Mobility of additives in ethylene polymers

Enikő Földes

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary

Summary
    Diffusion rate of different additives was studied in ethylene polymers. The measured values were evaluated on the basis of the free-volume theory. It was concluded from the results that the rate of diffusion is primarily determined by the fractional free-volume of the noncrystalline phase of the polymer, as well as the specific volume of the additive.

Introduction
    The additives used in practice for polymers (antioxidants, processing aids, etc.) have different chemical structures and molecular sizes. Most of them are considerably smaller than the macromolecules, but larger than the usual solvents. As migration plays an important role in their effectiveness [1,2], it is essential to know the quantitative relationships among the parameters influencing their mobility in the polymers. Recently Billingham published a review on the developments in the physical aspects of polymer degradation including the diffusion of additives in polymers [2]. The temperature dependence of the diffusion rate can be described by an Arrhenius equation. At the glass transition of the polymer, as well as at the melting point of the polymer crystallites the slope of the Arrhenius plot changes. The activation energy is reported to increase slowly with increasing molecular weight of the additive within the same homologous series, but the slope of the change is different for the different homologous series.
    In the present work mobility of additives of different chemical structure were studied in ethylene polymers. Changes of the physical structure of the polymers and the additives with temperature were determined. Quantitative relationships were found between the measured diffusion rates and some parameters characterizing the components.

Experimental
Materials
    Diffusion measurements were carried out in the additive-free ethylene polymers listed in Table 1. The polymers were processed into 70-100 μm films by extrusion blowing. Fusion characteristics of the materials hint at some differences not only in their crystallinity (α_c), but also in the lamellar size distribution of the crystallites [3].
    The additives studied are given in Table 2. The first four of them are spherical and the others linear molecules. The molecular weights and the melting points change on large scales.

Table 1
Polymers studied

Designation	Trade name	Chemical name	T_m (°C)	α_c
LDPE	Tipolen PB 2212[a]	low density polyethylene	111.5	0.445
LDPE/LLDPE blend	Tipolen PB 2212[a] Tipelin FA 381[a]	60 wt % LDPE 40 wt % ethylene-1-hexene copolymer	111.5 125.0	0.525
EVA-9	Evatane 1020 VN3[b]	ethylene vinyl acetate copolymer (3 mole % VA)	99.0	0.360

[a] TVK (Hungary) product
[b] ATOCHEM product

Table 2
Additives studied

Designation	Chemical name	T_m[*] (°C)	MW
BHT	2,6-di-*tert*-butyl para-cresol	70.5	220
Topanol CA	1,1,3-tris(2'-methyl-4'-hydroxy-5'-*tert*-butylphenyl)-butane	186.0	545
Ultranox 626	bis(2,4-di-*tert*-butylphenyl)-pentaerythritol diphosphite	155.0	604
Irganox 1010	pentaerythrityl tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl propionate)	117.5	1178
Oleamide	oleic acid amide	71.0	281
Erucamide	erucic acid amide	81.0	338
DLTDP	dilaurylthiodipropionate	42.0	515
Irganox 1076	stearyl beta-(3,5-di-*tert*-butyl-4-hydroxy-phenyl)-propionate	55.0	531

[*] Measured at a heating rate of 10 °C/min

For the diffusion measurements "additive sources" were prepared by mixing 5 wt % additive with LDPE and EVA-9, respectively, in a Brabender internal mixer at 150 °C, then compression molding twice into 1 mm-thick plates.

Methods

Densities (ρ) of the materials were measured in sunflower oil in a special dilatometer between 25 and 80 °C.

Fusion and crystallization properties were determined by the DSC-30 unit of a Mettler TA 3000 thermal analyzer at a heating and cooling rate of 10 °C/min. Temperature dependence of the crystallinity (α_c) of the polymers was calculated by partial integration of the fusion endotherms.

From the measured density and crystallinity values specific volume (v_a) and volume

fraction (α_a') of the noncrystalline phase of the polymers were calculated, assuming that
- ethylene polymers consist of an impermeable crystalline and a permeable disordered phase;
- acetate groups are rejected from the crystalline phase;
- density of the crystallites does not depend on the type of the ethylene polymer, and can be calculated by the Chiang-Flory equation [4].

Fractional free-volume of the disordered phase (f_a) was calculated by

$$f_a = \alpha_a'(v_a - v_{0,p})/v_{0,p} \qquad (1)$$

where $v_{0,p}$ is the occupied specific volume at 0 K. $v_{0,p} = 1.0$ cm^3/g was used as an approximation [5,6].

Diffusion of the additives was studied by measuring the concentration profile in a stack of 50 additive-free polymer films placed between two additive sources, compressed by 2 N/cm^2 and kept in a vacuum oven of controlled temperature for different periods. The diffusion experiment was terminated before the additive reached the middle of the stack. Additive concentration of each layer was measured by UV and IR spectroscopy, respectively, and plotted as a function of distance from the additive source. The diffusion coefficient (D) was calculated with the initial conditions of [7,8]

$$c = c_0, \quad x < 0, \quad t = 0$$
$$c = 0, \quad x > 0, \quad t = 0$$

where $x=0$ is the position of the interface between the additive source and the first polymer layer, c is the actual concentration; c_0 is the concentration of additive in the source contacting the polymer surface. Under the experimental conditions described above c_0 equals the solubility of the diffusant, and can be considered constant when the rate of dissolution of the excess additive exceeds that of the diffusion. The concentration at time t can be described by

$$c(x,t) = S[1 - erf(x/K)] \qquad (2)$$

where S is the solubility and

$$K = 2\sqrt{Dt} \qquad (3)$$

For the determination of D an interactive curve fitting program was used.

Results and discussion

The diffusion experiments were conducted at 45, 55 and 80 °C. Effect of the structure of the polymer, as well as that of the additive on the diffusion rate was studied by comparing the changes of D with different physical characteristics of the components.

According to the free-volume theory developed for the transport of small molecules (vapors of liquids) in amorphous polymers, the diffusion coefficient changes exponentially with the fractional free-volume of the polymer (f) [9,10]:

$$D = D_0 \exp(-B_d/f) \qquad (4)$$

where B_d is related to the minimum hole size required for the displacement of the penetrant [10].

96
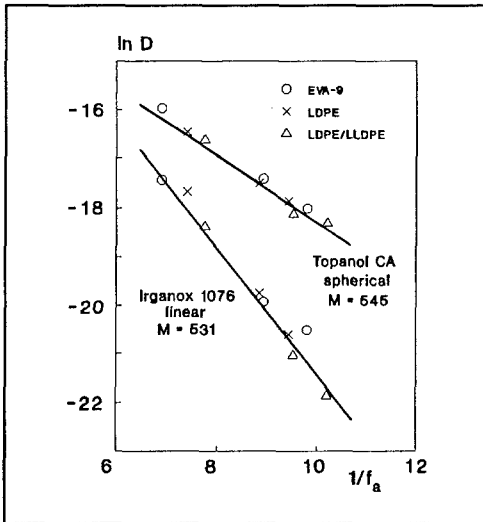
Figure 1 *Relationship between the diffusion rate and the free volume of the polymer*

It is accepted that the transport of additives in semicrystalline polymers takes place only in the noncrystalline phase [2]. Therefore f must correspond to the free-volume of that phase $(f = f_a)$. Although the experimental results proved that the additives swell ethylene polymers proportionally to their concentration, the additive uptake of the film layers during the diffusion experiments is so small, that the effect can be neglected in the calculations.

Effect of the polymer structure

Diffusion experiments were carried out in various polymers with freshly prepared additive sources at different temperatures. The logarithms of the diffusion coefficients were plotted as a function of the reciprocal fractional free-volume of the noncrystalline phase of the polymer $(1/f_a)$. Linear relationship was obtained for all of the eight investigated additives. *ln D* values measured in the different polymers fall on the same line, as it is shown by Figure 1. This result indicates that the mobility of the additives is independent of the type of the ethylene polymer, consequently of the size of the crystallites. The determining parameter is the magnitude of the fractional free-volume of the noncrystalline phase.

B_d and *ln D_0* values calculated from the *ln D* vs. $1/f_a$ functions are compared in Figure 2. The logarithm of D_0 changes close to linearly with B_d suggesting that both values are influenced by the same parameters.
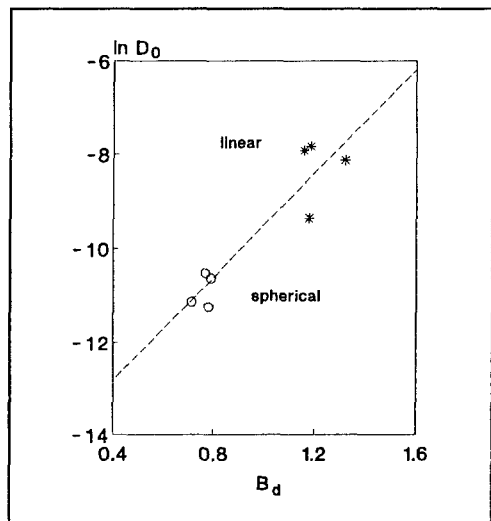
Effect of the additive structure

The chemical nature of the additives strongly influences the diffusion process. It was found that the diffusion rate of additives which crystallize easily on cooling from melt (for Irganox 1076 see [11]) is independent of the thermal history of the polymer-based additive source. Although some of these additives have their melting point in the temperature range of the investigations, the linear relationship of the *ln D* vs. $1/f_a$ functions indicates no direct influence of phase change on their mobility.

When the additive has a high melting point, crystallizes slowly after melting and/or forms different crystal modifications, the thermal history of the addi-

Figure 2 *Relationship between the measured parameters of Equation (4)*

tive source affects the concentration profile and also the calculated diffusion rate [12,13]. This effect is even more pronounced when the additive of different physical state is used itself as an additive source. For demonstration concentration profiles of I1010 are shown in Figure 3. The experiments were carried out in LDPE with different additive sources at 80 °C for the same time. The smallest concentration values were obtained for the pure unmelted crystalline additive source, and the largest ones for that prepared by mixing the additive with the polymer at high temperature. The glassy additive rapidly cooled after melting resulted in intermediate concentrations. Such effects of the thermal history can be attributed to the different rates of dissolution from the various physical states. When the rate of dissolution of the penetrant becomes slower than that

Figure 3 *Effect of thermal history of the additive source on the concentration profile of Irganox 1010 in LDPE*

of the diffusion, the measured D values change with the thermal history of additive source.

Also the shape of the additive molecule affects considerably the mobility. *ln D* vs. $1/f_a$ functions of two antioxidants with similar molecular weights are compared in Figure 1. The linear chains diffuse more slowly in the temperature range of the investigations, but their diffusion rate changes more pronouncedly with the fractional free-volume of the polymer than that of the spherical molecules.
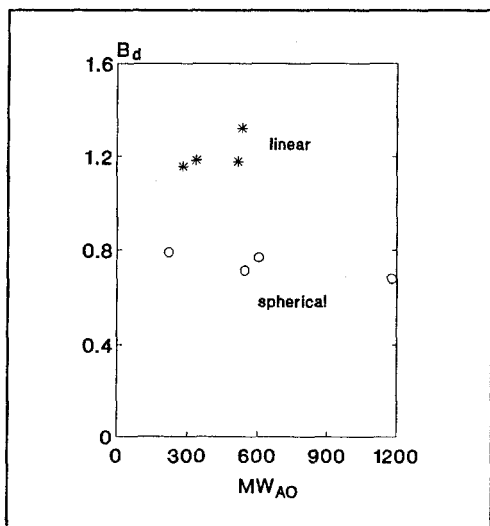

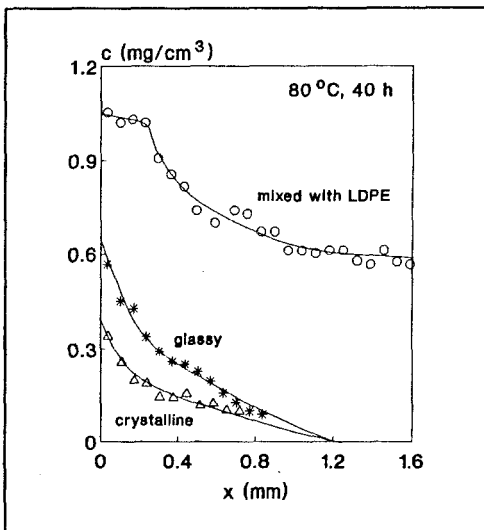**Figure 4** *Relationship between the molecular weight of the additives and B_d*

The slopes of the *ln D* vs. $1/f_a$ functions of the various additives were plotted in Figure 4 to study the effect of molecular weight on the mobility. As it can be expected from Figures 1 and 2, the linear molecules have higher B_d values than the spherical ones. There is no quantitative relationship between B_d and the molecular weight of additives.

According to the model of Cohen and Turnbull [9] B_d "must be near the molecular volume" of the diffusant, while Fujita defined that [10] as "the minimum hole required for a given diluent molecule to permit a displacement". The two definitions correspond each other, and express essentially the same condition of molecular transport.

The measured B_d values were plotted as a function of molar volumes of the additives calculated from the atomic and

group contributions given in Table 4.7 (Traube) and 7.4 (Fedors) in Ref. 14, respectively. Similar relationship was obtained as for the molecular weight dependence. For calculating the specific volumes, the molar volumes were divided by the molecular weights. Although different values were obtained according to the various data of the tables, the relationship shown in Figure 5 indicates that B_d increases with increasing specific volume of the additive.

For checking the validity of the specific volume dependence of B_d, densities of four antioxidants (BHT, Topanol CA, Irganox 1076 and Irganox 1010) were measured as a function of temperature, and the specific volumes were extrapolated to 0 K ($v_{0,AO}$). B_d vs. $v_{0,AO}$ function plotted in Figure 6 seems to prove that the mobility is influenced by the specific volume of the additive, beside the magnitude of the fractional free-volume of the noncrystalline phase of the ethylene polymers.
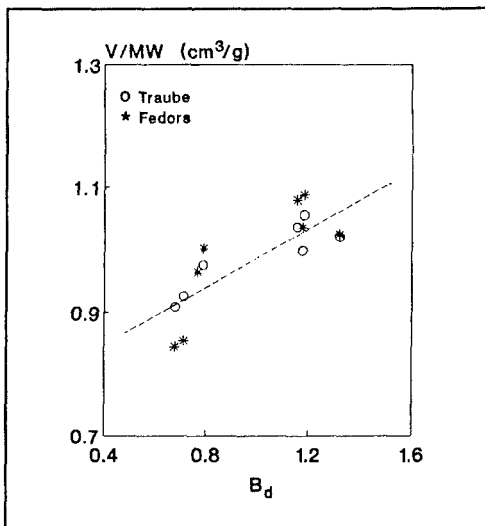

Figure 5 *Relationship between B_d and the specific volumes of additives calculated from the molar volumes [14]*
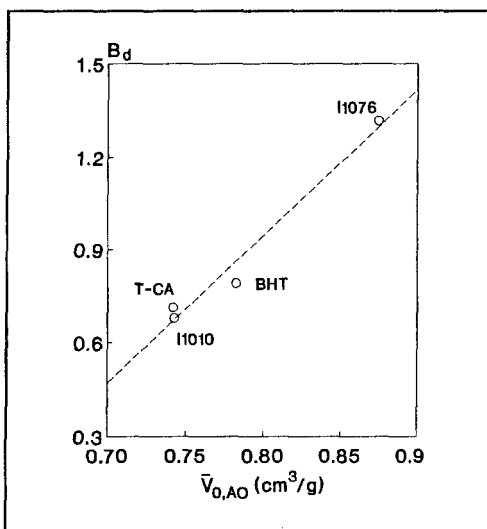

Figure 6 *Changes of B_d with the specific volumes of additives extrapolated from the measured values to 0 K*

Conclusions

Diffusion experiments of different additives in ethylene polymers proved that the mobility of additives above the glass transition temperature of the polymer can be treated quantitatively by the equations of the free-volume theory. Linear relationship was obtained between the logarithm of the diffusion coefficient and the reciprocal fractional free-volume of the noncrystalline phase of the polymer. For the studied polymers the slope of the function depends on the size of the additive, and changes linearly with the specific volume of the penetrant.

References
1 Moisan JY (1985) Effect of Oxygen Permeation and Stabiliser Migration on Polymer Degradation. In: Comyn J (ed) Polymer Permeability. Elsevier, London New York (chap 4, pp 119-176)
2 Billingham NC (1990) Physical Phenomena in the Oxidation and Stabilization of Polymers. In: Pospíšil J, Klemchuk PP (eds) Oxidation Inhibition in Organic Materials. CRC Press, Boca Raton FL (vol 2, chap 6, pp 249-297)
3 Wlochowicz A, Eder M (1984) Polymer 25: 1268
4 Chiang R, Flory PJ (1961) J Am Chem Soc 93: 2857
5 Doolittle AK (1951) J Appl Phys 22: 1471
6 Doolittle AK, Doolittle DB (1957) J Appl Phys 28: 901
7 Crank J, Park GS (1968) Methods of Measurement. In: Crank J, Park GS (eds) Diffusion in Polymers. Academic Press, London New York (chap 1 pp 1-39)
8 Crank J (1975) The Mathematics of Diffusion. Clarendon Press, Oxford
9 Cohen MH, Turnbull D (1959) J Chem Phys 31: 1164
10 Fujita H (1961) Fortschr Hochpolym-Forsch 3: 1
11 Földes E (1993) J Appl Polym Sci 48: 1905
12 Földes E, Turcsányi B (1992) J Appl Polym Sci 46: 507
13 Földes E (1994) J Appl Polym Sci 51: 1581
14 Van Krevelen DW, Hoftyzer PJ (1976) Properties of Polymers. Their Estimation and Correlation with Chemical Structure. Elsevier, Amsterdam Oxford New York