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Diffusion of hindered amine light stabilizers in low density polyethylene and isotactic polypropylene

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Diffusion coefficients and solubilities of some hindered amine light stabilizers (HALS) were measured in low density polyethylene (LDPE) and isotactic polypropylene(iPP). From the results obtained, activation energies and preexponential parameters of the Arrhenius equation were calculated. In the case of oligomeric HALS no measurable diffusion was found even after 10 months at room temperature.

An empirical model from the literature was used for the correlation of physical parameters obtained with the available experimental data on the efficiency of HALS. According to this model the solubility value seems to be more important for stabilizer efficiency than its rate of diffusion.

INTROUCTION

The discovery and commercialization of hindered amine light stabilizers, commonly referred to as HALS, represents significant progress in the stabilization of polyolefins. The efficiency of HALS is superior to that of other light stabilizers for polyolefins and even to carbon black.[1]

In recent years HALS have been one of the most actively investigated classes of polymer additives and there have been many publications which contribute to our understanding of the mechanism by which they function. It is generally accepted that hindered amines have multiple mechanisms of action and an important role in polymer stabilization is played by their transformation products—nitroxyl radicals—which can be regenerated in the stabilization process.[2,3]

It has been established that photo-oxidation of a stabilized polymer is accompanied by loss of most of the effective stabilizer.[4] The decrease in concentration of the stabilizer can be caused by its chemical consumption, which is directly associated with the stabilization mechanism, and by physical loss of the stabilizer from the polymer matrix, for example, by blooming, volatilization, extraction, etc. It is obvious that during the utilization of a stabilized polymer product, the stabilizer will be depleted in both ways.

Physical aspects of polymer stabilization have already been reviewed in the literature.[5–8] However, for HALS type stabilizers (transformation products of which can be regenerated during the stabilization process, thereby decreasing the importance of chemical consumption) there are few experimental data available concerning their physical behavior in a polymer matrix.

In this present work we have measured diffusion coefficients and solubilities of some HALS in low density polyethylene (LDPE) and isotactic polypropylene (iPP).

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EXPERIMENTAL

Materials

LDPE (Bralen FB 2–17, Slovnaft Bratislava) was pure and additive free. MFI = 2·0 g/10 min, density 0·921 g/cm^3. Film of thickness 90 μm was prepared by blow extrusion.

iPP (Tatren HPF, Slovnaft Bratislava) was pure and additive free, MFI = 10 g/10 min, density 0·905 g/cm^3. Film of thickness 50 μm was prepared by extrusion.

The stabilizers were as follows:

HALS 1: ester of 2,2,6,6-tetramethyl-4-piperidinol and stearic acid of technical grade (mixture of fractions C_{15}–C_{17}), light-yellow wax-like product (Dastib® 845); Mp = 28–32°C; M_n = 396–423.

HALS 2: bis(2,2,6,6-tetramethyl-4-piperidinyl)-sebacate (Tinuvin® 770) white crystals; Mp = 81–83°C; M_n = 480·7.

HALS 3: N-amino, N-amido bis(2,2,6,6-tetramethyl-4-piperidinyl)-β-amino propionamide; white crystals; Mp = 134–137°C; M_n = 366·6.

HALS 4; oligomeric HALS (Chimasorb® 944); white powder; Mp = 115–125°C; $\bar{M}_n$ = 2300;

HALS 5: 1,6-bis(2,2,6,6-tetramethyl-4-piperidinyl)hexamethylene diamine, crystaline product, Mp = 62–64°C; M_n = 394.

The structural formulae of the stabilizers are shown in Fig. 1.

Medicinal oil A1: (Petrochema Dubova) saturated paraffinic oil, kinematic viscosity 24 mm^2/s(40°C); density 853 kg/m^3.

Propoil K 300: (Slovnaft Bratislava) synthetic oil—mixture of branched hydrocarbons C_6–C_{90} containing 1–1·5 double bonds per average molecule; viscosity 300 mPa·s (20°C), density 835 kg/m^3.

Solvents: n-heptane, carbon tetrachloride, acetone and methanol were of analytical grade.

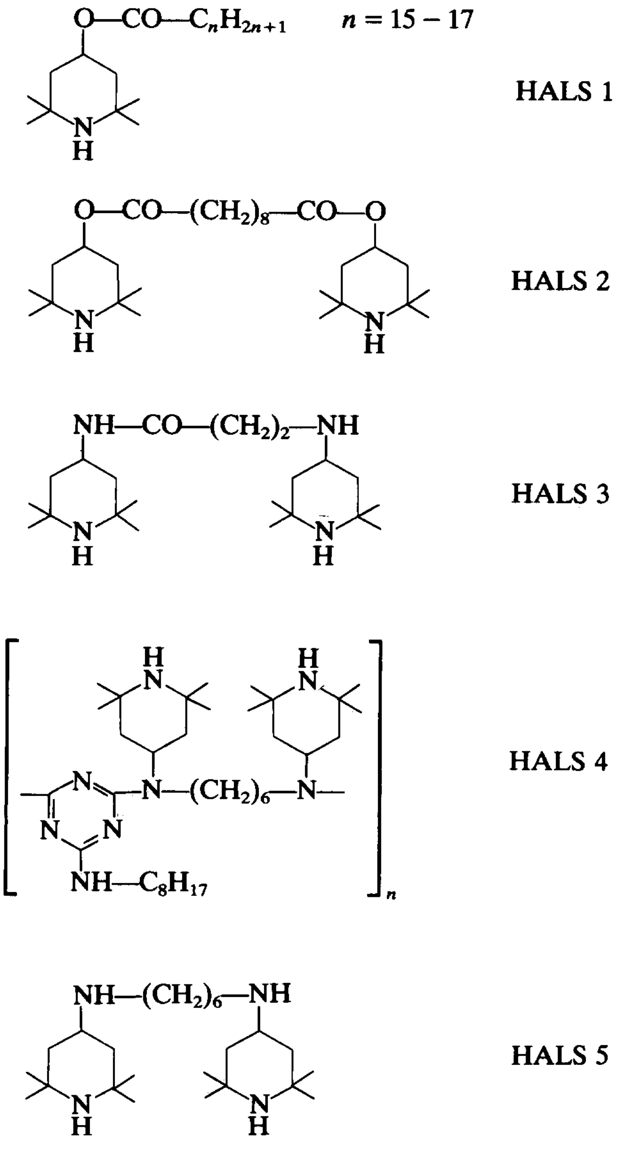

Fig. 1. Structural formulae of used HALS

METHODS

Diffusion and solubility of HALS in polymers

The diffusion and solubility of HALS in polyolefins were measured using the method described by Moisan.[7] The original method was modified because the mechanically pressed stack of foils always contained air bubbles between individual foils, which changed the diffusion area and thereby the results of the calculations. Individual foils were arranged in a stack, air bubbles were squeezed out by a rubber roller, and the stack was heated for 5 min between metal plates (90°C for LDPE and 130°C for iPP). This stack was then pressed (10 MPa) in a cold hydraulic press for 3 min. The stack thus obtained was compact and transparent, without air bubbles. Stabilizer was applied to the prepared stack in the form of a solution in methanol or acetone the solvent then being evaporated leaving a thin layer of the stabilizer deposited on the stack. The stack with the stabilizer was then placed in an oven for a defined time. The stabilizer was then carefully removed from the upper foil and individual foils were peeled from the stack and analyzed for stabilizer content. The analysis of HALS was done by UV-spectroscopy after the extraction of the stabilizer with CCl_4 for 24 h. The absorbance of HALS complex with iodine in CCl_4 was measured at 278 nm.

The diffusion coefficient (D) and solubility (S) were calculated from the appropriate solution of Fick's second law for the given initial and boundary conditions:

$$c_{x,t} = S\,.\,(1-\mathrm{erf}(x/K)) \qquad (1)$$

where $c_{x,t}$ is the concentration of HALS at position x and time t, S is the solubility and K is given by:

$$K = 2\,.\,\sqrt{D\,.\,t} \qquad (2)$$

The total amount of stabilizer which has entered the stack (Q_t) is given by:

$$Q_t = \frac{K\,.\,S}{\sqrt{\pi}} \qquad (3)$$

The ratio of the amount of diffusant which has entered the stack in the region $0-x(Q_x)$ to the total amount of diffusant in the stack (Q_t) is expressed by:

$$\frac{Q_x}{Q_t} = 1-\sqrt{\pi}\,.\,\int_{x/K}^{\infty}(1-\mathrm{erf}(x/K))\,\mathrm{d}(x/K) \qquad (4)$$

According to Petry and Keller[9] the function $1-\mathrm{erf}(x/K)$ can be approximated by the expression $\exp(-(x/K))^2\,.\,G(x/K)$, where G is a rational function defined by the authors.[9] For calculation of D and S, the method for the calculation of a root of a non-linear equation—regula falsi—was used.[10] The computation itself was done with a quickly emerging modification of the above method—Pegasus.[17] The accuracy of the calculations is expressed by the correlation index $I_{x,y}$. The coincidence of experimental values with the theoretical curve was simultaneously checked on a graphic display.

Solubility of HALS in model liquids

Saturated solutions of HALS in model hydrocarbons were prepared and analyzed by UV-spectroscopy for the stabilizer content as above after dilution in CCl_4.

RESULTS AND DISCUSSION

The results obtained (D and S) from diffusion measurements for HALS 1–3 in LDPE are summarized in Tables 1–3. It should be noted that the solubility parameter did not always reach the equilibrium value because of the computation condition according to which the concentration of stabilizer in the last film must be zero.[10] In addition, we observed a deviation of the theoretical curve from experimental data in the experiments where the solubility value exceeded 7–8%. This could be explained by concentration dependence of diffusion.

From Tables 1 and 2 it can be seen that the

Table 1. Diffusion coefficients and solubilities of HALS 1 in LDPE

T (°C)	t (h)	D (cm^2/s)	S (wt.%)
23	69·4	$6{\cdot}9\times10^{-10}$	1·96
23	69·7	$7{\cdot}1\times10^{-10}$	2·10
23	163·8	$7{\cdot}2\times10^{-10}$	2·22
23	381·0	$6{\cdot}8\times10^{-10}$	2·10
50	1·25	$2{\cdot}2\times10^{-8}$	3·9
50	1·5	$2{\cdot}1\times10^{-8}$	4·3
58	0·83	$3{\cdot}3\times10^{-8}$	4·3
58	1·0	$3{\cdot}5\times10^{-8}$	4·1
65	1·0	$5{\cdot}8\times10^{-8}$	6·0
65	1·25	$4{\cdot}1\times10^{-8}$	6·2
75	0·42	$1{\cdot}0\times10^{-7}$	6·1
75	0·75	$1{\cdot}1\times10^{-7}$	5·4

Table 2. Diffusion coefficients and solubilities of HALS 2 in LDPE

T (°C)	t (h)	D (cm^2/s)	S (wt.%)
23	456·75	$4{\cdot}7\times10^{-10}$	0·11
23	486·2	$4{\cdot}3\times10^{-10}$	0·1
23	651·8	$3{\cdot}7\times10^{-10}$	0·1
50	3·0	$6{\cdot}9\times10^{-9}$	0·26
50	4·0	$6{\cdot}6\times10^{-9}$	0·24
58	3·0	$2{\cdot}1\times10^{-8}$	0·32
58	5·0	$1{\cdot}8\times10^{-8}$	0·38
65	2·0	$3{\cdot}2\times10^{-8}$	0·66
67	3·0	$3{\cdot}5\times10^{-8}$	0·93
75	1·0	$5{\cdot}1\times10^{-8}$	1·38
75	2·5	$6{\cdot}2\times10^{-8}$	2·77

Table 3. Diffusion coefficients and solubilities of HALS 3 in LDPE

T (°C)	t (h)	D (cm^2/s)	S (wt.%)
49	7·0	$1{\cdot}4\times10^{-8}$	0·02
60	5·0	$2{\cdot}2\times10^{-8}$	0·02
65	5·0	$2{\cdot}8\times10^{-8}$	0·03
70	4·0	$3{\cdot}4\times10^{-8}$	0·04
75	4·0	$4{\cdot}0\times10^{-8}$	0·04
80	3·5	$5{\cdot}2\times10^{-8}$	0·05

values of D for HALS 2 are somewhat smaller than those for HALS 1, and the solubility values (especially at room tempeature) differ by one order of magnitude. This clearly indicates the influence of the long alkyl substituent of HALS 1 on its solubility in LDPE.

No measurable penetration of HALS 3 into the stack of films was found at room temperature after 2 months. The values of D at elevated temperatures (Table 3) are comparable to the D values for HALS 1 and 2 (Tables 1 and 2), but the solubilities were found to be very low. Oligomeric HALS 4 showed no measurable diffusion even after 10 months (7300 h) at room temperature.

The diffusion coefficients given in Tables 1–3 obey the Arrhenius law. Calculated values of activation energy of diffusion (E_D) and the logarithm of the preexponential factor ($\log D_0$) are summarized in Table 4. (For HALS 1, the values of D obtained below the melting temperature were not included in the calculation because they caused a discontinuity in the Arrhenius plot.) E_D and $\log D_0$ values for HALS 1 and 2 are comparable with the typical values for diffusion of organic stabilizers in LDPE[5]. The activation energy of diffusion of HALS 3, on the other hand, is very low and comparable to the activation energy of diffusion of oxygen in LDPE.[7]

The piperidine skeleton in oligomeric HALS 4 is bound in position 4 through the nitrogen atom as in HALS 3. This led to the suggestion that one of the reasons for the unmeasurable penetration of HALS 4 into the LDPE stack is the low solubility of this structural unit in the polymer (see Table 3). To verify the presumption of low solubility of the HALS stabilizers bonded in position 4 through a nitrogen atom experiments were carried out with HALS 5 which has a similar structure to HALS 3 and simultaneously is part of the structural unit of HALS 4. According to the results in Table 5 the D values are comparable but the solubility values differ by two orders of magnitude.

Table 4. Calculated parameters of Arrhenius equation for diffusion of HALS in LDPE

Stabilizer	E_D (kJ/mol)	$\log D_0$	Temperature range (°C)
HALS 1	57·2	1·55	50–75
HALS 2	83·1	5·3	23–75
HALS 3	38·3	−1·6	50–80

Table 5. Comparison of diffusion of HALS 3 and HALS 5

Stabilizer	T (°C)	D (cm²/s)	S (wt.%)
HALS 3	49	$1{\cdot}4\times10^{-8}$	0·03
HALS 5	49	$1{\cdot}4\times10^{-8}$	2·00
HALS 3	70	$3{\cdot}4\times10^{-8}$	0·04
HALS 5	70	$5{\cdot}6\times10^{-8}$	8·00

Because the solubilities of individual HALS compounds in the LDPE matrix differed significantly, the solubility of these stabilizers in non-polar liquid media was measured. The results, in Table 6, confirmed the very low solubility of HALS 3, and also the difference in solubilities of HALS 1 and HALS 2. Oligomeric HALS 4 showed surprisingly high solubility. This means that the unmeasurable diffusion of HALS 4 can be explained only by the size of its molecules and not by low solubility in the polymer matrix. Contrary to our presumption, the bond in position 4 through nitrogen seems to have a positive effect on the solubility of HALS in non-polar media (see, for example, HALS 5 and HALS 2 in Table 6).

Diffusion and solubility measurements in iPP were carried out in the same way as in LDPE. The results for individual HALS stabilizers are presented in Tables 7, 8, and 9. The values of D and S for HALS 1 are, in general, lower in iPP than in LDPE. In the case of HALS 2, the same trend is seen in D values, but solubilities are similar in iPP and LDPE. The D values for HALS 3 are also lower in iPP than in LDPE, and the solubility in iPP remains very low.

The parameters of the Arrhenius equation for diffusion of HALS in iPP were calculated from the data in Tables 7 and 8 and are shown in Table 10. From a comparison of these data with the results calculated for LDPE (Table 4) it is

Table 6. Solubility of HALS in model liquids at room temperature

Stabilizer	Solubility (wt.%)		
	n-heptane	med. oil A1	oil K 300
HALS 1	49·20	23·20	1·20
HALS 2	5·80	2·10	0·70
HALS 3	0·08	0·16	0·04
HALS 4	53·66	14·53	3·0
HALS 5	30·00	4·50	—

Table 7. Diffusion coefficients and solubilities of HALS 1 in iPP

T (°C)	t (h)	D (cm^2/s)	S (wt.%)
60	2·5	$1{\cdot}1\times10^{-9}$	2·15
60	3·5	$1{\cdot}2\times10^{-9}$	2.2
70	2·1	$4{\cdot}1\times10^{-9}$	3·0
70	2·1	$4{\cdot}0\times10^{-9}$	2·6
80	2·0	$1{\cdot}2\times10^{-8}$	2·5
80	1·25	$1{\cdot}1\times10^{-8}$	3·3
90	1·28	$3{\cdot}0\times10^{-8}$	3·1
90	1·28	$3{\cdot}0\times10^{-8}$	3·9

Table 8. Diffusion coefficients and solubilities of HALS 2 in iPP

T (°C)	t (h)	D (cm^2/s)	S (wt.%)
57	6·0	$4{\cdot}5\times10^{-8}$	0·31
63	5·0	$1{\cdot}1\times10^{-9}$	0·54
68	3·2	$1{\cdot}9\times10^{-9}$	0·63
68	5·2	$1{\cdot}4\times10^{-9}$	0·60
70	2·5	$1{\cdot}3\times10^{-9}$	0·86
70	4·0	$1{\cdot}5\times10^{-9}$	0·92
73	7·3	$2{\cdot}3\times10^{-9}$	1·16
73	4·0	$3{\cdot}8\times10^{-9}$	1·08
83	4·0	$5{\cdot}7\times10^{-9}$	2·08
83	6·0	$6{\cdot}5\times10^{-9}$	1·83

Table 9. Diffusion coefficients and solubilities of HALS 3 in iPP

T (°C)	t (h)	D (cm^2/s)	S (wt.%)
80	3·0	$3{\cdot}0\times10^{-9}$	0·06
80	4·0	$2{\cdot}8\times10^{-9}$	0·06
90	4·25	$7{\cdot}1\times10^{-9}$	0·09
90	4·5	$6{\cdot}2\times10^{-9}$	0·09

Table 10. Calculated parameters of Arrhenius equation for diffusion of HALS in iPP

Stabilizer	E_D (kJ/mole)	$\log D_0$	Temperature range (°C)
HALS 1	109·0	8·2	60–90
HALS 2	95·6	5·8	57–83

evident that for HALS 2, $\log D_0$ and E_D do not change significantly, but for HALS 1 there is a five-fold increase in the $\log D_0$ values and E_D for iPP is twice that for LDPE. A similar difference for an organic stabilizer with a long alkyl substituent has already been observed:[11,12] 2-hydroxy-4-*n*-octadecyloxybenzophenone in LDPE had values $\log D_0 = 0{\cdot}83$ and $E_D = 57$ kJ/mole, and $\log D_0 = 5{\cdot}49$ and $E_D = 99{\cdot}5$ kJ/mole in iPP, respectively.

Studying the efficiency of phenolic antioxidants in LDPE, Moisan[7] came to the conclusion that the ratio S^2/D is empirically linked to the protection time. The logarithm of the protection time for outdoors exposure increased with increasing $\ln S^2/D$. Values $\ln(S^2/D)$[13] ranged from 24·94 for the worst stabilizer to 39.73 for the best. When these values are calculated for HALS in LDPE we get 40·9 for HALS 1, 36·8 for HALS 2, and *ca.* 29 for HALS 3. The estimated ratio in iPP is again a little more favourable for HALS 1 than for HALS 2, but here the difference is much smaller. This means that according to this empirical relationship, HALS 1 should be more effective in the stabilization of LDPE than HALS 2. There are only a few experimental data available to make possible a comparison of these stabilizers under the same conditions.[14–16] These data confirm the higher efficiency of HALS 1 over HALS 2, in spite of the fact that HALS 2 has two active piperidine structures in the molecule, while HALS 1 has only one. (See Fig. 1). The experimental results available for HALS 3 depend on the testing conditions used.

It seems that the empirical relationship above can be used to estimate the effective protection of polyolefins by hindered amine stabilizers. In accordance with this empirical model, the solubility value seems to be a more important physical parameter for stabilizer efficiency than diffusion coefficient.

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