Dedicated to Prof. P.T. Frangopol on the occasion of his 75th anniversary

Prediction of Diffusion Coefficients in Plastic Materials

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Plastics properties can be tailored through control of their syntheses and processing to fit every desired application, packaging beeing a major one. Measurable residual amounts or conversion products from the many different raw materials and processing aids used in the various plastic synthesis processes can remain in the finished material along with many chemically different additives which are incorporated into the polymer matrix. All these compounds can diffuse from the plastics into its environment, for example into foodstuffs, pharmaceuticals or other goods packed in plastic materials, as well into the atmosphere and other environments. A theoretical modeling of diffusion coefficients of n-alkanes in a polymer, wich allows to better correlate the diffusion behavior with well defined properties of the polymer matrix, is presented.

Keywords: raw materials, polymer matrix, diffusion coefficients

Since the second world war a new class of useful materials has been developed whose properties can be tailored through control of their syntheses and processing to fit every desired application. With a yearly production of over 200 million tons, plastics form a pillar of the economy without which today's standard of living would not be attainable.

Plastics are defined as processable materials based on polymers. These materials can be transformed into finished products, such as bottles, containers, films, hoses, coatings, lacquers, etc. Packaging is one major field of application for plastic materials. As a result of today's multitude of plastic applications there is a corresponding enormous variety of plastic materials. Measurable residual amounts or conversion products from the many different raw materials and processing aids used in the various plastic synthesis processes can remain in the finished material. Knowledge of these materials is indispensable for the toxicological evaluation of the plastics and their analysis . The same applies for the many chemically different additives which are incorporated into the polymer matrix to allow better processing, to increase stability and to give the material specific properties.

All these compounds can diffuse from the plastics into its environment, for example into foodstuffs, pharmaceuticals or other goods packed in plastic materials, as well into the atmosphere and other environments. The mass transport by diffusion is denoted as "migration" and plays a key role as interaction between plastics and all kinds of environment.

During a diffusion process a change in the concentration c of the diffusing substance with time t takes place at every location x along the x axis throughout the plastic. The differential equation which describes the diffusion process is known as Fick's second law:

$$\frac{dc}{dt} = D \cdot \frac{d^2c}{dx^2} \qquad (1)$$

The diffusion coefficient D is a specific parameter depending on the properties of the plastic matrix, the diffusing compound and temperature T.

There are many solutions known for the diffusion equation (1) [1]. The key input parameter for all solutions is the diffusion coefficient, D_P, of the migrant in the plastic material P.

The literature reports a series of sophisticated models for the theoretical estimation of diffusion coefficients in polymers [2] but these models are, at least today, too complicated for practical applications. A recently developed equation for diffusion coefficients of organic compounds in polyolefins and other plastics [3] is presented in the following and experimental data obtained with polyethylene are compared with predicted values with this equation.

Experimental part

Diffusion coefficients of n-alkanes in polyethylene

The starting point for the development of an equation for diffusion coefficients in plastics was the homologous series of n-alkanes as a reference class of compounds with the elementary composition C_iH_{2i+2} with i carbon atoms in a molecule in this series. Specific properties like the melting point and critical temperature increase after a certain i value in a predictable way. Based on this characteristic behavior of a homologous series, the dimensionless ratio of a specific property $f(i)$ of an n-alkane with i carbon atoms and $f(\infty)$ for the polymethylene chain with $i >> 1$ can be approximated with the ratio

$$\frac{f(i)}{f(\infty)} = \frac{(1+2\pi/i)^{i/e}}{e^{2\pi/e}} = \frac{w_{i,e}}{w} \quad . \qquad (2)$$

The power sequence:

$$w_{i,e} = \left(1+\frac{2\pi}{i}\right)^{i/e} \quad \text{with} \quad \lim_{n\to\infty} w_{i,e} = e^{2\pi/e} = w \qquad (3)$$

with the members $w_{i,e}$ and the limit value w are designated as interaction functions and represent the mathematical backbone of the model for diffusion coefficients [3].

The following equation has been developed for the diffusion coefficient of an n-alkane with i carbon atoms and the relative molecular mass $M_{r,i}=(14i+2)$ in polyethylene with the relative molecular mass $M_{r,p}$ and the melting temperature $T_{m,p}$ [3]:

$$D_{P,i} = D_u \exp\left(w_{i,e} - w_{p,e} \cdot 0.14(14j+2)^{2/3} - \right.$$
$$\left. - ww_{j,e}^{2/3} T_{m,p} R/RT\right) \qquad (4)$$

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with $w_{i,e} = (1+2\pi/i)^{i/e}$, $j=(i^{1/3})$, $w_{j,e}=(1+2\pi/j)^{j/e}$, $p=(M_{r,p}/14)^{1/3}$, $w_{p,e}=(1+2\pi/p)^{p/e}$ and the unit $D_u = 1\ m^2/s$.

The product $0.14(14j+2)^{2/3}$ in the second term in the exponent represents the relative molar cross-sectional area of the diffusing particle. This area results as a measure of the relative resistance of the polymer matrix against the movement of the diffusing particle. In the special situation of a n-alkane $0.14(14i+2) = 0.14\ M_{r,i}^{2/3}$. But in contrast to the crystalline state, the diffusing molecules in the polymer matrix above the glass point can be considered in a first approximation to be present in form of spherical coils which offer a smaller cross-sectional area, than the sum of *i* methylene groups. As a consequence, a relative smaller diameter of the diffusing particle, $((M_{r,i}-2)/14)^{1/3} = j$ results in comparison to *i* and the factor $(14j+2)$ is used instead of $14i+2$. With *j* a corresponding interaction function, $w_{j,e} = (1+2\pi/j)^{j/e}$ results which is used in the third term of the exponent in equation (4). The numbers *i*, *j*, $w_{i,e}$ and $w_{j,e}$ refer to the diffusing molecule.

The change from a linear orientation to spherical coils in the whole matrix can be understood as a gradual process which occurs only to a small degree at very low temperatures, e.g. near the glass point, with short chains of small molecules. With increasing temperature and longer chains the transformation to spherical coils takes places to a much higher extent. In any case the diffusing particles can be assumed to exist in all situations in a more or less well coiled form.

For the polymer matrix the interaction function $w_{p,e} = (1+2\pi/p)^{p/e}$ is used, where $p = (M_{r,p}/14)^{1/3}$, with the relative molecular mass of the polymer. The product $w \cdot w_{j,e}^{2/3} \cdot T_{m,p} \cdot R = E_A$ between *w*, the melting temperature, $T_{m,p}$, *K* of the polymer, the factor $w_{j,e}^{2/3}$ and the gas constant *R* in the third term in the exponent of equation (4) represents the activation energy of the diffusion coefficient.

Results and discussion

Figure 1 shows a comparison between calculated and experimental [3-7] values of diffusion coefficients for n-alkanes and other organic compounds from table 1 in low density polyethylene (LDPE) at 23°C . Although eqation(4) has been developed starting from the homologous series of n-alkanes, the diffusion coefficients of other structures, as shown from this comparison, fits well with the predicted values. That means the major input parameter for the prediction of a diffusing compound is its relative molecular mass, $M_{r,i}$.

Polyethylene is the most widely used mass-produced plastic. At the present time many hundreds of grades of polyethylene, most of which differ in their properties in one or other way, are available. All polyethylenes are semicrystalline. Their densities and melting temperatures decrease with increasing of ramification. The crystalline melting temperatures are ca 108°C for LDPE , 135°C for high density polyethylene (HDPE) and 144°C for the ideal crystallites of linear PE. The softening temperatures of the wax like thermoplastic are between 80 and 130°C. The glass-temperatures are between –80°C until –30°C. A polymer like LDPE is polydisperse, in the sense that a sample spans a large range of molar masses. From the diffusion point of view, the smaller molecules probably play a relatively more important role in comparison with the bigger molecules due to the easier movement of the diffusing solute through a matrix with a large portion of small molecules. The molecular mass ranges between 3000 and 100000 for $M_{r,p}$ and the temperature ranges

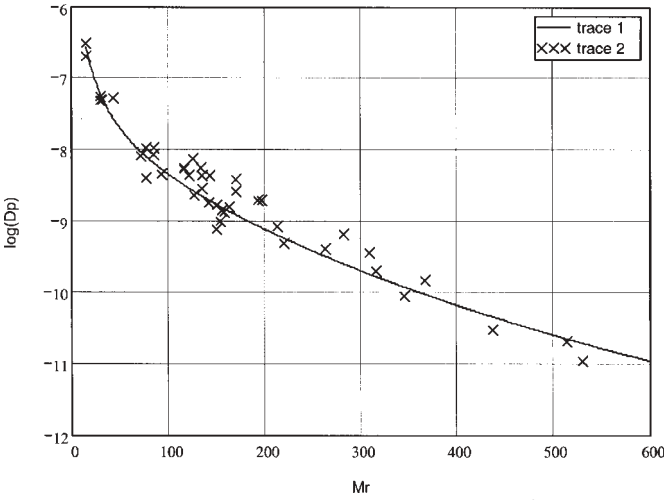

Fig. 1. Comparison of the diffusion coefficients (cm^2/s) at 23 °C calculated with Eq. (4)) (trace 1) for LDPE ($M_{r,p}$ = 25000, $T_{m,p}$ = 373 K (100 °C) and experimental values (trace 2) obtained with compounds from table 1

between 80 and 120°C for $T_{m,p}$, correlate well with the properties of LDPE.

This relative large range of $M_{r,p}$ and $T_{m,p}$ values explain the large range of diffusion coefficients obtained for similar substances measured in different PE samples. Nevertheless one could define a mean set of parameters for each type of PE which allow a good prediction of diffusion coefficients for practical applications. For LDPE, as an example, good prediction is possible for diffusion of organic compounds with relative molecular masses $M_r < 2000$ at temperatures < 90 °C, if $M_{r,p} = 25000$ and $T_{m,p} = 363\ K\ (90°C)$ are used in equation (4). Figure 2 shows the $log(D_p)$ curves obtained with these conditions.

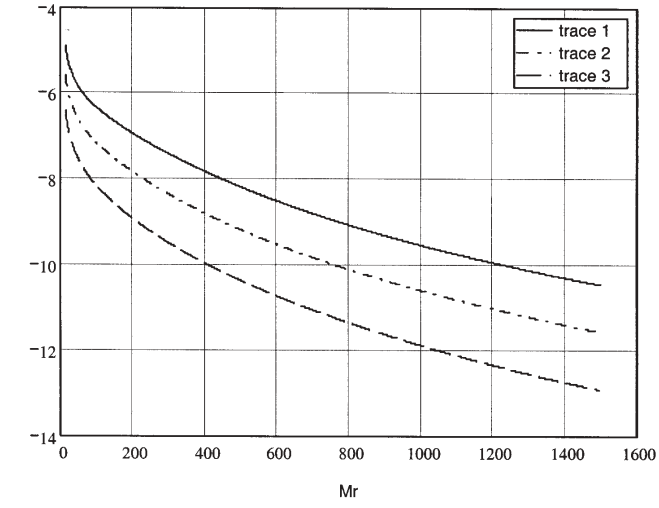

Fig. 2. Diffusion coefficients (cm^2/s) for relative molecular masses $M_r < 1600$ calculated with Eq.(4) for LDPE ($M_{r,p}$ = 25000, $T_{m,p}$ = 363 K (90 °C) at 80 °C (trace 1), 50 °C (trace 2) and 20 °C (trace 3)

The activation energy values of diffusion, E_A for LDPE are functions of $M_{r,i}$ and in a range between 49 kJ/mol for methane and 84 kJ/mol for M_r = 2000.

Diffusion coefficients of additives at temperatures below the glass point T_g of polyethylene are not known, due to the low value of these temperatures. But for polyethyleneterephthalate (PET) with $T_g \approx 80$ °C values of D_p exist below and above this temperature. Although the matrix structure of PET differs significantly from that of PE, one can use in a first approximation the above equation

Table 1

DIFFUSION COEFFICIENTS MEASURED AT 23 °C FOR ORGANIC COMPOUNDS WITH DIFFERENT RELATIVE MOLECULAR MASSES M_r AND STRUCTURES IN LDPE

Compound	M_r	$10^{10} \times D_P$ (cm^2/s)
Methane	16	1940
Methane	16	2980
Ethane	30	480
Ethane	30	538
Methanol	32	480
Propane	44	520
n-Pentane	72	80.5
Benzene	78	105
Benzene	78	40
n-Hexane	86	105
n-Hexane	86	84
Phenole	94	45
Heptanol	116	53
2,3-Benzopyrole (Indole)	117	55
2-Phenyl-ethyl-alcohol	122	43
3-Octene-2-one	126	73
n-Octanal	128	23
4-Isopropyl-toluene	134	54
4-Isopropenyl-1-methyl-1-cyclohexene (Limonene)	136	43
3-Phenyl-1-propanol	136	28
n-Nonanal	142	18
7-Methyl-chinoline	143	43
2,3,5,6-Tetramethyl-phenol	150	16
Dimethyl-benzyl-carbinol	150	7.5
3,7-Dimethyl-6-octene-1-al	154	10
n-Decanal	156	14
3,7-Dimethyl-octane-3-ol	158	13
2-Methoxy-4-propenyl-phenol	164	15.5
Diphenyl-oxide	170	37
n-Dodecane	170	26
Dimethyl-phthalate	194	19
n-Tetradecane	198	19
Tetradecanol	214	8.2
2,6-Di-tert-butyl-4-methyl-phenol (BHT)	220	4.8
Cedrylacetate	264	4.1
Eicosane	282	6.3
Docosane	310	3.5
2-(2-Hydroxy-3.t-butyl-5-methylphenyl-5-Chloro-benztriazol (Tinuvin 326)	315.8	2.0
2-Hydroxy-4-ethandiol methyl-thioacetic acid ester	346	0.9
Methyl-tricosanate	368	1.5
Methyl-octacosanate	438	0.3
Didodecyl-3-3-thio-dipropionate	514	0.2
3-(3,5-di-tert-butyl-4-hydroxy phenyl)-propionate (Irganox 1076)	531	0.11

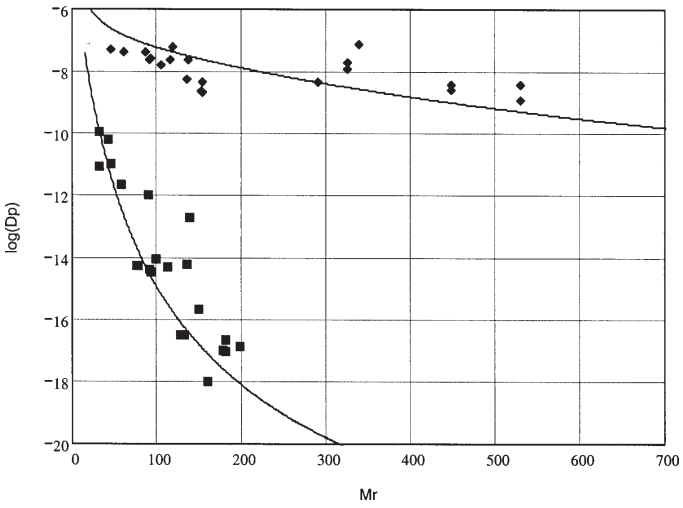

Fig. 3. Diffusion coefficients (cm^2/s) calculated with Eq.(4) for PET ($M_{r,p}$ = 10000, $T_{m,p}$ = 255 °C) at 175 °C (upper curve) and with Eq.(5) (T_g = 80 °C) at 40 °C (lower curve) in comparison with experimental data obtained at corresponding temperatures

for estimation of the diffusion coefficients in PET. For $T < T_g$ an equation analogous to (4) can be used:

$$D_{P,i} = D_u \exp\left(w_{i,e} - w_{p,e} \cdot 0.14 \cdot w_1^{2/3}(14j+2)^{2/3} - ww_{i,e}^{2/3} T_g R / RT\right) \quad (5)$$

with T_g instead of $T_{m,p}$ and $w_1 = (1+2\pi)^{1/2}$. At temperatures $T >> T_g$ but below the melting point $T_{m,p}$ equation (4) for the rubbery phase is used.

In figure (3) a comparison between the diffusion coefficients obtained for additives in PET with the two equations (5) at 40 °C and (4) at 175 °C with experimentally obtained data [8] are shown. In these equations, $T_g = 353$ *K (80 °C),* $T_{m,p} = 528$ *K (255 °C) and* $M_{r,p} = 10000$ are used. Due to the big range over more than 10 orders of magnitude, a good agreement between experimental and calculated values results from this comparison.

Conclusions

A general conclusion from the above results obtained with the theoretical modeling of diffusion coefficients is the possibility to correlate much better the diffusion behavior with well defined properties of the polymer matrix. A still actual limitation of the modeling is the lack of experimental data obtained with samples with well defined properties. To fill this gap is a challenge for the next future.

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