Transport of Small Molecules in Polyolefins. II. Diffusion and Solubility of Irganox 1076 in Ethylene Polymers

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SYNOPSIS

Diffusion coefficient and solubility of Irganox 1076 antioxidant in different ethylene polymers (LDPE, LDPE/LLDPE blend, and EVA) were studied between 45 and 80°C. For correct evaluation of the results, physical characteristics of the polymers and the additive were determined as a function of temperature. Good correlation was found between the diffusion rate of the additive and the free volume of the noncrystalline phase in the polymer. Measured solubilities were much higher than reported in the literature. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

It is well established (e.g., Refs. 1–4) that the effectiveness of the thermo- and photooxidative stabilizers in polymers depends not only on the chemical characteristics of the additive but also on physical loss of the small molecules. The rate of the additive loss is determined by its volatility, solubility and diffusion rate in and extractability from the polymer.

At given external conditions, volatility of a stabilizer is determined mainly by its molecular characteristics, but the rate of evaporation from a polymer matrix is strongly influenced also by diffusion processes.[2] When the polymer gets into contact with liquids, physical loss of the additive is accelerated by extraction.[5]

The rate of diffusion of small molecules in polymers is governed by the mobility of both the penetrant and the polymer chains. It is determined by the size and shape of the diffusing material and by the magnitude and distribution of free volume in the polymer.[6–12] It is accepted that transport of small molecules in semicrystalline polymers takes place only in the noncrystalline region. Therefore, the behavior of small molecules can be described by a two-phase model[6] assuming an impermeable crystalline and a permeable disordered phase. It was shown[6,7,13] that the penetration rate of small molecules depends

only on the amount of the free volume in the polymer. Diffusion of long-chain molecules (longer than 30 CH_2 units) is also influenced by the structure of the noncrystalline phase.

Solubility of small molecules in polymers is determined by the free volume of the polymer, the size and shape of the penetrant, and the polymer–polymer as well as the polymer–additive interaction (e.g., Refs. 6, 10, 14, and 15).

Transport properties of small molecules in polymers can be treated on the basis of the fractional free-volume concept (e.g., Refs. 6, 9, and 16–18). According to Peterlin,[6] the fractional free volume has to be considered "as an entropic quantity measuring in a simple manner the probability for creating a sorption site, i.e., a hole for accommodation of a molecule of the penetrant, or a diffusion channel through which a diffusing molecule can jump from one sorption site to the next one" and not as a distribution of actual voids. The free-volume concept for entropy of mixing was given by Hildebrand and Scott,[14] and for the diffusion coefficient by Cohen and Turnbull.[16]

Moisan conducted extensive studies on the diffusion rate and solubility of different additives in polyethylene.[4,19–21] He found a change in the slope of the Arrhenius plot of the diffusion coefficient at the melting point of the diffusant and explained it by the mobility change of the additive at that temperature. This explanation was argued by other authors: Billingham[10] attributed the effect to morpho-

logical changes of the polymer during the experiment, whereas Spatafore and Pearson[22] suggested that under the melting temperature the rate is determined by the separation speed of additive molecules from the crystals. The latter consideration fits into the general description of the diffusion behavior of penetrants in polymer membranes.[17]

In this work, diffusion rate (D) and solubility (S) of Irganox 1076 were studied at different temperatures in three ethylene polymers. Results were evaluated on the basis of the free-volume theory. For the calculations, physical changes of the polymers and the additive were also determined as a function of temperature.

EXPERIMENTAL

Materials

Irganox 1076, chemical name stearyl β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate (SBHP), MW = 531, was kindly provided by Ciba-Geigy AG as commercial material. For the diffusion measurements, "additive sources" were prepared by mixing 5 and 20 wt % of SBHP with additive-free LDPE and ethylene vinyl acetate copolymer (EVA) in a Brabender mixing chamber at 150°C, subsequently compression-molding them twice at 150 and 130°C, respectively, in argon atmosphere into 1 mm-thick plates.

Three types of additive-free ethylene polymers were studied:

- low density polyethylene (LDPE);
- blend of 60 wt % LDPE and 40 wt % linear low-density polyethylene (LDPE/LLDPE);
- ethylene vinyl acetate copolymer with 3 mol % (9 wt %) vinyl acetate content (EVA-9).

A detailed description of the materials is given in Table I. For the diffusion measurements, the polymers were processed into 70–90 μm films by extrusion blowing.

Methods

Thermal properties of the materials were characterized by a Mettler TA 3000 thermal analyzer. Melting and crystallization properties were measured by the DSC-30 unit of the system with a rate of heating and cooling of 10°C/min. Volatility of the additive was determined by the TG 50 thermobalance unit using 10°C/min rate of heating and by heat treatment at 80°C in an atmospheric oven.

Densities of the materials were measured as a function of temperature in a special dilatometer in sunflower oil. SBHP dissolved in it at each measuring temperature.

For the diffusion and solubility measurements, the same system was used as described by Roe et al.[23] A stack of additive-free polymer films was placed between two additive source plates. The whole system was put into a diffusion cell, compressed by 2 N/cm^2, and kept in a vacuum oven of controlled temperature for a given time. Diffusion measurements were carried out by using 50 additive-free polymer films and LDPE-base additive sources containing 5 wt % SBHP. The diffusion process was terminated before the additive reached the central layers of the film stack. After the diffusion process at a constant temperature, additive concentration was determined in each polymer film layer as a function of distance from the additive source by UV spectroscopy. Calibration was made in *n*-octane solution. The diffusion coefficient was calculated using the principle given by Moisan[4] and also described in our previous work.[24] For the solubility measure-

Table I   Polymers Investigated

Notation	Trade Name	Characterization	T_m (°C) Measured by DSC
LDPE	Tipolen PB 2212[a]	Low density polyethylene	111.5
LDPE/LLDPE	Tipolen PB 2212[a] Tipelin FA 381[a]	60 wt % LDPE 40 wt % ethylene-1-hexene copolymer	111.5/125
EVA-9	Evatane 1020 VN3[b]	Ethylene vinyl acetate copolymer (3 mol % VA)	99

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

Table II   Melting and Crystallization Properties of Irganox 1076 Measured by DSC

History	Measurement	T_1 (°C)	T_m (°C)	T_2 (°C)	ΔH (J/g)
As received	Melting	45.3	55.1	72.0	123.0
Quenched[a]	Melting	45.3	54.5	71.0	115.8
Annealed[b]	Melting	45.7	54.9	72.3	124.1
From melt	Cooling	14.7	6.3	−12.7	−74.2

Rate of heating and cooling: 10°C/min.
[a] Melted in a sealed aluminum pan at 150°C for 5 min, then dropped into liquid nitrogen.
[b] After quenching, annealed at 45°C for 160 h.

ments, six additive-free films were placed between two additive sources prepared by mixing 5 or 20 wt % SBHP with LDPE or EVA-9 and long measuring times were applied to reach equilibrium concentration in the film stack. Additive concentration was determined by measuring the weight gain of each layer.

RESULTS

Characterization of the Additive

Volatility of SBHP was determined in air. At 80°C, no weight loss was obtained after 300 h storage in an atmospheric oven. The results of the thermogravimetric analysis, measured at a rate of 10°C/min, showed that the material is not volatile under 195°C.

Melting and crystallization characteristics of the additive were determined by DSC. The results are summarized in Table II. (Heat of fusion of the material measured after cooling from melt by the rate of 10°C/min is shown in Fig. 6 as a function of temperature.) The melting range was obtained between 45°C (T_1) and 72°C (T_2) with a peak around 55°C (T_m) and heat of fusion (ΔH) about 120 J/g. Although the material can be supercooled considerably, it crystallizes during cooling. Melting and crystallization curves suggested that the additive was free from impurities. For studying the effect of heat treatment on the properties of SBHP, the material was sealed in aluminum pan, heated to 150°C for 5 min, then quenched in liquid nitrogen. Melting curves were measured after quenching and also after annealing the quenched material at 45°C for 160 h. It was found that thermal history of the material does not affect considerably the melting properties.

Density values of SBHP (ρ_{add}) measured as a function of temperature in sunflower oil are plotted in Figure 1. Within the accuracy of the measurement, density of the dissolved additive changes linearly with temperature.

Characterization of the Polymers

Melting properties of the polymers were studied by DSC and the melting curves are shown in Figure 2. Crystallinity was calculated by using 293 J/g as specific heat of fusion for polyethylene (PE) crystals.[25,26] Crystallinity of EVA-9 was determined by the same way assuming that acetate groups are excluded from the crystals.

Melting peak temperatures (T_m in Table I) and crystallinity ($\alpha_{c,H}$ in Table III) of the three samples are different. Comparing the polymers, the LDPE/LLDPE blend is the most crystalline material with the highest melting temperatures, whereas EVA-9 has the lowest crystallinity with the lowest melting temperatures. DSC studies revealed that the com-
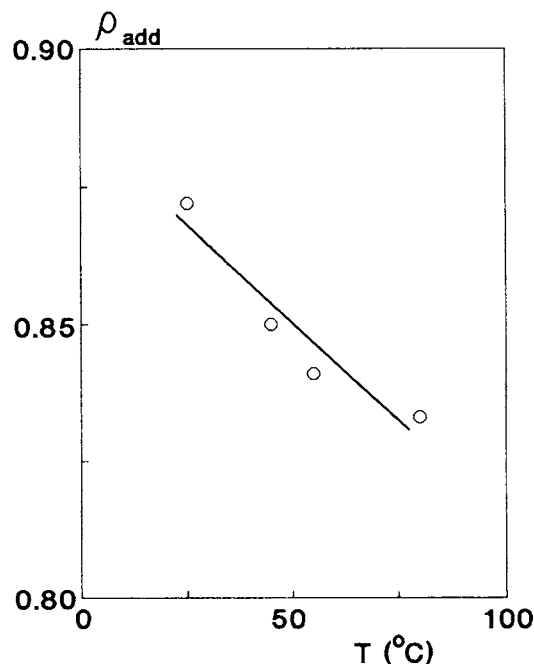
Figure 1   Temperature dependence of the density of Irganox 1076 dissolved in sunflower oil.
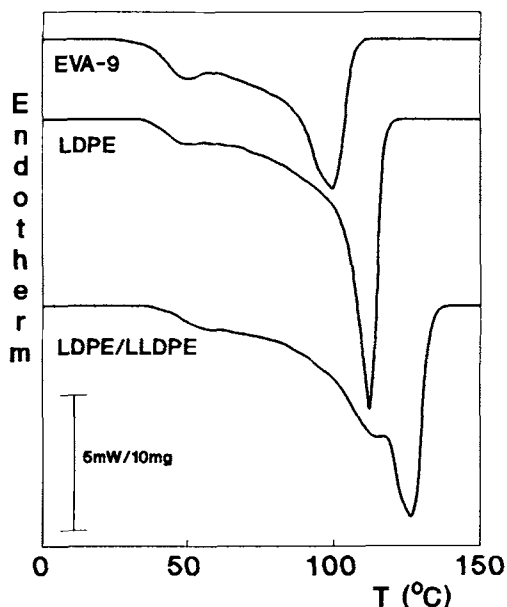
Figure 2 Melting curves of the investigated ethylene polymers measured by DSC with a rate of heating of 10°C/min.

ponents crystallize separately in the LDPE/LLDPE blend.

Temperature dependence of polymer crystallinity was determined by two methods and the results were compared. Before the measurements, the polymer films were annealed at 80°C for 4 h and cooled to room temperature at the same rate.

Table III Density and Crystallinity Values of the Polymers

| Polymer	Temperature (°C)	Density (g/cm³)	$\alpha_{c,H}$[a]	$\alpha_{c,d}$[b]
EVA-9	25	0.9220	0.360	
	45	0.9075	0.326	
	55	0.9016	0.299	
	80	0.8741	0.221	
LDPE	25	0.9180	0.445	0.488
	45	0.9031	0.423	0.456
	55	0.8976	0.407	0.452
	80	0.8769	0.354	0.399
LDPE/ LLDPE	25	0.9234	0.525	0.525
	45	0.9114	0.500	0.510
	55	0.9039	0.479	0.493
	80	0.8878	0.436	0.467

[a] Measured.
[b] Calculated according to Ref. 27.

1. $\alpha_{c,H}(T)$ was determined by measuring the heat of fusion as a function of temperature in the whole melting range, and ΔH below T temperature was calculated by partial integration.

2. $\alpha_{c,d}(T)$ was calculated from densities measured at different temperatures using the Chiang–Flory equations.[27] This method can be used only for PE, as the amorphous density of EVA is different.

The measured density and calculated crystallinity data are summarized in Table III. $\alpha_{c,H}$ and $\alpha_{c,d}$ values of PE samples are compared in Figure 3; they show a linear relationship. In accordance with literature data,[28,29] $\alpha_{c,d}$ values are somewhat higher than those of $\alpha_{c,H}$. The difference decreases with increasing crystallinity. The reason for the differences lies in the calculating methods and were discussed in detail previously.[29] As $\alpha_{c,H}$ is closer to the real crystallinity of PE than is $\alpha_{c,d}$, it was used for further calculations.

Free volumes of the polymers were calculated from the measured data with the following assumptions:

- The two-phase model[6] was used that considers the semicrystalline polymers consisting of an impermeable crystalline and a permeable dis-
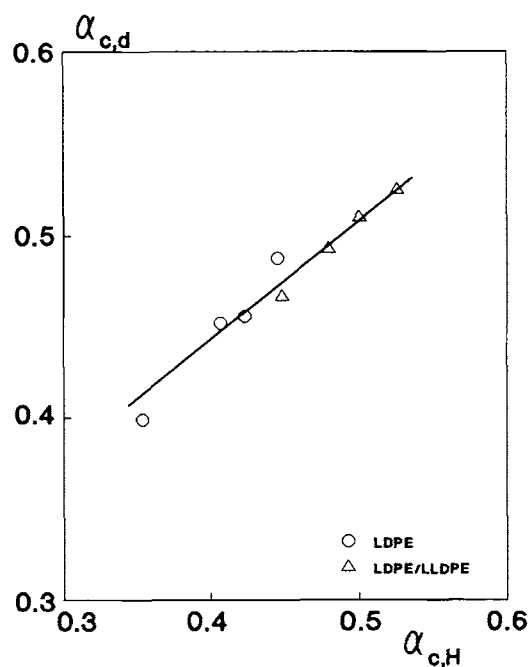
Figure 3 Relationship between crystallinity values of the investigated polymers determined by DSC ($\alpha_{c,H}$) and calculated from density data ($\alpha_{c,d}$).

ordered phase. For the transport of small molecules, only the amorphous free-volume is available.

- In EVA copolymer, acetate groups are rejected from the crystallites.

- Density of the crystallites depends only on the temperature (at constant pressure) and is independent of the ethylene polymer type; therefore, it can be calculated by the Chiang–Flory equation[27] that was originally determined from the data of linear PE.

Density (ρ_a) and volume fraction (α'_a) of the disordered phase was determined from the measured crystallinity ($\alpha_{c,H}$) and density (ρ) values and from the calculated densities of the crystalline phase. The results are given in Table IV. A linear relationship was found between $\alpha_{c,H}$ and ρ_a in the measured temperature interval. From the data of Table IV it can be also seen that, although the volume fraction of the disordered phase at given temperature is the largest in EVA-9, the density is the highest in it.

According to the definition, fractional free-volume of the amorphous phase can be described as

$$f_a = \alpha'_a (v_{f,a}-v_0)/v_0 \qquad (1)$$

where $v_{f,a}$ is the specific volume of the disordered phase, and v_0, the occupied specific volume of the polymer at 0 K.

As v_0 cannot be measured directly, different methods are given in the literature for the calculation.[9,16,30-33] For simplicity, Doolittle's equation[30,31]

Table IV   Calculated Data of the Investigated Polymers

Polymer	Temperature (°C)	ρ_a (g/cm³)	α'_a	f_a (cm³/g)
EVA-9	25	0.883	0.624	0.083
	45	0.871	0.660	0.098
	55	0.868	0.689	0.105
	80	0.847	0.772	0.139
LDPE	25	0.862	0.526	0.084
	45	0.847	0.549	0.099
	55	0.843	0.567	0.106
	80	0.829	0.626	0.129
LDPE/ LLDPE	25	0.852	0.431	0.075
	45	0.842	0.459	0.086
	55	0.837	0.517	0.101
	80	0.823	0.517	0.111
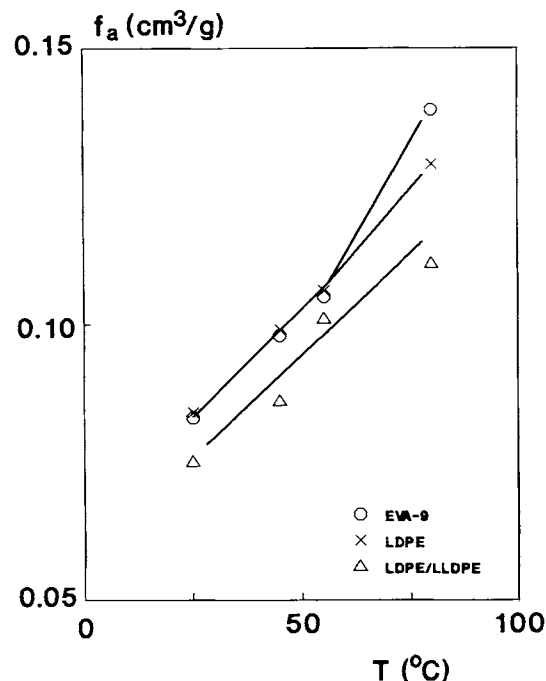
Figure 4   Changes of the fractional free-volume of the noncrystalline phase in the polymers as a function of temperature.

was used, which predicts $v_0 = 1.0$ cm³/g occupied volume for high alkanes. It is only a rough approximation in our case where branched ethylene polymers were investigated (especially for EVA, which contains also a small amount of heterogroups), but if we consider the free-volume as a probability factor,[6,18] it seems to be acceptable.

Calculated f_a data of the polymers are given in Table IV and plotted as a function of temperature in Figure 4. It can be concluded that in the measured range f_a increases linearly with temperature only up to a given value. The closer we are to the melting peak of the polymer crystals, the larger is the deviation from linearity.

Diffusion of SBHP in Ethylene Polymers

Diffusion of SBHP was measured at 45, 55, and 80°C using LDPE-base additive source with 5 wt % penetrant. The diffusion coefficient (D) data calculated from the concentration vs. penetration depth curves are given in Table V.

According to the free-volume theory,[6,16,18] the mobility of a small molecule in a given medium depends upon the probability that the molecule finds in its neighborhood a hole large enough for its displacement, so the diffusion coefficient can be ex-

Table V   Measured Diffusion Coefficient and Solubility of Irganox 1076 in Ethylene Polymers

Polymer	Temperature (°C)	$D \times 10^9$ (cm²/s)	S (w/w %)
EVA-9	45	1.22	10.9
	55	2.24	10.1
	80	26.70	12.9
LDPE	45	1.13	10.9
	55	2.67	12.1
	80	21.10	11.8
LDPE/LLDPE	45	0.32	12.3
	55	0.73	12.4
	80	12.10	10.4

pressed by the fractional free-volume (f) of the polymer:

$$D = D_0 \exp(-A_D/f) \qquad (2)$$

where D_0 is considered to be dependent primarily upon the size and shape of the diffusant and A_D corresponds to the minimum hole required for a penetrant to permit its displacement.

In our case, the fractional free-volume available for additive diffusion equals that of the amorphous phase (f_a). It was determined in each experiment before the diffusion measurement. In Figure 5, natural logarithm of the diffusion coefficient is plotted as a function of $1/f_a$. As can be seen, a linear relationship was obtained, independently of the polymer type. From the $\ln D$ vs. $1/f_a$ function, $D_0 = 2.96 \times 10^{-4}$ cm²/s and $A_D = 1.32$ values were calculated.

Solubility of SBHP in Ethylene Polymers

Before the experiments, solubility data of SBHP in LDPE were calculated by Moisan's equations given in Ref. 4. $S < 2.5$ wt % was obtained for the temperature range used in our experiments. Therefore, a 5 wt % SBHP containing additive source was prepared and solubility in the three polymers was measured at 45, 55, and 80°C, determining the concentration by UV spectroscopy; 20–45 mg additive/cm³ polymer values were obtained depending on the polymer type but independently of the temperature. From the results, two conclusions were drawn:

1. Solubility of SBHP in ethylene polymers must be higher than 5 wt % because the measured values correspond to about 5 wt % additive dissolved in the amorphous phase.

2. As the UV absorption of dissolved and crystalline SBHP is different and calibration was made in solution, at high concentrations, values determined from UV data correspond to the concentration of dissolved additive in the polymer at room temperature, not to the amount dissolved at the measuring temperature.

New additive sources were prepared with 20 wt % SBHP. The LDPE-base additive source was used for the experiments with LDPE and LDPE/LLDPE films and the EVA-base one for EVA-9 films. Solubilities were calculated from the weight gain of the additive-free polymers. At 45°C, equilibrium values were reached after a relatively long time, during which time dependent concentration was measured. At 55 and 80°C, the additive concentration in the film stack became independent of the measuring time after a short experimental period. Thickness of the films were also determined before and after the experiment. The measured solubility data are given in Table V. These are higher by an order of magnitude than those given in Ref. 4 and not dependent on the polymer type and temperature. Considering the crystallinity of the polymers, we obtain solubility in the noncrystalline phase around 20 wt %. It can be assumed that solubility of Irganox 1076 in ethylene polymers between 45 and 80°C is higher
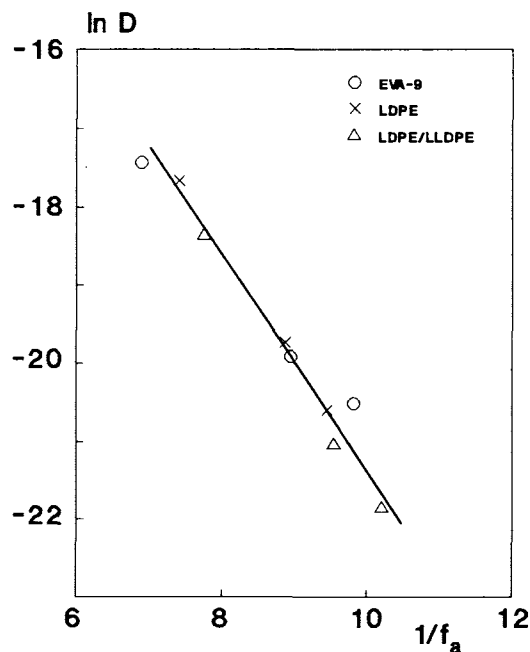
Figure 5   Changes of the diffusion coefficient of Irganox 1076 as a function of the fractional free-volume of the polymer noncrystalline phase.
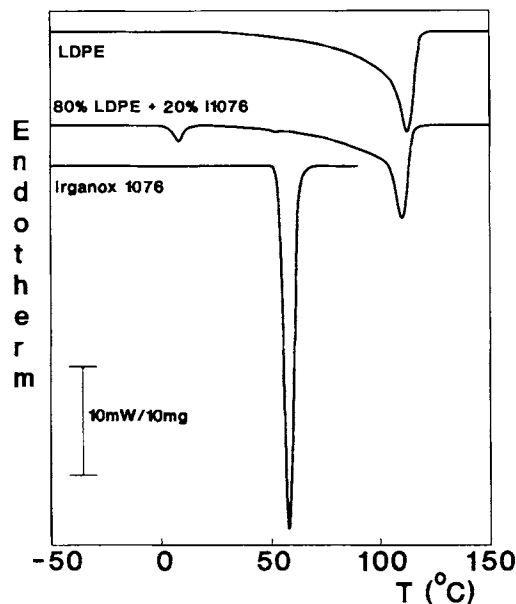
than the measured values. Dissolution of the additive resulted also a film thickness increase of about 5–6%. All these results suggest that Irganox 1076 is miscible—at least up to 20 wt %—with the non-crystalline region of the ethylene polymers in this temperature range and the measured solubility data were limited by the concentration of SBHP in the additive source.

Miscibility, i.e., interaction between the components in a blend of a semicrystalline polymer with a low molecular weight soluble compound or with another polymer, results in a melting-point depression and a decrease of crystallinity.[34,35] Heat of fusion of the two additive sources containing 20 wt % SBHP was measured. To eliminate the effect of history on the samples, melting properties of the blends measured in the second heating run after cooling from melt by 10°C/min were compared with those of the components. The results are given in Table VI. The expected effects were obtained: The melting peaks of both the polymer and the additive shifted to lower temperatures and the heat of fusion decreased. The changes are more pronounced in the properties of the additive. In the blends used as additive sources, the melting peak of SBHP is between −5 and 25°C. A graphic account on the changes can be seen in Figure 6, where the melting curve of the LDPE-base additive source is compared with that of the components. These results seem to confirm the suggestion that SBHP is miscible with the non-crystalline fraction of ethylene polymers.

Figure 6 Heat of fusion of LDPE, Irganox 1076, and their blend measured in the second run of DSC measurement. Rate of heating and cooling: 10°C/min.

DISCUSSION

The ethylene polymers used in this work for studying the transport properties of Irganox 1076 have different types of branching, therefore, also different crystallization properties. According to the literature,[36] the distribution of the specific heat of fusion measured as a function of temperature corresponds with the lamellar thickness distribution of the crystallites. The results of the polymer characterization measurements suggest that not only the amount of crystallinity but also the lamellar thickness distribution and the density of the disordered phase is different in the three investigated ethylene polymers.

Solubility data obtained between 45 and 80°C and the thermal properties of 20 wt % additive-containing blends revealed good miscibility of Irganox 1076 with ethylene polymers. It can be attributed to the chemical nature of the additive, which has a long paraffinic chain, being a stearyl ester. Using the so-called equilibrium method, we obtained much higher solubilities than reported in Ref. 4, where the data determined by the "dynamic method" are given. In our experiments, by increasing the concentration of Irganox 1076 in the additive source up to 20 wt %, the measured solubility values increased simultaneously, suggesting miscibility between the disordered polymer chains and the additive in the measured concentration range. This conception was confirmed by DSC measurements of the additive sources. To decide whether this additive is miscible

Table VI Melting Properties of Two Additive Sources and Their Components

Sample	T_m (°C)	ΔH (J/g) Measured	ΔH (J/g) Expected
LDPE	110.8	113.2	
EVA-9	97.2	87.8	
Irganox 1076	54.8	121.0	
20 wt % I1076			
+ 80 wt % LDPE	7.1	6.3	
	50.5	0.3	
	107.5		
		Σ 104.2	Σ 114.8
20 wt % I1076			
+ 80 wt % EVA-9	7.6	6.4	
	95.6		
		Σ 83.4	Σ 94.6

Rate of heating: 10°C/min. History: cooling from melt by the rate of 10°C/min.

with disordered paraffinic polymer chains in the total concentration range, it is necessary to conduct experiments with noncrystalline olefinic polymers using another experimental arrangement.

Transport property measurements were conducted between 45 and 80°C. In this temperature range, not only the additive suffers phase transition but also a part of the polymer crystals is melted. Changes in the polymer structure are different in the three systems. When we evaluate the results of the diffusion measurements, all these parameters have to be taken into account because the rate of diffusion is determined by the mobility of both the penetrant and the polymer.

DSC measurements revealed that Irganox 1076 is in liquid state in the used additive sources above room temperature; therefore, the melting properties of the penetrant did not affect the diffusion rate in the measured temperature range.

As to the effect of the polymer properties, in studying the changes of the diffusion coefficient as a function of temperature in an Arrhenius plot or as a function of the disordered phase volume fraction (α'_a), it is not taken into account that higher temperatures result not only an increase of α'_a but also changes of the specific volume of the polymer in a nonlinear manner. For correct evaluation of the results, the diffusion rate has to be compared with the free-volume in the polymer available for transport processes. Results showed that natural logarithms of the diffusion coefficient data measured in three different types of ethylene polymers give a straight line as a function of the reciprocal fractional free-volume of the noncrystalline phase in the polymer. It indicates that the rate of diffusion of Irganox 1076 in ethylene polymers does not depend on the size and distribution of the crystallites; it is primarily determined by a probability factor that represents the average fractional free-volume in the disordered phase.

CONCLUSIONS

In this work, compatibility of Irganox 1076 with three different ethylene polymers (LDPE, LDPE/LLDPE blend, and EVA) were studied. The results were evaluated on the basis of the free-volume theory.

Fractional free-volume of the disordered phase in the polymer (f_a) was determined by density and DSC measurements. It was found that f_a changes differ-

ently in the investigated ethylene polymers between 25 and 80°C.

Diffusion and solubility measurements were carried out at 45, 55, and 80°C. Results showed that the morphology of ethylene polymers does not influence the penetration rate of this additive; the diffusion coefficient changes exponentially with the reciprocal fractional free-volume of the noncrystalline phase in the polymer. Solubility measurements provided much higher values than given in the literature. Results suggest miscibility of the additive with the noncrystalline polymer chains in the measured temperature range.

REFERENCES

1. J. Crank and G. S. Park, in *Diffusion in Polymers*, J. Crank and G. S. Park, Eds., Academic Press, London, 1968, Chap. 1, p. 1.
2. J. Lustoň, in *Developments in Polymer Stabilisation-2*, G. Scott, Ed., Applied Science, London, 1980, Chap. 5, p. 185.
3. N. C. Billingham and P. D. Calvert, in *Developments in Polymer Stabilisation-3*, G. Scott, Ed., Applied Science, London, 1980, Chap. 5, p. 139.
4. J. Y. Moisan, in *Polymer Permeability*, J. Comyn, Ed., Elsevier, London, 1985, Chap. 4, p. 119.
5. W. L. Hawkins, M. A. Worthington, and W. Matreyek, *J. Appl. Polym. Sci.*, **3**, 277 (1960).
6. A. Peterlin, *J. Macromol. Sci. Phys.*, **B11**, 57 (1975).
7. J. Klein, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 2057, 2065 (1977).
8. R. Kosiyanon and R. McGregor, *J. Appl. Polym. Sci.*, **26**, 629 (1981).
9. V. M. Shah, S. A. Stern, and P. J. Ludovice, *Macromolecules*, **22**, 4660 (1989).
10. N. C. Billingham, in *Oxidation Inhibition in Organic Materials*, J. Pospíšil and P. P. Klemchuck, Eds., CRC Press, Boca Raton, FL, 1990, Vol. 2, Chap. 6, p. 249.
11. J. Koszinowski, *J. Appl. Polym. Sci.*, **31**, 1805 (1986).
12. J. Durmis, M. Karvaš, P. Čaučik, and J. Holčik, *Eur. Polym. J.*, **11**, 219 (1975).
13. J. Klein and B. J. Briscoe, *Proc. R. Soc. Lond. A*, **365**, 53 (1979).
14. J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolites*, 3rd ed. Reinhold, New York, 1950.
15. V. Stannett and H. Yasuda, in *Crystalline Olefin Polymers*, R. A. V. Raff and K. W. Doak, Eds., Interscience, New York, 1964, Part II, Chap. 4, p. 131.
16. M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).
17. H. L. Frisch, *Polym. J.*, **23**, 445 (1991).
18. H. Fujita, *Fortschr. Hochpolym.-Forsch.*, **3**, 1 (1961).
19. J. Y. Moisan, *Ann. Télécommun.* **34**, 53 (1979).
20. J. Y. Moisan, *Eur. Polym. J.*, **16**, 979, 989, 997 (1980).

21. J. Y. Moisan, *Eur. Polym. J.*, **17**, 857 (1981).
22. R. Spatafore and L. T. Pearson, *Polym. Eng. Sci.*, **31**, 22 (1991).
23. R.-J. Roe, H. E. Bair, and C. Gieniewski, *J. Appl. Polym. Sci.*, **18**, 843 (1974).
24. E. Földes and B. Turcsányi, *J. Appl. Polym. Sci.*, **46**, 507 (1992).
25. L. Mandelkern, J. G. Fatou, R. Denison, and J. Justin, *Polym. Sci. B*, **3**, 803 (1965).
26. B. Wunderlich, *Macromolecular Physics-3*, Academic Press, New York, 1980, p. 40.
27. R. Chiang and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 2857 (1961).
28. L. Mandelkern, *Polym. J.*, **17**, 337 (1985).
29. E. Földes, G. Keresztury, M. Iring, and F. Tüdos, *Angew. Makromol. Chem.*, **187**, 87 (1991).
30. A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).
31. A. K. Doolittle and D. B. Doolittle, *J. Appl. Phys.*, **28**, 901 (1957).
32. A. Bondi, *J. Phys. Chem.*, **58**, 929 (1954).
33. R. N. Haward, *J. Macromol. Sci.-Rev. Macromol. Chem.*, **C4**, 191 (1970).
34. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York, 1979.
35. B. Pukánszky, F. Tüdős, A. Kalló, and G. Bodor, *Polymer*, **30**, 1399 (1989).
36. A. Wlochowicz and M. Eder, *Polymer*, **25**, 1268 (1984).