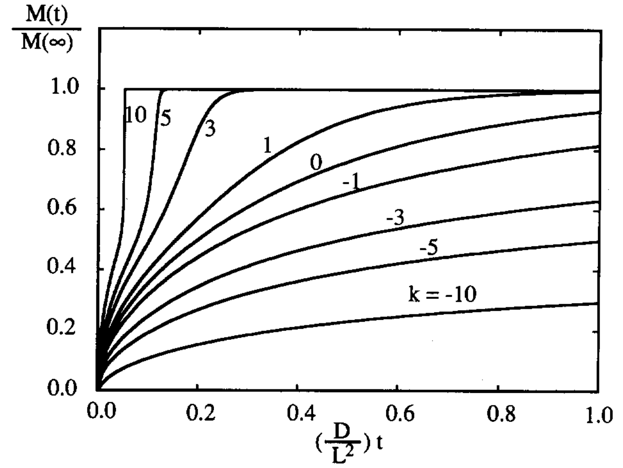


Figure 7 Mass sorption curves for a number of exponential factors. Parameters as for *Figure 3* but showing only the linear time scale

STABILIZER CHEMISTRY AND PHYSICS

Solubility, volatility and loss

Solubility of the stabilizer in the polymer will determine how much additive can exist in the polymer matrix at equilibrium. The solubility depends on both the interactions between the small molecule and the polymer and on the physical states of the polymer and additive[6,13,76].

Modelling solubility has been a difficult problem, since most theory is only strictly applicable to the liquid state (e.g. Hildebrand, Flory–Huggins). This restriction has been circumvented by describing solids as supercooled liquids[13]. Experimental measurements of equilibrium solubilities are equally difficult since they must be done by extrapolation from the liquid phase to the solid phase[77] or by measuring related phenomena, such as diffusion profiles, which can be theoretically related to solubility[6,13].

The standard theory of solubility of an additive in a polymer is calculated, or measured, from the free energy change associated with the transformation of the additive from its equilibrium state as a pure material into the polymer matrix. This is state-dependent, e.g. the solubility of an amorphous additive is greater than that of the crystalline additive. Also, one must correct for the fact that additives dissolve only in the amorphous phase of the polyolefin (i.e. include the degree of crystallinity). It is usual to assume that the (negative) free energy of mixing for the liquid additive at the desired temperature is equal to the (positive) free energy required to convert the crystalline additive to liquid at that temperature. Following the treatment given by Billingham and co-workers[6,76] this can be formulated in more concrete terms. The free energy of fusion , ΔG_f, for a crystalline solid is:

$$\Delta G_f = \Delta H_f - T\Delta S_f \qquad (6)$$

or, using the relation $\Delta S_f = \Delta H_f / T_m$, where T_m is the melting temperature of the additive, gives:

$$\Delta G_f = \Delta H_f\left[1 - \frac{T}{T_m}\right] \qquad (7)$$

Using the Flory–Huggins theory of mixing of liquids with polymers implies that the partial molar free energy of mixing, ΔG_m, can be written:

$$\Delta G_m = RT[\ln \phi_1 + (1 - V_1/V_2) + \chi\phi_2^2] \qquad (8)$$

where ϕ_1, ϕ_2 are the volume fractions of additive and polymer, respectively, V_1 and V_2 are their molar volumes, and χ is the solvent–solute interaction parameter. The first and second terms are the entropy of mixing and the third term represents the non-ideality of the solution due to the interaction between the polymer and the additive. Since $\Delta G_f + \Delta G_m = 0$ and $\phi_2 \approx 1$, one obtains:

$$-\ln \phi_1 = \frac{\Delta H_f}{RT}\left[1 - \frac{T}{T_m}\right] + \left[1 - \frac{V_1}{V_2}\right] + \chi \qquad (9)$$

If χ is constant for a solvent–additive combination at all temperatures then the first term in equation (9) contains the temperature dependence of the solubility of the additive. The χ parameter can be expressed in various forms, such as a free energy, or as a relationship involving solubility parameters of the solute and solvent[76]. A plot of solubility *versus* temperature is shown in *Figure 8* for a benzophenone (Cyasorb UV531) in polypropylene[6]. The transition in slope at T_m can be related to the heat of fusion of the additive[6] by equation (9).

For one system of interest, experiment showed that the χ parameter was not constant with temperature or molecular weight, and it was not possible to extrapolate from solubility measurements at high temperatures in a series of homologous alkanes to polyolefins at room temperature[76]. The study[76] examined a series of phenolic antioxidants in PP and PE, and consequently this is quite significant to actual applications. Since this result disagrees with previous work by Roe *et al.*[77] an experimental concern was that small amounts of polar contaminants could easily change the solubility measurements; however, this was not found to be a factor in this study[76].

Equilibrium solubilities at room temperature for stabilizers are typically less than 1 wt%, and usually much less. However, many formulations incorporate excess stabilizer to retard oxidation during processing. Much of this excess is lost during processing, but the final product is usually supersaturated with stabilizer regardless. The excess often forms glassy inclusions and surface blooming. After time, it would be expected that

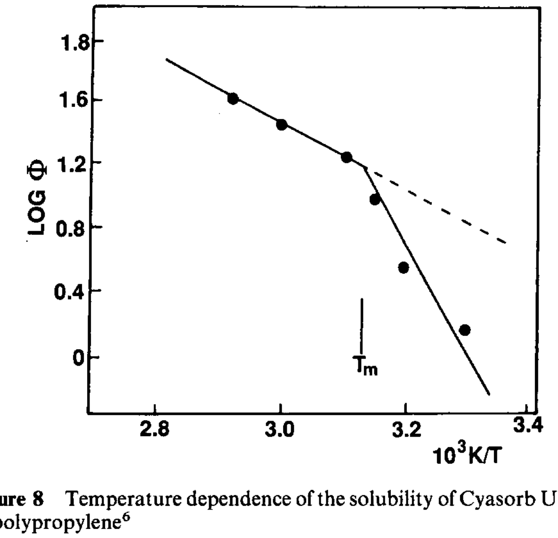


Figure 8 Temperature dependence of the solubility of Cyasorb UV531 in polypropylene[6]

volatilization would remove these excesses and the equilibrium saturation will be reached. However, the equilibrium saturation concentration may not contain enough stabilizer to protect the polymer. There may be additional surface depletion of the polymer if air flow is present through a combination of diffusion and volatilization, which has also been found to be dependent on the polymer geometry. The loss of stabilizers by volatilization has been widely observed[5,78–81]. Additionally, polymers in contact with solvents can suffer further extraction of stabilizer depending on the strength of the interaction between the stabilizer and the solvent. (If the stabilizer is more 'compatible' with the solvent, the thermodynamics of the system will establish a concentration gradient favouring extraction of the stabilizer from the polymer, thereby lowering the free energy of the system.) Many of these effects have been observed experimentally. For example, in LDPE stabilized by Santonox, the extrusion of stabilizer followed by surface crystallization and sublimation was reported[82]. Similarly, the extrusion of 4,4′-thiobis(3-methyl-6-tert-butyl phenol) from polyethylene has been monitored by SEM. In this case it was found[83] that, for a starting concentration of 0.08 wt%, 70% has migrated to the surface after 3 days at 70°C.

Molecular size effects have been hard to prove, possibly because of the complex interactions involved. In one case, the solubility of n-alkanes was found to vary inversely with molecular weight[74], but other studies indicate that solubility is more nearly constant as a function of molar volume or weight[75]. An example of a modifying detail is that the amount of polymer branching has been found to lower the interactions of a solvent with the polymer[84] and, consequently, has large effects on the solubility of the polymer. It is usually hard to draw reliable conclusions because of the sensitivity of transport to the polymer morphology, since the polymer systems used are often not characterized to the necessary degree.

Other additives in the polymer can compete for stabilizer[81]. Pigments and metal stabilizers may be more compatible with the stabilizer and these particulates can then absorb a large amount of stabilizer. This has been observed for carbon black, some metal chelates[7], and some antioxidants[85].

One model of stabilizer loss combines solubility, volatility and diffusion[7]. One very interesting conclusion was that sample geometry is quite important to the loss rate. For Irganox 1010 in LDPE at room temperature it was calculated that 90% of the stabilizer would be lost from a bulk sample after 3500 years. However, in a film 1 mm thick this drops to 22 years, for a 100 μm thick film it is only 2.2 years, and for a 10 μm thick film it takes only 80 days. When combined with higher temperatures and oxidative loss of stabilizer one would expect rapid mechanical failure in wire coatings, as was observed in the field for LDPE coatings. It should also be noted that a fibre (cylindrical) geometry has about half the lifetime of the analogous film geometry for stabilizer loss according to this model. The above loss times were calculated for a model where the surface evaporation rate controlled the process. If the process is diffusion-controlled, where all the material reaching the surface is removed by a solvent, for example, the times for 90% stabilizer loss for bulk, 100 μm and 10 μm films fall to 130 years, 3 days, and 4.5 min, respectively! Rapid migration of oleamide or stearamide to surfaces has been noted experimentally in LDPE at temperatures only slightly above room temperature (35–45°C), but beyond suggesting defects, no mechanism was determined[86]. Experiments on PP also suggest that volatility will be a dominating factor for high surface-to-volume geometries[80]. It should be noted that in addition to dimension dependence, the mechanism of stabilizer loss varies as a function of temperature and oxygen concentration. This also implies that accelerated ageing tests would not correlate with field performance.

Morphology effects on performance

Stabilizer is predominately found in the amorphous regions of polyolefins. *Figure 9* shows a schematic representation of the semicrystalline structure of PE. Generally, it is believed that embrittlement due to thermal oxidation involves chain scission in the amorphous regions. The details of the mechanism are unresolved at present, but the morphology is an important part of the process. Stress on load-bearing interlamellar chains has been suggested as a possible enhancement of the reaction of these chains with oxygen. This leads to radial fracture through spherulites and along the boundaries between spherulites. Alternatively, as the amorphous regions oxidize, shrinkage occurs which may give rise to enough stress to generate and propagate cracks, again radially in the spherulites and along the spherulite boundaries.

Clearly, changes in the spherulite dimensions and organization will affect the growth of cracks in the polyolefin. Most notably, any orientation that might have occurred in processing will channel the crack propagation direction. One relevant observation is that the rapid cooling of the polyolefin surface leads to a surface morphology quite different from that of bulk polymer. The rapid cooling leads to growth of lamellae perpendicular to the surface and organized in long, thin spherulites, also perpendicular to the surface. This is shown in *Figure 10* (from reference 87). As oxidation occurs in the surface it is expected that surface cracks will form, which will grow inward into the bulk rather than randomly. The importance of this in relation to failure of the bulk coating is unclear, but it suggests a mechanism for rapid crack propagation into the bulk[7,87].

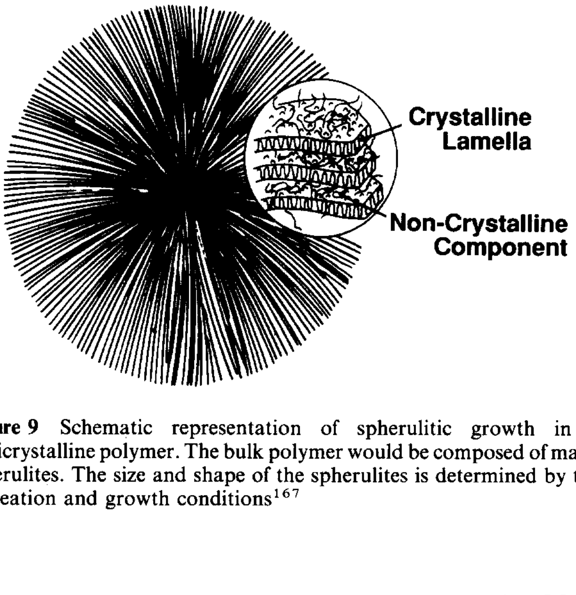


Figure 9 Schematic representation of spherulitic growth in a semicrystalline polymer. The bulk polymer would be composed of many spherulites. The size and shape of the spherulites is determined by the nucleation and growth conditions[167]

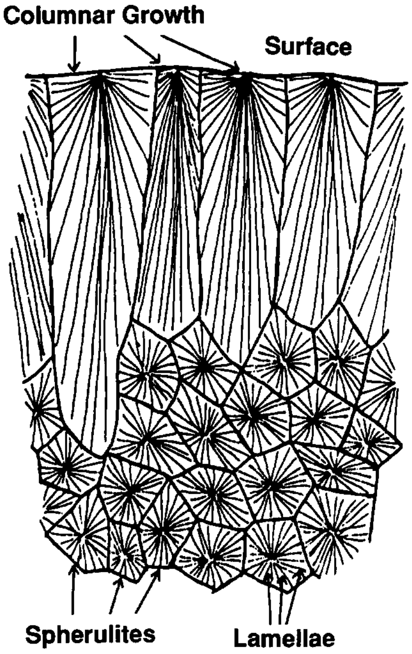


Figure 10 Effect of surface cooling on crystallite and spherulite growth in a semicrystalline polyolefin[87]

Degradation

Oxygen. Oxygen diffuses through the amorphous regions of the polyolefin. The crystalline regions are resistant to both oxygen diffusion and oxidation. Thus the crystallites act as a barrier to diffusion and a two-phase model has been developed for diffusion in polyolefins. However, oxygen diffusion is fast enough that it is not the rate limiting step in the oxidation process for bulk polymer at room temperatures. Only in the case of processing, such as hot extrusion, would one expect an oxygen-diffusion-limited peroxidation reaction[1]. These resulting peroxides will be much more susceptible to thermal or photo-oxidation leading to premature surface cracking. It has been suggested that thermal oxidation has several mechanisms. The initial reaction is affected by polymer structure and the extent of this reaction is governed by the polymer morphology[88]. At later times a slower oxidation rate was observed; the transition between mechanisms was related to the degree of crystallinity[88].

In their study of the effect of structure on oxidation of polyolefins, Hansen *et al.*[88] observed that the greater the number of branches, the more easily the polymer is attacked by the oxygen. Consistent with this is the observation that the order of ease of oxidation is: PP > LDPE > HDPE[88]. However, bulky side groups that reduce the access of oxygen to the chain backbone modify this situation, implying that both the existence of and the accessibility to tertiary carbons are important in the oxidation reaction.

Thermally induced and photo-induced oxidative degradation require oxygen to complete the formation of a variety of peroxides, ketones, aldehydes, alcohols and carboxylic acids of the polymer. Additionally, a variety of oxides of the stabilizers can be formed. The degradation of polymer properties is often tied to the oxidation process. The dielectric properties deteriorate with increasing polar oxidation products[1]. Similarly, mechanical properties also deteriorate, but the time to failure is specific to the given property being tested. An example of this is given in *Figure 11* where the product of ultimate tensile elongation (UE) and the ultimate tensile strength (UTS) *versus* time is plotted with the oxygen uptake *versus* time. The product of UE and UTS is related to embrittlement and ageing. However, failure of the different properties frequently occurs at different oxidation levels[89].

Embrittlement seems to occur at very low levels of oxygen uptake. Observed decreases in molecular weight of the polymer show a decrease of two at embrittlement. Further, remoulding can recover nearly all of the original toughness in PE[7]. The exact mechanism of embrittlement is not proven at present. It is expected that the amorphous region is the main site of embrittlement. The factor that contributes most to embrittlement, whether crack propagation, enhanced reactivities, reactions specific to tie chains or stress from shrinkage, is under investigation[7].

Other mechanisms. Non-oxygen related mechanisms of failure are known. Recently, processing temperatures have been increased to improve production in polyolefin applications. In some cases temperatures as high as 350°C have been used, which can cause pure thermal degradation of polyolefins[9]. Solubility is a factor in another form of degradation. During the melt processing stage in PE, water can be absorbed which condenses on cooling, forming water-filled void defects; these can significantly reduce dielectric performance[9]. Other factors related to polymer degradation, such as mechanical, radiation, hydrolytic, photo- and biodegradation, are discussed by Cassidy and Aminabhavi[8].

OBSERVED DIFFUSION RESULTS

As a function of polymer morphology

In this review we are concerned with the diffusion of small molecules (small in comparison to the polymer molecules) moving through the polymer matrix. Such movement depends, in part, on the polymer morphology, which controls the propagation of a molecule from one site to another and the flexibility of the polymer chains required to cooperate with the movement. Any morphological factors that modify either the structure or the flexibility of the polymer chains will be expected

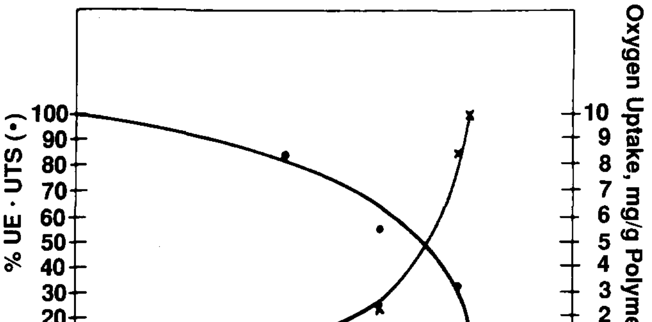


Figure 11 Oxygen uptake (×) and impact toughness index (●) (the product of the ultimate tensile elongation (UE) and strength (UTS)) *versus* time for stabilized polypropylene at 120°C in pure oxygen[9]

to change the diffusivity of the molecule. Since most polyolefins are semicrystalline materials and the primary diffusion pathways will be in the amorphous regions, it is especially important to consider the effects of the crystalline structure on the amorphous structure. Whether by interfacial induced order, or by defining oriented channels, the amorphous material in a semicrystalline polymer is modified by the crystalline content.

Polymer morphology is controlled by both the defect content and the processing history. The number of random branches will modify both the crystalline lamellar thickness and the surface perfection of the lamellae. This occurs during the crystal growth process as the defects are excluded to the lamellar surfaces. The thermal history determines how many defects are actually moved to the lamellar surfaces, and the annealing temperature and time will determine the lamellar thickness. The presence of solvents and/or stress can modify the effects of the thermal history. Solvents can provide additional chain mobility and chain–chain isolation (plastization and solvation). A typical example of this is the growth of single crystal lamellae from dilute solutions. Stress in processing can be applied in a number of ways. Flow during processing can occur in both the melt and solid phases and the resulting induced orientations can have different morphologies. Sample thickness plays a role in morphology because of surface effects on crystal growth and orientation effects due to geometry. Finally, the polymer morphology can be modified by the extent of crosslinking present and the timing of the introduction of crosslinks into the processing history.

Crystallinity and crystal morphology (quenched, annealed, solvent-induced and stress-induced). Polyolefins are typically formed with flat crystalline plates, the lamellae, embedded in an amorphous matrix. The lamellae are connected to each other and to the amorphous material by polymer chains that extend from the lamellar surfaces and edges. This structure is significant to diffusion in the polyolefin due to the extreme permeation differences between the crystalline and amorphous structures. Typical polymer additives, as well as oxygen, dissolve only in the amorphous phase of semicrystalline polymers[63,64,88,90]. In addition, the crystalline regions are much less readily oxidized than the amorphous regions[1,88]. This is supported by the observation that increasing crystallinity in polyolefins reduces solubility, as would be expected if the crystalline regions exclude the penetrant molecules[84]. In fact oxygen uptake can be used to determine the degree of crystallinity in polyolefins based on the transition point between oxidation processes[88]. Thus the crystallites act as a barrier to the transport of diffusants and only the amorphous phase supports diffusion. This should result in an increase in the diffusion path length which in turn causes a decrease in the diffusion coefficient, possibly analogous to a percolation problem. This was exactly the behaviour found by Moisan[10,91] when he studied an antioxidant, Plastanox 2246 (see *Table 1*), as a function of density for PE samples between 50 and 80°C. In this case the diffusion coefficient decreased as the density increased at each temperature. It has also been observed[90] that diffusing ethane molecules in PE tend to travel more rapidly along lamellar boundaries. In unoriented material this leads to a diffusion constant (and solubility constant) that varies inversely with the lamellar thickness. It is worth noting that a surface orientation effect was found in melt crystallized PE; this occurs because thermal cooling first causes nucleation at the surface, which then induces spherulitic growth normal to the surface[87,90,92,93]. A schematic view of this is shown in *Figure 10*.

The preceding results were for unoriented, melt crystallized polyolefins. In a similar way, Michaels *et al.*[92] measured the diffusion constants for helium, argon and ethane in a series of linear PE films which had been subjected to various rates of cooling from the melt followed by subsequent annealing near the melting temperature. A monotonic decrease in the 'geometric impedance' to diffusion with increasing amorphous content of the polymer was observed in films cooled directly from the melt, as in the above work[92]. However, upon annealing these films at elevated temperatures, this impedance was found to decrease markedly, despite an increase in crystallinity. This suggests the formation of thicker lamellae that contain a high concentration of intralamellar imperfections similar to that observed in the annealing of PE single crystals. The anomalous helium diffusion constants that were observed have been explained in terms of a slow diffusion of gas into defects in the crystalline phase from which the larger molecules were excluded. The apparent activation energies for diffusion of argon and ethane were essentially constant, irrespective of thermal history. Also, the so-called chain immobilization factor was not a result of restricted chain-segment mobility via crystalline crosslinking in the amorphous polymer, but was rather a penetrant-size-dependent geometric impedance to diffusion arising from the molecular dimensions of the 'channels' in the polymer.

Constant diffusion activation energies were also measured in mixed ethylene–propylene copolymers (for carbon tetrachloride, benzene and n-hexane diffusants); however, in this work, a free volume model was used to model the diffusion rates[94]. A similar result was found by Lowell and McCrum[93] (HDPE, small hydrocarbons) who further noted that the larger the amorphous content in the quenched sample (faster cooling), the larger the diffusion coefficient, and on annealing, the larger the diffusion constant (assuming annealing to equal densities). They concluded that it is not the amorphous region that controls diffusion, but the 'structure factor', which relates to the length of the path that a diffusant must take between two points in the amorphous material to avoid the blocking crystalline regions (sometimes referred to as a tortuosity factor)[7,95]. An interesting conclusion from the constant activation energies for diffusion in the solid is that the molecular interactions are independent of the crystal geometry and the amorphous fraction[93]. In this case, the measurements were taken as a function of temperature from below the melt to above. It was determined that the melt was actually more liquid-like than the amorphous material (different diffusion coefficients, etc.), but the equilibrium concentration of diffusants are essentially the same, in support of a two-phase model for the solid. The above transport results are supported by a study by Araimo *et al.*[96], where three different thermal treatments (quenched, quenched then annealed, and slowly cooled) on undrawn LDPE were used. It was found that the diffusion coefficient was appreciably influenced by the thermal history. The slowly cooled sample yielded the smallest value, while the quenched then annealed sample had the highest. The concentration coefficient was practically the same for all three samples. This is an indication of the importance of morphology on the transport behaviour in polyolefins.

In contrast, increases in diffusion rates in larger crystalline spherulitic polyolefins may be a sign of large defects forming on the surfaces[97] and in the amorphous boundaries. An indication of this was found in a study by Billingham[6] who used u.v. microscopy, to study the diffusion of a benzophenone in two PP samples (a quenched amorphous sample and a slowly cooled sample resulting in large, crystalline spherulites). It was found that diffusion was a factor of two faster in the more crystalline sample. However, a non-uniform diffusion front with 'fingering' of the additive along the spherulitic boundaries was also observed. Similarly, Klein and Briscoe[98] reported that long chain esters diffuse more rapidly in slowly cooled PE than in quenched samples. However, they explained their results using a self-diffusion model which takes into account entanglement of the diffusant within the matrix. Two concepts are embodied in this description: 'structured' amorphous material and reptation (a snake-like motion of the diffusant through the polymer matrix). It is not clear from smaller molecule work, where reptation is not involved, whether the concept of structured amorphous material is valid, since the opposite trend of smaller diffusion coefficients with increasing crystallinity is observed. A similar size effect has been seen in LDPE for a wide range of antioxidant molecules[91]. In the melt, Klein and Briscoe[99] support a reptation model for diffusants greater than 30 methylene backbone units in length. Polymer structure length scales were related to the diffusant size in a similar study by Moisan[100].

At present there is little evidence to support non-Fickian transport. This is partly due to the quality of the data available and partly to the expectation of Fickian behaviour from analogies with studies of rubbery materials. Most studies of diffusion in polyolefins support classical Fickian behaviour[99]. However, the study of other semicrystalline polymers suggests that the possibility exists. For example, Billovits and Durning[101] examined the non-steady state transport of liquid methanol, acetone, and dimethylformamide (DMF) in thin films of unoriented, semicrystalline poly(ethylene terephthalate) (PET). Three different semicrystalline fine structures were prepared, one by solvent-induced crystallization (SINC) and two by thermal annealing procedures. They found that for films prepared by thermal annealing, the methanol transport is classical, while in SINC films the process shows some non-classical (non-Fickian) characteristics. Further, for both acetone and DMF, the transport is non-Fickian; the non-Fickian effects are consistent with current phenomenological models. They reported that the influence of semicrystalline fine structure on the transport is subtle for the methanol, but very strong for acetone and DMF. This suggests that if the right processing conditions were found, similar behaviour might be possible in the semicrystalline polyolefins. In a supporting study[102] on the effect of orientation on the sorption of toluene by HDPE, the sorption curves suggest that the diffusion behaviour of the oriented samples was non-Fickian.

Branches. The polyolefins can be characterized by their branches. The absence of branches corresponds to HDPE while the existence of random branches corresponds to LDPE. Organized branch structure, such as methyl side groups in PPs, can be formed as atactic, syndiotactic and isotactic structures. The degree of order in the polyolefins can be related to their degree of crystallinity. More subtly, the crystalline lamellar structure is dependent on the branch order and size.

The effect of changing branch content is seen in changes in the diffusion coefficient. Westlake and Johnson[63,64] studied diffusion of stabilizers (2,4-dihydroxybenzophenone and 4-octoxybenzophenone) in polyolefins between 44 and 75°C. The magnitude of the diffusion coefficient was found to decrease in the order isotactic PP < HDPE < LDPE. This is consistent with saying the diffusion rate decreases as the crystallinity increases.

Orientation. Orientation in polyolefins can form by a variety of processes and with different morphological structures that will impact the observed transport behaviour. Sorting the different orientation effects that occur is often difficult because the morphology is rarely directly determined. However, some general correlations are possible.

First, annealing oriented LDPE causes a change in the structure that can increase the diffusion coefficient compared to the unannealed material[96]. Second, time dependence in the transport properties is observed as ageing of the annealed films occurs[103]. As expected, mechanical properties and the density also exhibit an ageing response[104]. Third, when transport was studied in relation to the draw direction it was found that the diffusion decreased parallel and increased perpendicular to the draw[10,105,106]. The effect of drawing PE is schematically shown in *Figure 12*. These points will be discussed in more detail in following sections.

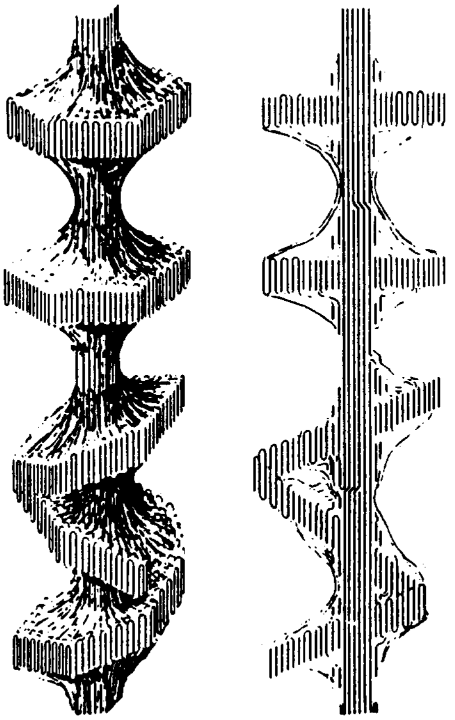


Figure 12 Schematic illustration of draw-induced structure in semicrystalline polyolefins due to mechanical forces exerted on the lamellae by connecting tie-molecules followed by recrystallization[168]

A variety of transport studies have involved LDPE. The conflicting results often arise from slight differences in the preparation of the samples. A clear understanding of the relations between drawing, annealing, ageing and quenching and the morphology and resulting transport properties is yet to be determined. For example, Araimo *et al.*[96] studied the transport properties of quenched, quenched then annealed, and slowly cooled drawn LDPE. They found orientation effects similar to, but less drastic than, the effects on linear HDPE, i.e. smaller sorption and diffusivity and a higher concentration dependence of diffusivity. They reported that the transformation is not yet complete, even at the highest draw ratio of 6, just before the sample breaks. They also observed that, when annealed at 90°C, the drawn sample with free ends restores or even increases the transport properties beyond those of the undrawn sample without causing the fibrous structure to revert to the original lamellar structure. DeCandia *et al.*[103] found that the transport properties of drawn LDPE upon annealing are in good agreement with those for slow crystallization at room temperature (the drawn sample had been annealed with ends fixed). The transport properties did show a time-dependent behaviour, in that immediately after annealing and cooling to room temperature they were found to be similar to those of the undrawn lamellar material, but gradually returned to values characteristic for samples as drawn. However, this results in a very different micromorphology; the initial amorphous, taut tie-molecules are now in the crystalline state, and such a sample is not identical with drawn material at any draw ratio.

Measurements of orientation effects on transport must be evaluated carefully since the transport is no longer isotropic. Moisan[106] studied the orientation effect on the diffusivity of the antioxidants. He found that the rate of diffusion of the stabilizer Irganox 1076 along the orientation direction in LDPE decreased with increasing orientation, and the rate of diffusion perpendicular to the orientation direction increased. Similarly, Eby[90] presented data for the diffusion of ethane in PE together with the results of optical microscopy and of large- and small-angle X-ray diffraction for the same sample. He found that the orientation of the lamellar boundaries with respect to the concentration gradient of the diffusing molecules was important in determining the diffusion rate.

When drawn, HDPE shows a general lowering of the diffusion coefficient to a minimum at a given draw ratio (presumably an average of the parallel and perpendicular components discussed above)[107–109]. Annealing the drawn HDPE reduced the diffusion coefficient and, possibly, changes the diffusion mechanism[102]. Peterlin and co-workers studied the effect of orientation by determining the sorption and diffusion coefficient of methylene chloride in drawn HDPE[107–109]. They found the sorption and diffusion coefficient in HDPE decreased drastically for draw ratios between 8 and 9. Ng *et al.*[110] studied diffusion of toluene vapour in linear PE and found that drawing reduces the diffusion coefficient by a factor of 60 when the draw ratio increases to 10. The orientation effect on reducing the diffusivity of the diffusant was attributed to a transformation of the initially spherulitic material into a fibrous structure composed of aligned microfibrils with taut tie-molecules lying on the outer boundaries[107–110]. Bischoff and Eyerer[102] studied the effect of orientation on the sorption of toluene by HDPE. They found from the sorption curves that the diffusion behaviour of the oriented samples was non-Fickian. The annealing of the samples resulted in a decay of the orientation and a change of the diffusion mechanism. The latter was manifested by the decrease of the exponent n which describes the time dependence of the solvent uptake in the equation:

$$M(t)/M(\infty) = kt^n \qquad (10)$$

where $M(t)$ is the mass sorption at time t, $M(\infty)$ is the saturated mass sorption, and k is a constant.

Ng *et al.*[110] studied the sorption and diffusion of toluene in isotropic and oriented linear PE with mass fraction crystallinity between 0.48 and 0.82 and draw ratio up to 10 at 30°C. They found that the sorbed concentration in the amorphous phase is little affected by crystallinity, indicating that the 'free volume' fractions are roughly the same for all isotropic samples. Drawing reduces the sorbed concentration in the amorphous phase by a factor of four as draw ratio increases to 10. Ng *et al.*[110] also observed, for the toluene–PE system, smaller increases in the concentration coefficient upon drawing compared with the effect in the methyl chloride–HDPE system[107,109]; they explained this as being a result of different strengths of interaction between the penetrants and the polymer. *Figure 13* shows the effect of drawing on equilibrium sorption in different PEs[110]. In all cases the equilibrium concentration decreases with increasing draw ratios.

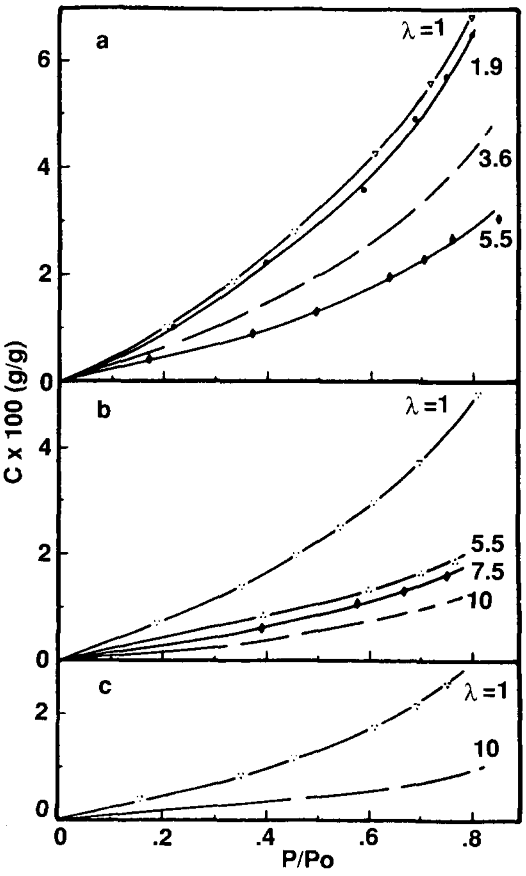


Figure 13 Equilibrium sorption concentration of toluene in linear PE of various draw ratios at 30°C as a function of vapour activity P/P_0. (a) LLDPE; (b) MDPE medium density polyethylene, formed from a 1-butene/ethylene copolymerization; (c) HDPE[110]

Film thickness. Billingham and Calvert[7] have developed a theory that shows an explicit relationship between small molecule loss from a polymer matrix and the polymer bulk geometry. Thinner films have faster loss rates than thick films; likewise thinner fibres lose dopants faster than thick fibres, and fibres of diameter similar to a given film thickness lose dopant at nearly twice the rate of the film. Supporting observations were made by Britton *et al.*[111] who studied the effect of film thickness on the diffusion behaviour of eight organic permeants in HDPE samples using a standard ASTM permeation cell. Their results showed that a decrease in permeation rate was associated with an increase in film thickness (0.8–2.5 mm). The importance of sample geometry is further supported if the assumption that stabilizer loss is related to the oxidative gain is correct. This was shown in the work of Hansen *et al.*[88] in which they observed that overall oxidation occurs less rapidly and less extensively at the centre of thick polyolefin films. Further, the rate of oxidation of thick samples is less than the rate in thin samples even for temperatures where oxygen permeation should be occurring faster than oxygen consumption.

In another study on semicrystalline polymers it was found that the sorption kinetics depend on sample thickness[112]. This also suggests that polyolefins may have non-Fickian transport properties under some conditions. Berens[112] found that in the sorption of organic liquids and vapours by rigid poly(vinyl chloride) (PVC) at high sorption levels, increasing film thickness produces a shift of the kinetics from Case II (linear with time) to Fickian (linear with $t^{1/2}$) with apparent diffusivity values typical of rubbery polymers.

Crosslinking. Crosslinking seems to have little effect on solvent transport until the polymer is deformed. At this point the crosslinking pins the morphology to approximately the original structure. This is demonstrated in a study by DeCandia *et al.*[113] of the transport properties (the concentration of the sorbate in the amorphous component, the zero-concentration diffusivity, D_0, and the exponential concentration coefficient) of drawn CLPE. They found that the drawing dependence of the equilibrium concentration of sorbed methylene chloride in the amorphous component and the zero-concentration diffusion coefficient of CLPE was similar to uncrosslinked branched material of similarly low density. They reported that the main difference is in the concentration dependence of the diffusion coefficient. While the experimental coefficient rises quite drastically in LDPE as draw ratio goes from 5 to 6, the increase in CLPE is small, indicating that the crosslinked material is substantially further from complete transformation of the lamellar into the fibrillar structure than is the case with uncrosslinked LDPE. As a consequence of the higher amorphous content of CLPE, as compared with branched but uncrosslinked LDPE, there is also a higher equilibrium concentration of sorbed methylene chloride in the amorphous component, a concentration which is closer to that of the fully relaxed rubbery structure.

As a function of diffusant

Size and shape. Some common stabilizers with their corresponding molecular structure and properties are listed in *Table 1*. The size of the molecule has a significant influence on the diffusion coefficient[91,106,114,115]: as size increases, diffusion decreases. In addition to overall size, the shape is also important. If the diffusants are of relatively large diameter, the effect of the length of the molecule is less than the effect of the diameter of the diffusant. Conversely, if the diffusants are of comparable diameter but of varying length, the effect of the length will play a dominant role[114,115]. However, as expected, these are not independent variables.

Molar volume correlates with increasing solubility coefficients for classes of molecules such as n-paraffins and monosubstituted benzenes[75]. At the same time low molecular weight molecules have been seen to diffuse as gases while higher molecular weight diffusants behave like polymer chains in self-diffusion[91]. It has been found (e.g. hydrocarbons in LDPE) that the extrapolated zero-concentration diffusion coefficient decreased with increasing hydrocarbon length. Also, the activation energies of diffusion increase with chain length, but are independent of temperature[114]. Similarly, in a study on the diffusion of a series of esters and benzophenones in isotactic PP, the activation energy was found to increase linearly with the number of carbons in the diffusant[116]. This result was modified to a linear increase in the activation energy *versus* penetrant size up to the energy of self-diffusion of the polymer segments[117]. In this case the maximum in the activation energy for diffusion was explained as a result of the increasing compatibility between the larger diffusants and the polymer which lowers the energy of self-diffusion.

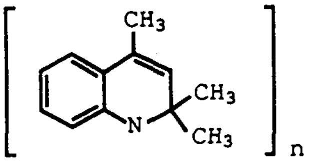
Conversely, for DLTP, Irganox PS800 and *N*-octadecyldiethanolamine in PE, PP and poly-4-methylpentene-1, the activation energy for diffusion was found to be essentially constant, independent of the size and shape of the molecule[118].

Chemical nature. In addition to size and shape, chemical interactions between the penetrant and the polymer (and polymer–polymer, penetrant–penetrant) are important in the transport process. Moisan[91,106] studied the dependence of the diffusion coefficient on length for methyl esters in PE films at various temperatures (20–80°C). For the methyl esters, he observed a decrease in the diffusion coefficient with an increase in length while the activation energies for diffusion increased with increasing aliphatic chain length, demonstrating that diffusant/polymer interactions do modify the transport[106]. The diffusion behaviour is shown in *Figure 14*. The most noticeable effect was the sudden change at a length of about 26–27 Å. Moisan suggested that small molecules diffuse as gases, whereas larger molecules behave like polymer chains in self-diffusion. However, the suggestion was at variance with several earlier studies on the self-diffusion of normal alkanes in low molar weight PE[119,120]. More recently, Moisan's results for small molecules have been duplicated using hydrocarbons in LDPE[114]. Moisan also noticed that only a few of the long chain stabilizers are long enough to follow the self-diffusion model[91]. Klein and Briscoe[98] studied the diffusion behaviour of long molecules through semicrystalline polyethylene. Their results indicated that these diffusants diffuse faster in the slowly cooled matrix than in the fast-quenched matrix, in marked contrast to the behaviour of gaseous diffusants. They applied a self-diffusion model to explain these results.

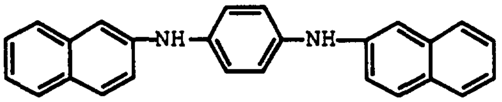
Asfour *et al.*[114] studied the diffusion of saturated

Table 1 Stabilizer additives listed in text (see also ref. 169)

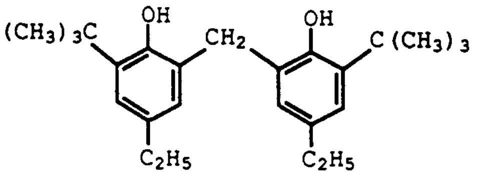
AgeRite resin D (R.T. Vanderbilt Company, Inc.) (ref. 142)
Polymerized 1,2-dihydro-2,2,4-trimethyl quinoline
M_w 172, M.p. 74°C



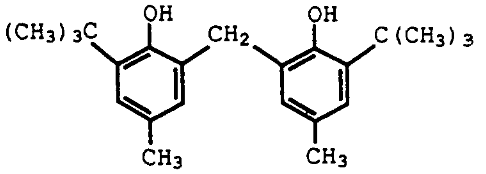
AgeRite White (R.T. Vanderbilt Company, Inc.) (ref. 145)
Symmetrical di-beta-naphthyl-*p*-phenyldiamine
M_w 360, M.p. 224–230°C



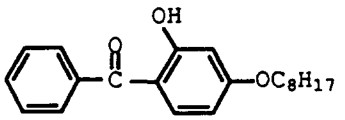
Cyanox 425
[also CAO-5 (Catalin Corp.), Plastanox 425]
2,2′-Methylene bis(4-ethyl-6-tert-butyl phenol)
M_w 368, M.p. 124°C, *L* 13.33 Å



Cyanox 2246
[also Plastanox 2246 (refs 6, 76, 91)]
2,2′-Methylene bis(4-methyl-6-tert-butyl-phenol)
M_w 340, M.p. 131°C, *L* 13.3 Å



Cyasorb UV 531
[also HOB (refs 6, 7, 91)]
2-Hydroxy-4-octoxybenzophenone
M_w 326, M.p. 50°C, *L* 19.37 Å



DLTP, see Irganox PS800 (refs 6, 91, 118)

Eastman Inhibitor
[also OABH (refs 142, 145)]
1,2-Bis(benzylidenehydrazino)ethanedione
M_w 294, M.p. 330°C

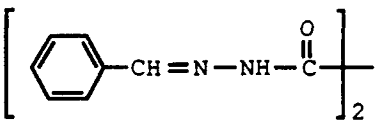
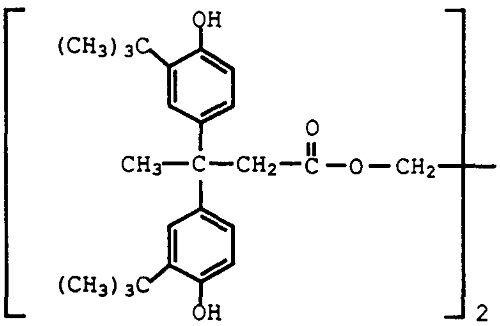


Table 1 *continued*

Hostanox 03 (Hoechst AG, Germany) (ref. 147)
Butyric acid [3,3′-bis(3-tert-butyl-4-hydroxyphenyl) ethylene ester
M_w 794, M.p. 170°C

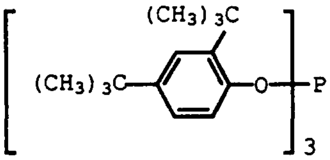


Hostanox SE10 (Hoechst AG, Germany) (ref. 147)
Di-octa-decyl disulphide
M_w 571, M.p. 55°C

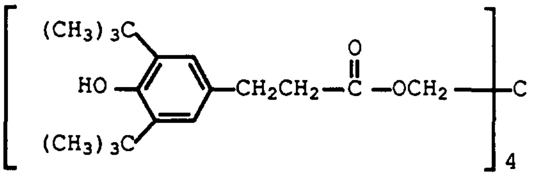
$H_{37}C_{18}—S—S—C_{18}H_{37}$

Hostanox VP PAR 24 (Hoechst AG, Germany) (ref. 147)
See Irgafos 168

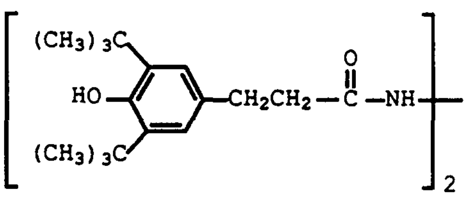
Irgafos 168
[also Hostanox VP PAR 24 (Hoechst AG, Germany) (ref. 147)]
Tri(2,4-ditert-butyl phenyl)phosphite
M_w 647, M.p. 183°C



Irganox 1010
[also THM (Ciba-Geigy) (refs 7, 123), AO-1 (ref. 151), THPM (ref. 91)]
Tetrakis[methylene-3-(3′,5′-di-tert-butyl-4-hydroxy phenyl) propionate] methane
M_w 1178 (1176), M.p. 107–115°C, 118–123°C, *L* 25.88 Å



Irganox MD 1024 (ref. 151)
N,N′-bis[3,5-di-tert-butyl-4-hydroxy phenyl)propionic acid] hydrazide
M_w 552, M.p. 227°C



Irganox 1076 (Ciba-Geigy) (refs 91, 145)
Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyl-phenyl)propionate
M_w 531, M.p. 56–62°C, *L* 35.08 Å

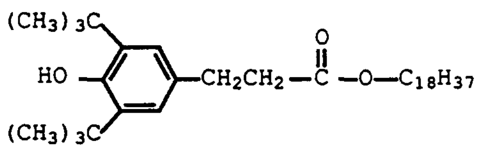
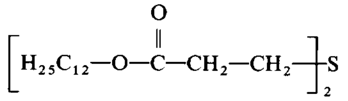


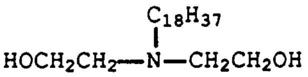
Table 1 *continued*

Irganox PS800
[also DLTP, DLTDP (refs 6, 91, 118)]
Dilauryl thio dipropionate
M_w 514, M.p. 42°C, *L* 42.97 Å



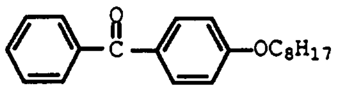
$$\left[H_{25}C_{12}-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2\right]_2 S$$

N-octadecyldiethanolamine (ref. 118)
M_w 357



$$HOCH_2CH_2-\overset{C_{18}H_{37}}{\overset{|}{N}}-CH_2CH_2OH$$

4-Octoxybenzophenone (refs 63, 64)
M_w 310

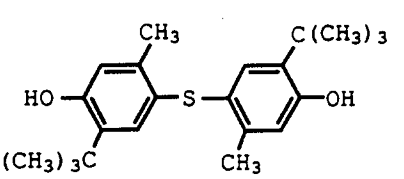


OABH, copper deactivator, see Eastman Inhibitor, OABH (ref. 142)

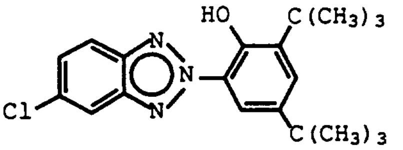
Plastanox 2246, see Cyanox 2246 (refs. 6, 76, 91)

Santonox, see Santonox R (ref. 91)

Santonox R
[also Santonox (Monsanto) (refs 85, 145)]
4,4′-Thiobis(6-tert-butyl-3-methylphenol) or 4-4′-thio bis (6 tert-butyl-*m*-acresol)
M_w 358, M.p. 166°C, *L* 13.89 Å



Tinuvin 327 (ref. 91)
2(2′-Hydroxy-3′,5′-ditert-butyl-phenyl)-5-chlorobenzotriazole
M_w 357



THM, see Irganox 1010 (refs 7, 123)

THPM, see Irganox 1010 (ref. 91)

Carbon Blacks
United BB (United Carbon Co.) (ref. 145)
Monarch 74 (Cabot Corp.) (ref. 145)
  Channel carbon black
Vulcan 9 (Cabot Corp.) (ref. 145)
  Furnace carbon black
Graftol 300 (Sandoz de Venezuela) (ref. 147)
CK3/S (Degusa)
  Sulphur-activated carbon black
  8.7% chemically combined sulphur (ref. 85)
Kosmos BB (United Carbon Co.)
  Normal channel carbon black
  6.5% oxygen (ref. 85)

1,1,3-tri(2-methyl-4-hydroxy-5-t-butyl phenyl) butane (ref. 118)

N-octadecyldiethanolamine (ref. 118)

hydrocarbons in LDPE films. They observed the diffusion coefficient at zero penetrant concentration, D_0, decreases linearly as the penetrant molecular size increases (molar volume = $130-200 \times 10^{-6}$ m^3 mol^{-1} at 25°C). The same relation was found for the diffusion of substituted benzenes and chlorinated solvents in LDPE[115]. The order of the ratio between $\log D_0$ and molar volume is: chlorinated solvents > hydrocarbons > benzenes. Thus when comparing the effect of size of penetrants on diffusion, the molecular structure of the penetrants as well as that of the polymer should be considered. Asfour and co-workers also found that the flexibility of the penetrant molecule has a profound effect on diffusion in LDPE[114,115]. As expected, linear and flexible molecules diffuse more quickly than rigid and unsymmetrical molecules. They observed that, at all temperatures, the values of D_0 for 2,2,4-trimethylpentane (TMP) are considerably lower than the expected values of a linear molecule of the same size[114] and xylenes of almost the same size have different diffusion coefficients[115]. This latter result has been utilized in separating mixtures of xylenes[115]. Britton *et al.*[111] studied the diffusion behaviour of eight organic permeants in HDPE and found the diffusion rate of methylene chloride to be the fastest, with 1,2-dichloroethane second and 1,1,2-trichloroethane third. Absorption behaviour of styrene, toluene and benzene appeared to be almost identical, suggesting that the substituted benzene derivatives behave like the parent benzene molecule, and their diffusion rates were comparable to that of dichloroethane. Both naphthalene and 2-methyl naphthalene demonstrated the lowest diffusivity among the studied permeants.

McCall *et al.*[121] studied the solubility and diffusion of water in LDPE by means of desorption experiments. They have developed a model to describe the bound oxygen dependence of solubility and diffusion coefficients. They reported that physically the oxygen groups act as traps that are strong enough to bind the water but not so deep as to remove the water from the diffusion process. They found that hydroxyl, hydroperoxide and carboxylic acid groups form the strongest traps, ketone groups are weaker and ester groups exhibit negligible trapping. They also reported that permeation is unaffected by bound oxygen.

Berens[112] studied the effect of activity and solvent strength of a number of organic penetrants (χ values = 0.5–1.0) upon their sorption kinetics and equilibrium values in PVC by gravimetric vapour and liquid sorption experiments at 30°C. He reported that T_g

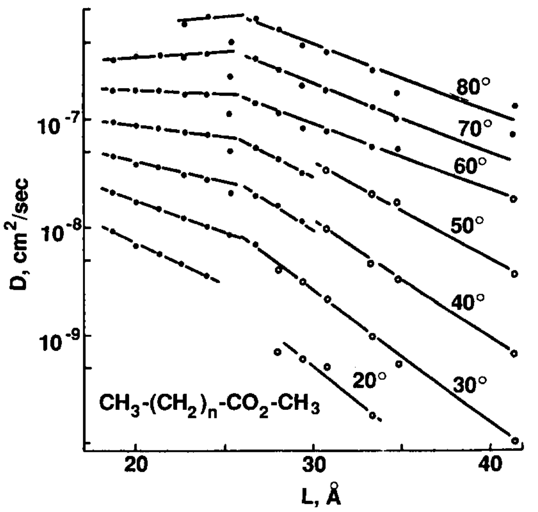


Figure 14 Diffusion coefficient of methyl esters as a function of molecular length at various temperatures. Solid symbols are for values of *D* below the melting temperature of the diffusant[10,106]

was depressed in direct proportion to the volume fraction of solvent absorbed and defined C_g as the composition corresponding to a T_g of 30°C. He observed that when the equilibrium sorption is less than about $C_g/2$, kinetics are Fickian, with the very low diffusivities typical of the glassy state. For sorption values between $C_g/2$ and C_g, anomalous kinetics are observed. When the sorption is greater than C_g, transport in the thin PVC films follows Case II kinetics; however, this changes to Fickian for thicker films.

As a function of temperature

McCall and Slichter[74] studied the diffusion of small molecules in both LDPE and HDPE as a function of temperature and pressure. Increasing temperature seems to increase the diffusion coefficient linearly for a given molecule. Temperature increases have also been found to correlate with accelerated solvation in a PE/benzene system under stress[122]. Similarly, Britton *et al.*[111] studied the diffusivity of eight organic permeants in HDPE at 22 and 50°C and found diffusivity values to increase with an increase in temperature. In contrast, in a study of saturated hydrocarbons in LDPE films, Asfour *et al.*[114] found that the dependence of D_0 on the penetrant size decreases with increasing temperature and becomes almost insignificant at 50°C. This was understood as the consequence of an increase in the 'free volume' of the polymer matrix resulting from an increase in temperature. In the temperature range 25–50°C, the activation energy for diffusion, E_d, was found to be independent of temperature. An increase of E_d with increasing size of the penetrant molecule was observed. For each additional CH_2 group, they reported an increase of about 7.5 kJ mol^{-1} in the activation energy. Due to its larger diameter, TMP has a higher E_d than its isomer n-octane of a similar size. It is expected that any modification of the molecular mobility of the diffuser or of the polymer matrix will affect the diffusion kinetics, and that every first order or second order transition will cause a change in the activation energy of diffusion.

Generally, diffusion is more rapid in the polymer melt and in the rubbery state than in the glassy state. Moisan[91] observed that the diffusion coefficients for several antioxidants did not increase linearly when plotted against reciprocal temperature, as would be expected from the Arrhenius relationship. He found that a discontinuity occurs in the Arrhenius plot at the melting points of the stabilizers and the activation energy is lower at temperatures above the discontinuity. Lowell and McCrum[93] reported that the diffusion characteristics of small molecules in molten PE and in the amorphous fraction of the solid are quite different. They found that the amorphous fraction exhibits higher activation enthalpy and higher diffusion coefficient than the melt, i.e. the melt shows liquid-like characteristics when compared with the amorphous fraction. Kuck[123] studied the equilibrium solubility of a phenolic antioxidant, Irganox 1010, in LDPE between 25 and 80°C. The melting range for Irganox 1010 is 107–115°C. Kuck found that a discontinuity occurs at about 50°C, which was attributed to a change in physical state of the antioxidant from a more soluble amorphous form to a less soluble crystalline phase. If a large portion of the stabilizer is in a supersaturated state or in the form of precipitates and not in solution in the material, it is expected that the stability of the stabilizer will be reduced, and the stabilizer diffusion is enhanced.

Temperature changes can modify the diffusant mobility in polyolefins even when the temperature is below the melt of the polymer due to molecular weight dispersion. Gilroy[124] studied the melting behaviour of LDPE, HDPE and PP by differential thermal analysis (d.t.a.). This study was motivated by the observed increase in resistance to oxidation of stabilized HDPE and PP. The results suggest that the poor stability of LDPE is due to the existence of a molten fraction of LDPE below the melt (40–110°C) with subsequent easy diffusion of stabilizers out of the bulk polymer. The effect is accelerated by secondary crystallization upon annealing (exclusion of non-PE species from the growing crystals) and the formation of microvoids within the LDPE (resulting in a more effective diffusion path). The existence of a pure molten phase and recrystallization below the melting temperature was not evident in HDPE and PP.

As a function of cosolvents

Westlake and Johnson[63,64] investigated the rate of loss of stabilizers (2,4-dihydroxybenzophenone and 4-octoxybenzophenone) in HDPE and LDPE samples immersed in water at 44°C. For 2,4-dihydroxybenzophenone, the diffusion coefficients are somewhat greater when water is present for the LDPE and considerably smaller in the case of HDPE. For 4-octoxybenzophenone, the rate of loss of the stabilizer from both HDPE and LDPE was found to be extremely low, as a result of the octoxy substituent and the resulting increase in compatibility between the stabilizer and polymer.

Fleischer[125] measured the diffusion coefficient of each component in benzene–cyclohexane and benzene–toluene mixtures in LDPE with deuterated and protonated diffusants using the pulsed field gradient n.m.r. technique. He found the diffusion coefficient of the diffusant under consideration was increased by the other diffusant. He also reported, for the benzene–cyclohexane mixture dissolved in PE, that the diffusion coefficient of benzene is about twice that of cyclohexane and is nearly independent of the mixture ratio and the concentration.

As a function of small molecule concentration

Although there seems to be no general consensus, it is often found that the diffusion coefficient depends on the concentration of the solvent[74]. Rogers *et al.*[75] studied the sorption and diffusion of different organic vapours in three different types of PE. They observed that the sorbed vapour concentration, C, is proportional to the amorphous content of the samples and the diffusion coefficient, D, decreases substantially with increasing crystallinity. At low sorption concentration, D increases exponentially with C, and this relation can be explained by a free volume theory[75]. Essentially[126]:

$$D = D_0\, e^{\Gamma C} \tag{11}$$

defining

$$D_0 = A\, e^{-B/f_2} \tag{12}$$

and

$$\Gamma = \frac{B(f_1 - f_2)}{f_2^2} \tag{13}$$

where A and B are constants and f_1 and f_2 are the fractional free volumes of the pure diffusant and the pure polymer, respectively. Therefore, the concentration coefficient, Γ, is proportional to the interaction between the diffusant and the matrix and inversely proportional to the square of the free volume of the polymer matrix. It is thus expected that the concentration dependence will become stronger with an increase in crystallinity and an increase in the interaction between the penetrant and the polymer. At temperatures less than 100°C above T_g, a strong concentration dependence of the diffusion coefficient at low solvent concentrations in the polymer–solvent systems was reported by several authors and, in some cases, the dependence was explained using the free volume theory of diffusion[103,126–133]. Vrentas *et al.*[134] presented diffusivity data for the *o*-xylene/PE system in the temperature range 125–175°C, which is more than 200°C above the polymer T_g. They found that the diffusion coefficient increases slightly as the solvent concentration increase nears the pure polymer limit. Further, the concentration dependence of the diffusivity, for this system, is different from that typically observed for polymer–solvent systems. However, it is consistent with a free volume theory of diffusion. In this version of the free volume theory hole concentrations are an explicit component as well as interaction parameters.

The free volume theory has been mentioned several times without details. One reason for this is that there is no single theory. Also, it has not been shown to hold generally (i.e. adjustable parameters are used to fit experimental data). Finally, direct measurements of voids in the amorphous phase of PE samples, ranging from 20 to 69% amorphous, have mean sizes[135] of 0.119–0.176 nm^3. This corresponds to cubes of 4.9–5.6 Å on a side. Small molecules could be accommodated, but many stabilizers have larger molar volumes and could not easily diffuse in such a matrix by free volume pathways.

DIFFUSION AND TRANSPORT EFFECTS IN APPLICATIONS

A major use of polyolefins is in wire and cable coatings. Problems that have occurred in such coatings will be used to illustrate typical application problems that can be related to transport. First, extrapolation of lifetimes from high temperature testing is not straightforward. Several models used for predicting polymer lifetimes and the problems that can occur in actual application have been reviewed[9]. Discovery of differing rates of oxidation[88,136] dependent on polymer morphology, structure and temperature suggest that extensive characterization of the polymer sample or system is needed to attempt lifetime predictions at lower temperatures. Deviations of the oxidation rate as a function of temperature from the Arrhenius equation have been observed[1]. A particular example of this is the case of carbon black. High temperature studies (above the polymer melt) suggest rapid failure when extrapolated linearly to field temperatures. However, the relationship between inverse temperature and the logarithm of the oxidation induction time becomes highly non-linear at lower temperatures and, as a result, carbon black is actually an outstanding antioxidant below the melt[1]. Another feature that is changing is the structure of the amorphous region as a function of oxidation. It becomes more crystalline as the entanglement constraints are released by chain scission and the short chains can reorganize. This is shown in *Figure 15*. Additives also significantly complicate reliable predictions[81,83,137]. Another complication is the choice of what constitutes failure. In wire it is often the cracking of insulation[138], which can be unpredictable; when LDPE that had failed earlier by cracking was aged further, it was found to no longer crack when stressed[139]. This was demonstrated to involve the formation of crosslinked structure in the LDPE which was still extensively oxidized.

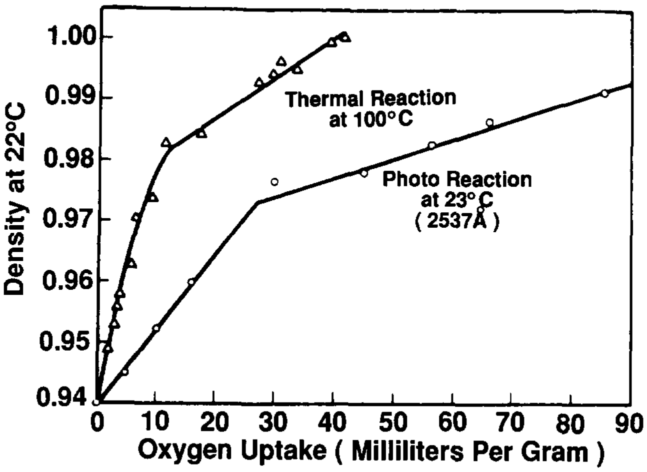


Figure 15 Effect of thermal oxidation (△) and photo-oxidation (○) on the density of linear polyethylene[9]

Additives and contaminants modify the stability of the polyolefin. The oxidative stability of LDPE stabilized with 0.1% Santonox as well as with 0.1% Irganox 1010 is compromised in the presence of copper, which acts as a very effective catalyst for the oxidation of the system. Further, the oxidative stability of LDPE was increased by adding copper inhibitors (e.g. Oxanilide)[137]. Pigments were shown to reduce oxidative stability[81,137]. It was also noted that the stability of black wire is an order of magnitude greater than the green or slate coloured wires. However, this is no longer the case; there is little observed difference in lifetimes due to the colouring additives[138–140]. Additionally, it was shown that the inclusion of 5% of a low molecular weight PP, used as a processing aid, causes a substantial decrease in the oxidative stability[137]. Toughening agents can also sensitize polyolefins to photo-oxidation[141]. Even above the melt the choice of stabilizer additives can easily vary the oxygen induction times by an order of magnitude[142].

Physical defects can also contribute to failure. Rarely considered, but critical to some applications, are tracks from heavy ions. These tracks form channels compatible with water and consequently have much higher transport rates than bulk polymer[143].

The possibility of stabilizers that are fixed (by size or chemical attachment) in the polymer matrix and consequently not subject to loss by diffusion are of interest[85]. Carbon black has been the main example of this type of stabilizer but it has not been acceptable since it cannot be easily colour coded for multi-wire cables. However, Verne *et al.*[144] reported a new type of stabilizer, which when incorporated into PE, is made non-extractable by processing above 210°C. The new stabilizers, which are a group of nickel derivatives of hydroxybenzyl phosphonic acid, function as both antioxidant and copper inhibitor.

Combinations of stabilizers that may address different oxidation processes have proven to be more effective[81]. Gilroy[145] evaluated the stability in LDPE wire insulation formulated in 227 different antioxidant and metal deactivator combinations. Insulation stabilized with Santonox R failed in 6–9 months and that stabilized with Irganox 1010 and OABH failed in 16–22 months. AgeRite White with metal deactivators and tertiary stabilization systems were found to be equal to or better than 1010/OABH systems. Kokta[142] studied the oxidative stability of HDPE and LDPE using the d.t.a. induction time method; the best combination of PE stabilizers was found to be 0.05% Irganox 1010, 0.05% AgeRite Resin D, and 0.1% OABH as a copper deactivator. Choudhary *et al.*[146] evaluated the relative effectiveness of five stabilizers (Cyasorb 531, Irganox 1076, Irganox 1024, Tinuvin 327 and Tinuvin 770) on the photo-oxidation and thermal ageing of PP by following changes in mechanical properties. He found that Cyasorb 531 (2% w/w) was the most effective in stabilizing PP towards discolouration and brittleness. HDPE stabilized with Hostanox VP PAR 24, Hostanox 03, Hostanox SE 10, or carbon black (Graftol 300) was found to have concentrations which minimized changes in mechanical properties[147].

It is often overlooked that cables are actually complicated systems that have to address many other issues besides oxidative stability. Current accelerated ageing test procedures for polyolefin-insulated cable (PIC) used in phone lines have been discussed[140]. The testing approach has been to duplicate field conditions and installations as closely as possible during the ageing step, with the exception of a higher temperature. Drawbacks to this approach are the length of time required to run the test and temperature variations within the test fixture[140]. The difficulty in controlling the test variables is reflected in an analysis of test data from nine independent laboratories. Ageing tests at 110°C were in agreement while tests at 90°C and 80°C showed variations by factors of 5 and 3.5 in times to cracking, respectively. These tests were run on wires from one manufacturer and, presumably, all from the same lot[148]. Related studies on PP have shown a similar problem in testing consistency[79].

In a related approach, the measurement of the concentration of stabilizer additives followed by a determination of oxidative induction time for that sample should be reasonably correlated to the lifetime of the system. In reality, measurement of the stabilizer concentration has been difficult (high performance liquid chromatography seems to be a successful method) and correlation with field samples suggests that the oxidation/loss mechanisms are too different from those in oxidative induction time procedures to be a reliable indicator of field lifetimes in most instances[81,149]. One feature that should be considered in both tests is the need for a preconditioning step, run at about the high temperature limit found in the field, to bring the concentration of stabilizer(s) down to their solubility limit[81]. For filled cable this needs to be done in contact with the filling compound if it can extract more stabilizer than would volatilize in air.

A good review of cable properties and structures can be found in reference 150. It is important to note that many cables for underground telephone lines are 'jelly'-filled. The jelly is a PE-modified petrolatum. Also, earlier cable had wires coated with PP or HDPE followed later by 'foam-like' HDPE, which has cells within the solid material forming the insulation. The combination of hydrocarbon filler and increased porosity is a flaw in this system since the marginally soluble stabilizers will be easily extracted from the wire coating. The extraction of stabilizer by filling compound has been shown to be the most significant loss process (followed by thermal-oxidative and chemical reaction during the foaming process) in foam-skin cable[151]. Failures in this system are being observed, starting in the hotter regions of the United States[138,140] and in related cellular insulation in Australia[81]. Current recommendations are to use solid HDPE (but with improved stabilizer packages), although the jelly filler can still swell and extract stabilizers from HDPE, albeit over a longer time.

Another aspect of testing that is often overlooked is the effect of stress on polymer ageing. Chemical contact during applied mechanical force can lead to failure through swelling and/or stress cracking. Both PE and PP[152] in contact with aliphatic and aromatic hydrocarbons exhibit a strong swelling effect. If the solvents should contain functional groups (apart from chlorine), swelling is less. The reduction in strength depends mainly on the degree of swelling. When swelling is negligible, the class of material and the concentration becomes important. PP shows a tendency towards oxidative degradation on wetting with oxidizing substances, and its swelling in solvents is somewhat greater than PE. Both rigid PE and PP are permeable to many organic substances. PE is also susceptible to environmental stress cracking[153]. Deformation of PE in environmental stress cracking agents (methanol, isopropanol, Igepal, water) results in changes in both the mechanism of deformation and structure of the resulting drawn material. Stress-cracked failure surfaces are highly fibrillar, the fibrils having less elastic recovery than those in samples drawn in air. The environmental stress cracking agents are suggested to weaken the cohesion between the fibrils in samples drawn beyond yield. The stress is thus supported by a number of independent, non-uniform fibrils rather than a coherent structure; the weakest of the fibrils fail in turn as the crack propagates through the sample. The enhanced cracking rate due to applied stress was seen where wires were tightly wrapped in coils[140]. It is also believed that stress can accelerate chemical reactions at the strained bonds, which leads to localized oxidation in the amorphous regions of polyolefins. Finally, typical methods of toughening polymers by the addition of colloidal particles can fail in PE (and by extension of the proposed model in all semicrystalline polymers). This is because it is thought that the interfacial binding between the colloidal particle and the polymer can induce a weak layer in the polymer adjacent to the colloidal surface[154].

Mechanisms of failure while in contact with solvents are highly dependent on the conditions. Studies on linear PE and ethylene–hexene copolymer (slightly branched) in a stress cracking agent (10% solution in water of nonylphenoxy-poly(ethyleneoxy)ethanol) and in swelling solvents (hexane, dodecane or *o*-dichlorobenzene), at 296 and 300 K, show different failure mechanisms which involve flow, bond rupture, crack formation and propagation, depending on material, load, temperature and chemical environment[155,156]. Crazing and fracture can be modified even at liquid nitrogen temperatures; it was found[157] that liquid nitrogen can act as a plasticizer at 77 K. Stabilizer extraction by water has been documented[85]. In cases where more than one failure mechanism is present, a note of caution is appropriate with regard to using high temperatures as a means of accelerating failure and predicting lifetimes.

Electrical failure can be associated with solvent penetration of the polymer coating (see reference 158 for a review of mechanisms). Water treeing is a pre-breakdown phenomenon associated with dielectric failure in high voltage cables. A void, contaminant or a protrusion in the insulation when subjected to a high electrical stress forms a tree-like burn pathway at failure. These tree structures have high concentrations of polyaromatic stabilized free radicals in the defect regions[159]. Additives, crosslinking and graft-modified PE have been used to control the spherulitic growth during crystallization to reduce water treeing[160]; direct observation of this morphology has been made[87]. Indirect measurements such as volume changes as a function of additives have also been used[161]. Progress is being made in accelerated ageing with regard to electrical failure. However, accelerated ageing with regard to electrical failures is subject to many of the problems mentioned above for other failure indicators (changing ageing mechanisms as higher voltages are used etc.)[162]. One study[163] showed that small amounts of water clearly degrade the electrical properties of insulations. Water content in polyolefins is dependent on the oxygen-containing defects in the polymer. The type of oxygen defect also determines the solubility and diffusion rate in the polymer by acting as traps of varying interaction strengths[121]. Various additives, including antioxidants, change the electrical charge storage and conduction properties of LLDPE[164]. Electrical breakdown may be stimulated by the antioxidants, or pigments, added to the resin, reinforcing the idea that the complete system must be tested when any minor production change is introduced. Other properties, such as crosslinking, could be shown to change the performance. Further development of tests with accelerating factors such as temperature, water, electrical stress, frequency and mechanical stress were suggested.

Remedial action to preserve existing material is possible. Methods to reduce further extraction (e.g. lower temperatures, less contact with oxygen, addition of stabilizers to the system) all have merit based on our knowledge of transport and oxidation. Simple exclusion of oxygen from the polymer was shown to be an effective approach in the laboratory[165]. Crosslinking could possibly improve the mechanical behaviour of oxidized PE, and should be investigated[166]. Field treatments will be complicated by many factors beyond modifications to the polymer and will probably be decided by cost/benefit analysis.

DISCUSSION

Transport, or diffusion, was seen to be a function of structure of both the polymer and the diffusant. This includes both local chemical structure and longer range order described as morphology. Temperature, solubility, reactivity, orientation and composition modify the transport process.

Usually the diffusion process in polyolefins is close to classical Fickian behaviour. However, there is the strong possibility that regimes exist where other forms of diffusion dominate. This is a consequence of the semicrystalline structure present in polyolefins. Because there are two distinct materials there is the possibility that a time-dependent behaviour could manifest itself and dominate the diffusion process. Similarly in glassy polymers a time-dependent deformation is induced by the solvation process, which gives rise to a dramatic change in the diffusion rate. This question has not been explored for the polyolefins.

The issue of practical use is a difficult area to assess. It has been shown that seemingly slight changes in formulation or processing conditions may have a large impact on structure and consequently oxidative stability. Since it is currently difficult to establish reliable accelerated ageing tests, it is hard to demonstrate, on a short time-scale, the effects of such minor modifications. This can lead to modifications in processing being introduced for other, 'practical' reasons. Typical examples include higher processing temperatures to improve flow viscosity, additions of small quantities of chemicals to improve processing behaviour and/or finish, higher draw rates to speed rate of production, reduced cost polymer resins, reduced cost colour additives and, often, reductions or changes in antioxidant formulations to reduce costs. Until reliable accelerated ageing tests can be demonstrated there is little that can be done to control this situation.

CONCLUSIONS

Although it is clear that diffusion is important to polyolefin stability, it is much harder to pinpoint guidelines in polymer preparation that will assure one of an oxidatively stable polymer. This is because one is really discussing a system which includes the polymer, level and nature of defects in the polymer, thermal antioxidants, contaminants present in end use, processing history, thermal environment when in use, geometry of polymer in use and chemical contacts when in use.

Clearly, the relationship between polyolefin morphology and diffusant behaviour is vague. In part, this is because it is very hard to quantify morphology, except at its extreme limits: totally amorphous and totally crystalline. Also, our understanding of solubility in the solid state is marginal. Again, as in diffusion models, our knowledge is formulated in bulk terms rather than in molecular terms. This tends to obscure the detailed nature of the problem, making it difficult to develop a quantitative theory. Whether it is possible to start from first principles in such a complicated system is at present unclear.

ACKNOWLEDGEMENTS

The authors thank Dr T. Bowmer, Bell Communications Research, for many stimulating discussions and for reading and suggesting improvements to this manuscript.

REFERENCES

1 Hawkins, W. L. in 'Oxidative and Combustion Reviews', Vol. 1 (Ed. C. F. H. Tipper), Elsevier Publishing, Amsterdam, 1965, pp. 170–221

2 Allara, D. L. and Edelson, D. *Rubber Chem. Technol.* 1972, **45**, 437

3 Mill, T., Mayo, F., Richardson, H., Irwin, K. and Allara, D. L. *J. Am. Chem. Soc.* 1972, **94**, 6802

4 Gugumus, F. in 'Oxidation Inhibition in Organic Materials', Vol. I (Eds J. Pospisil and P. P. Klemchuk), CRC Press, Boca Raton, 1990, pp. 61–172

5 Moisan, J. Y. and Lever, R. *Eur. Polym. J.* 1982, **18**, 407

6 Billingham, N. C. in 'Oxidation Inhibition in Organic Materials', Vol. II (Eds J. Pospisil and P. P. Klemchuk), CRC Press, Boca Raton, 1990, pp. 249–297

7 Billingham, N. C. and Calvert, P. D. in 'Developments in Polymer Stabilisation – 3' (Ed. G. Scott), Applied Science Publishers, London, 1980, Ch. 5

8 Cassidy, P. E. and Aminabhavi, T. M. *J. Macromol. Sci., Rev. Macromol. Chem.* 1981, **C21**, 89

9 Bandyopadhyay, P. K., Shaw, M. T. and Weiss, R. A. *Polym. Plast. Technol. Eng.* 1985, **24**, 187

10 Moisan, J. Y. in 'Polymer Permeability' (Ed. J. Comyn), Elsevier Applied Science, London, 1985, pp. 119–175

11 Pospisil, J. and Klemchuk, P. P. (Eds) 'Oxidation Inhibition in Organic Materials', Vols I and II, CRC Press, Boca Raton, 1990

12 Flynn, J. H. *Polymer* 1982, **23**, 1325

13 Barton, A. F. M. 'Handbook of Solubility Parameters and Other Cohesion Parameters', CRC Press, Boca Raton, 1983

14 Mirabella, F. M. Jr, Westphal, S. P., Fernando, P. L. and Ford, E. A. *J. Polym. Sci., Part B: Polym. Phys.* 1988, **26**, 1995

15 Chiou, J. S., Maeda, Y. and Paul, D. T. *J. Appl. Polym. Sci.* 1985, **30**, 4019

16 Hartley, G. S. *Trans. Faraday Soc.* 1949, **45**, 820

17 Thomas, N. L. and Windle, A. H. *Polymer* 1977, **18**, 1195

18 Thomas, N. and Windle, A. H. *Polymer* 1978, **19**, 255

19 Klier, J. and Peppas, N. A. *Polym. Bull.* 1986, **16**, 359

20 Mills, P. J. and Kramer, E. J. *J. Mater. Sci.* 1986, **21**, 4151

21 Alfrey, T. *Chem. Eng. News* 1965, **43**(41), 64

22 Alfrey, T. Jr, Gurnee, E. F. and Lloyd, W. G. *J. Polym. Sci.: Part C* 1966, **12**, 249

23 Thomas, A. G. and Muniandy, K. *Polymer* 1987, **28**, 408

24 Tonyali, K., Rogers, C. E. and Brown, H. R. *Polymer* 1987, **28**, 1472

25 Park, G. S. *Trans. Faraday Soc.* 1951, **48**, 11

26 Crank, J. *J. Polym. Sci.* 1953, **11**, 151

27 Long, F. A. and Richman, D. *J. Am. Chem. Soc.* 1960, **82**, 513

28 Hui, C.-Y., Wu, K.-C., Lasky, R. C. and Kramer, E. J. *J. Appl. Phys.* 1987, **61**, 5129

29 Mandelkern, L. and Long, F. A. *J. Polym. Sci.* 1951, **6**, 457

30 Peterlin, A. *Polym. Lett.* 1965, **3**, 1083

31 Michaels, A. S., Bixler, H. J. and Hopfenberg, H. B. *J. Appl. Polym. Sci.* 1968, **12**, 991

32 Garcia-Fierro, J. L. and Aleman, J. V. *Eur. Polym. J.* 1985, **21**, 753

33 Scherer, J. R., Bailey, G. F., Kint, S., Young, R., Malladi, D. P. and Bolton, B. *J. Phys. Chem.* 1985, **89**, 312

34 Turner, D. T. *Polymer* 1987, **28**, 293

35 Hui, C.-Y., Wu, K.-C., Lasky, R. C. and Kramer, E. J. *J. Appl. Phys.* 1987, **61**, 5137

36 Korsmeyer, R. W., Von Meerwall, E. and Peppas, N. A. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 409

37 Korsmeyer, R. W., Lustig, S. R. and Peppas, N. A. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 395

38 Petropoulos, J. H. and Roussis, P. P. *J. Membr. Sci.* 1978, **3**, 343

39 Thomas, N. and Windle, A. H. *Polymer* 1980, **21**, 613

40 Gostoli, C. and Sarti, G. C. *Polym. Eng. Sci.* 1982, **22**, 1018

41 Thomas, N. L. and Windle, A. H. *Polymer* 1982, **23**, 529

42 Korsmeyer, R. W. and Peppas, N. A. *Polym. News* 1984, **9**, 359

43 Hopfenberg, H. B. and Frisch, H. L. *Polym. Lett.* 1969, **7**, 405

44 Thomas, N. L. and Windle, A. H. *Polymer* 1981, **22**, 627

45 Truong, V. T., Williams, D. R. G. and Allen, P. E. M. *Eur. Polym. J.* 1987, **23**, 41

46 Prager, S. and Long, F. A. *J. Am. Chem. Soc.* 1951, **73**, 4072

47 Kokes, R. J. and Long, F. A. *J. Am. Chem. Soc.* 1953, **75**, 6142

48 Aitken, A. and Barrar, R. M. *Trans. Faraday Soc.* 1955, **51**, 116

49 Hayes, M. J. and Park, G. S. *Trans. Faraday Soc.* 1955, **51**, 1134

50 Fujita, H., Kishimoto, A. and Matsumoto, K. *Trans. Faraday Soc.* 1960, **56**, 424

51 Green, P. F., Mills, P. J., Palmstrom, C. J., Mayer, J. W. and Kramer, E. J. *Phys. Rev. Lett.* 1984, **53**, 2145

52 Kramer, E. J., Green, P. and Palmstrom, C. J. *Polymer* 1984, **25**, 473

53 Mills, P. J., Green, P. F., Palmstrom, C. J., Mayer, J. W. and Kramer, E. J. *Appl. Phys. Lett.* 1984, **45**, 957

54 Green, P. F., Palmstrom, C. J., Mayer, J. W. and Kramer, E. J. *Macromolecules* 1985, **18**, 501

55 Koszinowski, J. *J. Appl. Polym. Sci.* 1986, **32**, 4765

56 Sada, E. and Kumazawa, H. *J. Appl. Polym. Sci.* 1986, **32**, 5567

57 Iwai, Y., Kohno, M., Akiyama, T. and Arai, Y. *Polym. Eng. Sci.* 1987, **27**, 837

58 Ito, T., Seta, J. and Urakawa, H. *Colloid Polym. Sci.* 1987, **265**, 557

59 Kalachandra, S. and Turner, D. T. *Polymer* 1987, **28**, 1749

60 Pawlisch, C. A., Macris, A. and Laurence, R. L. *Macromolecules* 1987, **20**, 1564

61 Turner, D. T. and Abell, A. K. *Polymer* 1987, **28**, 297

62 Ryan, T. G. and Calvert, P. D. *Polymer* 1982, **23**, 877

63 Johnson, M. and Westlake, J. F. *J. Appl. Polym. Sci.* 1975, **19**, 1745

64 Westlake, J. F. and Johnson, M. *J. Appl. Polym. Sci.* 1975, **19**, 319

65 Rhee, C.-K. and Ferry, J. D. *J. Appl. Polym. Sci.* 1977, **21**, 773

66 Park, G. S. and Hoang, T. V. *Eur. Polym. J.* 1979, **15**, 817

67 Manjkow, J., Papanu, J. S., Soong, D. S., Hess, D. W. and Bell, A. T. *J. Appl. Phys.* 1987, **62**, 682

68 Tong, H. M., Saenger, K. L. and Durning, C. J. *J. Polym. Sci., Part B, Polym. Phys.* 1989, **27**, 689

69 Aboul-Nasr, O. T. and Huang, R. Y. M. *J. Appl. Polym. Sci.* 1979, **23**, 1819

70 Aronhime, M. T., Neumann, S. and Marom, G. *J. Mater. Sci.* 1987, **22**, 2435

71 Czanderna, A. W. and Thomas, T. M. *J. Vac. Sci. Technol.* 1987, **5**, 2412

72 Windle, A. H. in 'Polymer Permeability' (Ed. J. Comyn), Elsevier Applied Science, London, 1985, pp. 75–118 (and references therein)

73 Crank, J. 'The Mathematics of Diffusion', 2nd Edn, Oxford University Press, London, 1975

74 McCall, D. W. and Slichter, W. P. *J. Am. Chem. Soc.* 1958, **80**, 1861

75 Rogers, C. E., Stannett, V. and Szwarc, M. *J. Polym. Sci.* 1960, **XLV**, 61

76 Billingham, N. C., Calvert, P. D. and Manke, A. S. *J. Appl. Polym. Sci.* 1981, **26**, 3543

77 Roe, R.-J., Bair, H. E. and Gieniewski, C. *J. Appl. Polym. Sci.* 1974, **18**, 843

78 Newland, G. C. and Tamblyn, J. W. *J. Appl. Polym. Sci.* 1964, **8**, 1949

79 Blumberg, M., Boss, C. R. and Chien, J. C. W. *J. Appl. Polym. Sci.* 1965, **9**, 3837

80 Plant, M. A. and Scott, G. *Eur. Polym. J.* 1971, **7**, 1173

81 Board, B. L. and Ruddell, H. J. in 'Proceedings of 31st International Wire and Cable Symposium', 1982, pp. 300–312

82 Roe, R. J., Bair, H. E. and Gieniewski, C. Bell Laboratories Technical Memorandum, TM-73-1515-38, 1973

83 Bair, H. E. *Polym. Eng. Sci.* 1973, **13**, 435

84 Rogers, C. E., Stannett, V. and Szwarc, M. *J. Phys. Chem.* 1959, **63**, 1406

85 Hawkins, W. L., Worthington, M. A. and Matreyek, W. *J. Appl. Polym. Sci.* 1960, **3**, 277

86 Rennie, A. R. *J. Polym. Sci., Polym. Lett. Edn* 1985, **23**, 241

87 Muccigrosso, J. and Phillips, P. J. *IEEE Trans. Electr. Insul.* 1978, **EI-13**, 172

88 Hansen, R. H., Martin, W. M. and DeBenedictis, T. Bell Telephone Laboratories Technical Memorandum, MM-63-1122-8, 1963

89 Akay, G., Tincer, T. and Ergoz, H. E. *Eur. Polym. J.* 1980, **16**, 601

90 Eby, R. K. *J. Appl. Phys.* 1964, **35**, 2720

91 Moisan, J. Y. *Eur. Polym. J.* 1980, **16**, 979

92 Michaels, A. S., Bixler, H. J. and Fein, H. L. *J. Appl. Polym. Sci.* 1964, **35**, 3165

93 Lowell, P. N. and McCrum, N. G. *J. Polym. Sci., Part A-2*, 1971, **9**, 1935

94 Kreituss, A. and Frisch, H. L. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 889

95 Harland, R. S. and Peppas, N. A. *Colloid Polym. Sci.* 1989, **267**, 218

96 Araimo, L., DeCandia, F., Vittoria, V. and Peterlin, A. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 2087

97 Dorset, D. L. *Z. Naturforsch A. (Germany)* 1978, **33A**, 964

98 Klein, J. and Briscoe, B. J. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 2065

99 Klein, J. and Briscoe, B. J. *Proc. R. Soc. Lond. A.* 1979, **365**, 53

100 Moisan, J. Y. *Eur. Polym. J.* 1980, **16**, 989

101 Billovits, G. F. and Durning, C. J. *Polymer* 1988, **29**, 1468

102 Bischoff, M. and Eyerer, P. *J. Membr. Sci.* 1984, **21**, 333

103 DeCandia, F., Russo, R., Vittoria, V. and Peterlin, A. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 2083

104 Baum, J. S. and Schultz, J. M. *J. Appl. Polym. Sci.* 1981, **26**, 1579

105 Moisan, J. Y. *Eur. Polym. J.* 1980, **16**, 997
106 Moisan, J. Y. *Eur. Polym. J.* 1981, **17**, 857
107 Peterlin, A., Williams, J. L. and Stannett, V. *J. Polym. Sci., Part A-2* 1967, **5**, 957
108 Williams, J. L. and Peterlin, A. *J. Polym. Sci., Part A-2* 1971, **9**, 1483
109 Peterlin, A. *J. Macromol. Sci., Phys.* 1975, **11**, 57
110 Ng, H. C., Leung, W. P. and Choy, C. L. *J. Polym. Sci., Polym. Phys. Edn.* 1985, **23**, 973
111 Britton, L. N., Ashman, R. B., Aminabhavi, T. M. and Cassidy, P. E. *J. Appl. Polym. Sci.* 1989, **38**, 227
112 Berens, A. R. *J. Appl. Polym. Sci.* 1989, **37**, 901
113 DeCandia, F., Russo, R., Vittoria, V. and Peterlin, A. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 269
114 Asfour, A.-F. A., Saleem, M., De Kee, D. and Harrison, B. H. *J. Appl. Polym. Sci.* 1989, **38**, 1503
115 Saleem, M., Asfour, A.-F. A., De Kee, D. and Harrison, B. H. *J. Appl. Polym. Sci.* 1989, **37**, 617
116 Dubini, M., Cicchetti, O., Vicario, G. P. and Bua, E. *Eur. Polym. J.* 1967, **3**, 473
117 Cicchetti, O., Dubini, M., Parrini, P., Vicario, G. P. and Bua, E. *Eur. Polym. J.* 1968, **4**, 419
118 Jackson, R. A., Oldland, S. R. D. and Pajaczkowski, A. *J. Appl. Polym. Sci.* 1968, **12**, 1297
119 Douglas, D. C. and McCall, D. W. *J. Phys. Chem.* 1958, **62**, 1102
120 McCall, D. W., Douglas, D. C. and Anderson, E. W. *J. Chem. Phys.* 1959, **30**, 771
121 McCall, D. W., Douglas, D. C., Blyler, L. L. Jr, Johnson, G. E., Jelinski, L. W. and Bair, H. E. *Macromolecules* 1984, **17**, 1644
122 Nisizawa, M. *J. Appl. Polym. Sci.* 1969, **13**, 2506
123 Kuck, V. in 'Polymer Additives' (Ed. J. E. Kresta), Plenum, 1984, pp. 103–110
124 Gilroy, H. M. Bell Laboratories Technical Memorandum, TM-74-1511-2, 1974
125 Fleischer, G. *Polym. Commun.* 1985, **26**, 20
126 Fujita, H. *Fortsshr. Hochpol. Forsch.* 1961, **3**, 1
127 Fujita, H. in 'Diffusion in Polymers' (Eds J. Crank and G. S. Park), Academic Press, New York, 1968
128 Ventas, J. S. and Duda, J. L. *AIChE J.* 1979, **25**, 1
129 Duda, J. L., Ni, Y. C. and Vrentas, J. S. *J. Appl. Polym. Sci.* 1979, **23**, 947
130 Vrentas, J. S. and Duda, J. L. *J. Appl. Polym. Sci.* 1977, **21**, 1715
131 Vrentas, J. S. and Duda, J. L. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 403
132 Vrentas, J. S. and Duda, J. L. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 417
133 Fleischer, G. *Polym. Bull.* 1982, **7**, 423
134 Vrentas, J. S., Duda, J. L. and Lau, M. K. *J. Appl. Polym. Sci.* 1982, **27**, 3987
135 Serna, J., Abbe, J. Ch. and Duplatre, G. *Phys. Stat. Sol.* 1989, **115**, 389
136 Howard, J. B. and Gilroy, H. M. *Polym. Eng. Sci.* 1975, **75**, 268
137 Hawkins, W. L., Link, G. L. and Chan, M. G. Bell Telephone Laboratories Technical Memorandum, MM-69-1516-3, MM-69-1513-4, 1969
138 Bowmer, T. N. in 'Proceedings of 37th International Wire and Cable Symposium', 1988, pp. 475–483
139 Gilroy, H. M. in 'Proceedings of 23rd International Wire and Cable Symposium', 1974, pp. 42–45
140 Bowmer, T. N., Hjorth, E. P., Miner, R. J. and Gebizlioglu, O. S. in 'Proceedings of 37th Wire and Cable Symposium', 1988, pp. 490–499
141 Al-Malaika, S. and Amir. E. J. *Polym. Deg. Stab.* 1986, **16**, 347
142 Kokta, E. Bell Laboratories Technical Memorandum, TM-74-1511-3, 1974
143 Schaupert, K., Albrecht, D., Armbruster, P. and Spohr, R. *Appl. Phys. A*, 1987, **44**, 347
144 Verne, S., Puckowski, R. T. and Pointer, B. R. O. in 'Proceedings of 21st International Wire and Cable Symposium', 1972, pp. 350–360
145 Gilroy, H. M. Bell Laboratories Technical Memorandum, TM-73-1510-14, 1973
146 Chouhdary, V., Varshney, S. and Varma, I. K. *Ange. Makromol. Chemie* 1987, **150**, 137
147 Padron, A. J. C., Colmenares, M. A., Rubinztain, Z. and Albornoz, L. A. *Eur. Polym. J.* 1987, **23**, 723
148 Bowmer, T. N. and Hore, L. M. Bellcore Technical Memorandum, TM-ARH-016343, 1990
149 Plitz, I. Bellcore Technical Memorandum, TM-ARH-015578, 1990
150 Tyler, J. S. 'The Universal Cable Design for the Outside Plant – Cellular Insulated, Jelly Filled Telephone Cable', Essex Telecommunications Products Division, Decatur, Illinois, 1980
151 Dye, K. D., Kuck, V. J., Schilling, F. C., Chan, M. G. and Loan, L. D. in 'Proceedings of 38th International Wire and Cable Symposium', 1989, pp. 98–104
152 Gaube, F., Muller, W. and Diedrich, I. G. *Chem. Eng. World* 1971, **6**, 39
153 Singleton, C. J., Roche, E. and Geil, P. H. *J. Appl. Polym. Sci.* 1977, **21**, 2319
154 Kendall, K. and Sherliker, F. R. *Br. Polym. J.* 1980, **12**, 85
155 Crissman, J. M. and Zapas, L. J. *Am. Chem. Soc.* 1979, **95**, 289
156 Zapas, L. J. and Crissman, J. M. *Org. Coat. Plast. Chem.* 1979, **41**, 469
157 Olf, H. G. and Peterlin, A. *Macromolecules* 1973, **6**, 470
158 Nunes, S. L. and Shaw, M. T. *IEEE Trans. Electr. Insul.* 1980, **EI-15**, 427
159 Schaible, M., Hayden, H. and Tanaka, J. *IEEE Trans. Electr. Insul.* 1987, **EI-21**, 699
160 Henkel, H.-J., Muller, N., Nordmann, J., Rogler, W. and Rose, W. in 'Proceedings of 2nd International Conference on Conduction and Break. in Sol. Dielec.', 1986, pp. 267–274
161 Nunes, S. L. and Shaw, M. T. in 'Proceedings of Conference on Electrical Insulation and Dielectric Phenomena', 1981, pp. 238–243
162 Davies, A. E. and Hodgson, D. A. in 'Proceedings of 5th International Conference on Dielectric Materials, Measurements and Applications', 1988, pp. 254–257
163 Lyle, R. and Kirkland, J. W. *IEEE Trans. Power Syst.* 1981, **PAS-100**, 3764
164 Perlman, M. M. and Haridosa, S. in 'Proceedings of 5th International Symposium on Electrets', Heidelberg, 1985, pp. 83–93
165 Bowmer, T. N. Bell Communications Research, Technical Memorandum, TM-ARH-016639, 1990
166 Chen, Y. L. and Ranby, B. *Polym. Adv. Tech.* 1990, **1**, 103
167 Rabolt, J. F. personal communication
168 Bassett, D. C. 'Principles of Polymer Morphology', Cambridge University Press, Cambridge, 1981
169 Herman, T. J. 'World Index of Polyolefin Stabilizers', Kogan Page, London, 1982