ARIEL

University of Arizona Library
Interlibrary Loan
1510 E. University Blvd
Tucson, AZ 85721
(520) 621-6438 / (520) 621-4619 (fax)
OCLC: AZU
U of A Ariel: 150.135.45.156
askill@u.library.arizona.edu

Borrower: BUF

Trans.#: 24275

Call #: WEB

ILL Number: 8533676

Location:

University of Arizona Interlibrary Loan

Lending String: PMC,*AZU,CLE,CLE,CWR
Patron: Antoniou, Eleftheria

MaxCost: $30.00IFM

Journal Title: Progress in organic coatings.

Article Author:

Article Title: Van Der Wel GK and Adan OCG; Moisture in Organic Coatings-a review

Volume: 37
Issue: 1-2
Month/Year: November 1999
Pages: 1-14

Shipping Address:
SUNY AT BUFFALO
234 Lockwood Memorial Library, ILL
Buffalo, NY 14260-2200

Fax: (716)645-6298

Notice: This material may be protected by Copyright Law (Title 17 U.S.C.).

Rec'd: 8/22/2003 11:44 AM

ARIEL INFORMATION:

Ariel Address: 128.205.111.1

ELSEVIER

Progress in Organic Coatings 37 (1999) 1–14

PROGRESS IN ORGANIC COATINGS

www.elsevier.com/locate/porgcoat

Review

Moisture in organic coatings — a review

G.K. van der Wel[a,*], O.C.G. Adan[b]

[a]*Faculty of Architecture, Building and Planning, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands*
[b]*TNO Building and Construction Research, PO Box 49, 2600 AA Delft, The Netherlands*

Received 12 July 1999; accepted 19 August 1999

Abstract

A review is given on transport and equilibrium sorption of moisture in polymer films and organic coatings. Polymeric material forms the continuous phase of a coating and is therefore important for transport properties. Besides polymer, coatings consist of pigments and fillers and various additives, each of them affecting moisture transport. Firstly, in this paper typical transport and equilibrium characteristics of pure polymer films are covered, and secondly those of coatings, assimilating the impact of pigments, fillers and additives.

Discrimination between Fickian and non-Fickian effects is usually based on the appearance of kinetic absorption curves. Several types of curve are dealt with, and models that describe these curves are discussed. These include "two-stage" sorption, "sigmoidal" sorption and "Case II" sorption. The common practice of fitting Fick's law to kinetic data by means of relaxation parameters is criticized. Transport kinetics is modelled on the basis of kinetic plots, thereby introducing relaxation parameters in Fick's diffusion law. Although these models describe moisture transport in polymers reasonably, these models imply a lot of "curve-fitting", without a clear mechanistic foundation.

Equilibrium sorption of moisture in polymeric systems is reflected by their sorption isotherms. Type II and III isotherms of the BET classification are commonly encountered, together with linear isotherms according to Henry's law. The suitability of porous media adsorption models for polymeric systems is discussed. These models are treated in relation to interactions of water in polymers, since localized binding of water to specific groups may justify the use of these models.

Finally, the — substantial — effects of pigments and fillers, as well as coating additives on moisture transport and solubility in coatings are dealt with. Pigments may lower moisture permeation, but non-ideality of pigmentation reduces this effect. Coating additives increase moisture solubility, but only little is known in detail. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Polymer films; Organic coatings; Transport; Equilibrium sorption; Moisture

1. Introduction

The present review paper deals with transport and equilibrium properties of moisture in organic coatings. This field of research is of continuous interest when protection of substrates to moisture-related degradation is concerned, e.g. corrosion protection of metal substrates. In addition, biodegradation of organic coating systems, e.g. by fungal growth, is often closely related to the moisture balance of these systems, frequently in interaction with the underlying porous substrate [1,2]. As far as we know, the papers of Blahník [3] and Huldén and Hansen [4] published in this journal were the latest reviews dealing with the subject of moisture transport in coatings. In the present paper, the subject is reassessed starting from the point of view that overall kinetic data are not of primary interest, but rather the processes they result from. Our concern with the moisture balance of a combined system of coating and porous substrate also draws attention to differences and similarities in moisture transport mechanisms in these materials. Past decade, modelling of moisture transport in inert, rigid porous media — e.g. gypsum plaster [5] — has made a lot of progress as a consequence of improved and highly sophisticated measuring techniques.

Organic coatings normally consist of polymeric material, pigments, fillers and various additives (rheology modifiers, dispersion agents, etc.). The polymer functions as the binder material, and provides a matrix in which all other constituents are solubilized or dispersed. In the research of transport properties, polymer films are frequently used as the starting point to which effects of other constituents are subsequently related. In the past years, diffusion phenomena in polymers have been reviewed by Vieth [6], and more recently by Neogi [7]. However, despite the fact that most studies concern polymeric materials that are not normally used in

---

[*] Corresponding author. Tel.: +31-40-247-5064; fax: +31-40-243-8595.
E-mail address: g.k.v.d.wel@bwk.tue.nl (G.K. van der Wel)

0300-9440/99/$ – see front matter © 1999 Elsevier Science S.A. All rights reserved.
PII: S0300-9440(98)00048-4

coatings, many of the concepts may still be valid assuming that transport mechanisms basically remain the same.

The polymer content of a dry coating film is highly variable. In many manufactured decorative coatings, the amount of polymeric material is only just enough to bind the pigments and extenders in the paint film. Most common inorganic pigments and extenders are impermeable, and consequently, moisture transport primarily takes place in the binder material. On the other hand, pigments may have substantial influence on moisture transport in paint films since they decrease the volume fraction of the binder. Besides, additives contribute to moisture transport properties, especially for water-borne coatings, since many of these additives are applied in paint formulations to achieve compatibility between polar phases (inorganic pigments, and in case of aqueous paints, water) and the more hydrophobic polymer phase. Therefore, many additives are inherently moisture sensitive.

To avoid ambiguities, the terms sorption, absorption, desorption, adsorption, permeation, moisture and substrate are defined here. The meaning of these terms in polymer and coating sciences may differ from that in other fields of interest, such as transport phenomena in porous media. Throughout this paper, we will adopt the following definitions:

Sorption. Usually, a synonym for absorption. Sorption may also be used referring to equilibrium uptake.
Absorption. Uptake of liquids or vapours by a material.
Desorption. Loss of liquids or vapours from a material.
Adsorption. Physical binding of molecules, or clusters of molecules, at surfaces or specific binding sites.
Permeation. Transport of liquids or vapours through a material.
Moisture. Water in liquid and/or vapour phase.
Substrate. The base material to which the coating is adhered.

The paper is outlined as follows. In Section 2, transport and equilibrium sorption in polymer films are covered, being general concepts valid for many penetrant–polymer systems. In Section 2.5, the specific role of water as the penetrant is highlighted in relation to polymer structure. In Section 3, organic coatings are considered, starting with coating structure and other general aspects in Section 3.1, and the role of pigments, fillers and additives on the moisture balance in Sections 3.2 and 3.3. A general discussion of moisture in organic coatings in Section 4 concludes the present paper.

2. Polymer films

2.1. *Fickian and non-Fickian kinetics*

Unidirectional Fickian transport in polymer films is described by

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(D(C)\frac{\partial C}{\partial x}\right). \tag{1}$$

This equation is known as the general diffusion law or Fick's second law of diffusion (Fick's law, for short). C (kg m^{-3}) is the penetrant concentration, t (s) the time, x (m) the position in the film in the direction of diffusion, and D (m^2 s^{-1}) is the diffusion coefficient or diffusivity of the penetrant in the polymer. D is the pivotal parameter determining the rate of transport. It may depend strongly on concentration, but this is not necessarily the case in polymers. It is noted that concentration dependency implies dependency both on penetrant content (m^3 m^{-3}) and temperature. According to Hopfenberg and Frisch [8], isothermal diffusion of organic penetrants in polymers is concentration independent at very low activities over a wide temperature range. With increasing penetrant activities, however, they claim that diffusion is only concentration independent in the case of very low temperatures.

Fickian diffusion in polymers is an ideal case of penetrant transport, corresponding to free diffusion of penetrant without interference of polymer chain rearrangement — i.e., structural relaxation. Whether deviations from ideal Fickian behaviour occur, depends on the rate of relaxation compared to that of diffusion. If polymer relaxation is much faster than penetrant diffusion, diffusion is followed by instantaneous response of the system, resulting in Fickian behaviour. Instantaneous response of the system requires large flexibility of the polymer chains in the system. This is generally accepted to be the case for polymers above their glass transition temperature (T_g) (°C), which are 'rubbery' (systems below T_g are 'glassy'). Two things should be mentioned about this transition of state. Firstly, the T_g is not a real thermodynamic transition, since its value depends on the speed of heating or cooling of the system [9]. Secondly, the T_g is characteristic for the total system including possible penetrant. Since penetrant absorption may also induce a transition from glassy to rubbery state and vice versa, such transition under isothermal conditions should be considered in terms of a glass transition concentration (C_g) rather than in terms of a glass transition temperature. The effect of the glass transition on the diffusion behaviour of several water–polymer systems has been investigated, and summarized by Barrie [10]. Although the isothermal diffusion coefficients appeared to be clearly dependent on temperature, no discontinuities were found upon traversing the T_g. Instead, D increased smoothly with increasing temperature.

Vrentas et al. [11–13] introduced a diffusion Deborah number $(\mathrm{DEB})_\mathrm{D}$ (–) to indicate the presence of non-Fickian effects during absorption experiments. This number is defined as

$$(\mathrm{DEB})_\mathrm{D}=\frac{\lambda_m}{\theta_\mathrm{D}} \tag{2}$$

Here θ_D (s) is the characteristic time of penetrant diffusion and λ_m (s) can be considered as the characteristic time of polymer relaxation processes. θ_D is proportional to the square of film thickness l (m), and consequently, $(\mathrm{DEB})_\mathrm{D}$ is proportional to l^{-2}. Calculation of the diffusion Deborah

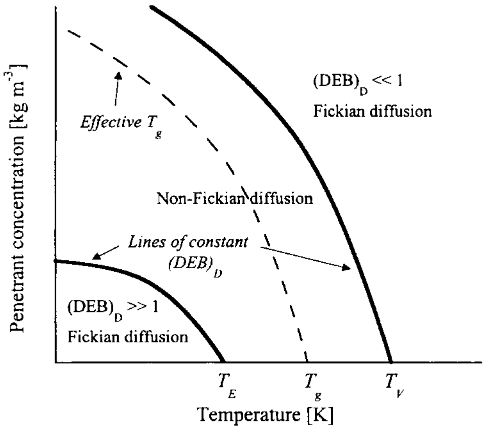

Fig. 1. Schematic picture of the different zones of diffusion, separated by lines of constant diffusion Deborah number $(DEB)_D$, as related to penetrant concentration and temperature. T_E is the temperature below which pure polymer acts like an elastic solid, T_g the glass transition temperature, and T_V is the temperature above which pure polymer acts like a viscous fluid. Reproduced from Vrentas et al. [11].

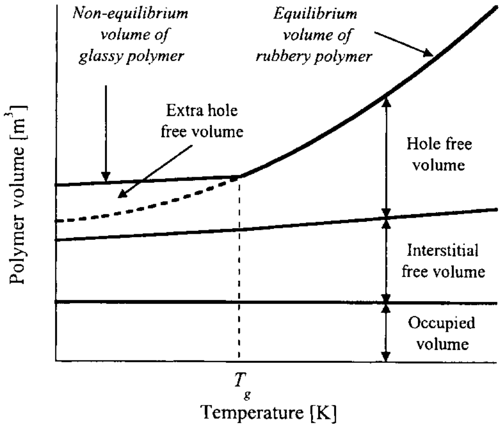

Fig. 2. Schematic picture of polymer volume as a function of temperature. Reproduced from Duda and Zielinski [19].

number is described in [12]. Since 'glassy' to 'rubbery' state transitions depend — at least — on both the concentration C and temperature T, $(DEB)_D$ may be expressed as a function of C and T. Vrentas et al. [11] suggested that three different zones in a C–T diagram can be distinguished, separated by lines of constant Deborah number (see Fig. 1).

They defined two threshold temperatures, T_V and T_E, respectively, characterizing these lines. T_V (°C) is the temperature at zero penetrant concentration above which the polymer acts like a viscous liquid, whereas T_E (°C) is the temperature at zero penetrant concentration below which the polymer acts like an elastic solid. They claim that Fickian behaviour is found both above T_V and below T_E. In the latter state, polymer segments move back to their original positions instantaneously after passage of a diffusing particle, resulting in a net unchanged matrix [11]. To our opinion, rigid structures should not be excluded from this point of view. As shown in Fig. 1, the (effective) glass transition temperature is in the area between these borderlines. Thus, in this respect Vrentas et al. disagree with the general opinion that the glass transition is the border between Fickian and non-Fickian diffusion characteristics.

2.2. *Porosity and free volume*

The kind of Fickian behaviour found for elastic solids may also result from a polymer film with a rigid structure containing free spaces which are able to accommodate penetrant molecules, therefore showing characteristics of porous materials. Philip and de Vries [14] provided a theory, dealing with moisture transport in inert porous materials. In this model, moisture transport is described by a diffusion type equation, similar to that for Fickian diffusion (1). However, the — macroscopic — moisture diffusion coefficient D assimilates various moisture transport mechanisms in the pore system and appears to be highly dependent on the moisture content φ (m^3 m^{-3}) [15].

There is clear evidence that penetrant transport in polymers may be connected to free volume. Vrentas et al. [16–18] suggested a model for describing the volumetric behaviour of glassy polymer–penetrant systems. This model has been reviewed by Duda and Zielinski [19]. According to this model, polymer volume is divided into three elements (see Fig. 2):

1. *Occupied volume.* This is basically the "van der Waals" volume [20] and is the volume of the material without any free volume. This volume can be calculated from bond distances and non-bonded contact radii — the so-called "van der Waals" radii — and is a constant for all temperatures.
2. *Interstitial free volume.* This inaccessible free volume stems from the vibrational energy of polymer bonds, and increases slightly with temperature.
3. *Hole free volume.* This is the volume stemming from volume relaxation and plasticization upon heating and cooling of the polymer. This free volume is accessible for penetrant transport, and may be altered by absorption and desorption of penetrants. Changes in the total polymer volume are largely governed by changes in the hole free volume. Rubbery polymers attain equilibrium volume, since polymer relaxations are fast. Glassy polymers, however, are non-equilibrium liquids in which relaxations are slow. Consequently, glassy polymers may have larger volume than would be the case at equilibrium, since extra hole free volume is trapped in the polymer. Although polymers seem to be porous viewed in this way, Duda and Zielinski [19] emphasize that volume trapped in a glassy polymer is continuously redistributed through the volume.

However, the nature of free volume is still open for discussion, since commonly polymers are considered non-porous.

For porous materials, the penetrant phase is clearly decisive for the transport mechanism, both at the surface and inside the material. However, for non-porous polymers, the penetrant phase within the polymer is not defined, and consequently, transport cannot be considered in terms of liquid and/or vapour.

2.3. *Typical sorption and permeation kinetics*

2.3.1. *Typical sorption kinetics*

In kinetic sorption experiments a quantity representing overall penetrant loss or gain is recorded as a function of time for a sample of polymer film or coating that is subjected to a certain penetrant activity. Usually, the mass of penetrant M (kg) is taken as this quantity [21]. Results of kinetic experiments are normally presented by plots of M as a function of time (t) or square root of time ($t^{1/2}$). Free films are usually subjected to a constant external penetrant activity at both sides of the film. For films applied to a substrate, single-sided moistening is commonly performed. In case the substrate is impermeable, experimental data used to be processed in the same way as for free films with the restriction that only half of the film thickness is used. However, due to factors like polarity and surface energy, such assumption may not be justified, i.e. free and applied films may show quite different characteristics. Corti et al. [22] studied the effect of steel and glass substrates on water absorption in epoxy-polyamide clear varnish and concluded that free films showed a tendency towards greater water uptake.

In the next section, a number of typical plots is given and categorized according to their appearance.

2.3.1.1. Fickian sorption. Fig. 3 is a typical plot for the so-called Fickian absorption kinetics. Characteristic features of such curve are [23]:

1. An initially linear plot of M as a function of $t^{1/2}$.
2. With increasing t, the absorption curve smoothly levels off to a saturation level M_∞.
3. When $M(t)/M_\infty$ is plotted as a function of $t^{1/2}/l$ (where l is the film thickness) a "reduced" plot is obtained, which is identical for different values of film thickness.

Fickian desorption curves show the same features. "Reduced" absorption and desorption curves coincide over the entire range of $t^{1/2}$ when D is constant. "Reduced" absorption curves lie above the corresponding desorption curves when D is an increasing function of concentration. The features that are described here only apply when two conditions are met: firstly, local equilibrium at the material surface must be maintained. Secondly, the external penetrant activity must be kept constant over the entire experiment. Analytical solutions for Eq. (1) that describe the curve in Fig. 3 have been obtained by Crank [24]. In these solutions, D is assumed to be constant. Actually, this assumption may not be valid. In that case, the solution may only be considered an averaged value. Practical approximations for constant D are given by Balik [25].

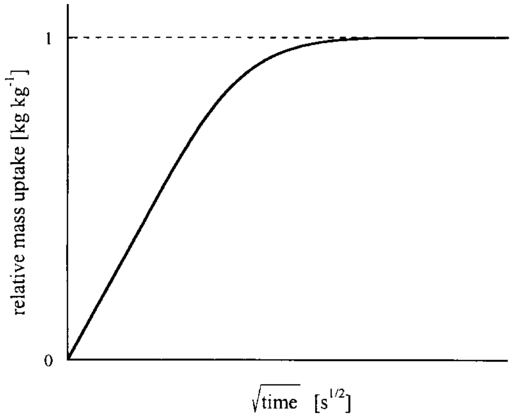

Fig. 3. Stylized picture of a typical Fickian absorption curve. The relative weight gain $M(t)/M_\infty$ is plotted as a function of the square root of time.

Absorption and desorption are normally classified as non-Fickian when anomalous plots are obtained under experimental conditions similar to those mentioned above. Non-Fickian effects are commonly classified according to their appearance in kinetic plots. Well-known anomalous appearances are two-stage, sigmoidal, and Case II sorption. Many models have been developed to link kinetics with presumed underlying transport mechanisms.

2.3.1.2. Two-stage sorption. 'Two-stage' sorption is a frequently encountered anomalous type of absorption. Its general appearance is shown in Fig. 4. The name 'two-stage' sorption is chosen since the curve appears to be composed from two different parts: (1) fast Fickian absorption; (2) slow non-Fickian absorption. In Fig. 4, the curve is Fickian from the start until the moment it starts to level off. However, instead of reaching the saturation level typical for Fickian absorption, the curve is extended through a non-Fickian part. Ultimately, saturation will be reached for all instances. A theory, satisfactorily describing the features of 'two-stage' sorption, has been proposed in 1978 by Berens and Hopfenberg [26].

In their diffusion–relaxation model they considered the absorption process to be composed of two phenomenologically independent contributions: a diffusion part $M_\mathrm{F}(t)$ that is governed by Fick's laws and a structural part $M_\mathrm{R}(t)$, resulting from polymer relaxations. The total weight gain at time t may be expressed as the linear superposition of these contributions:

$$M(t) = M_\mathrm{F}(t) + M_\mathrm{R}(t). \quad (3)$$

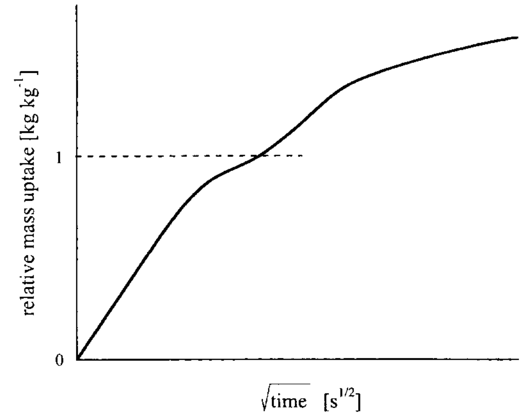

Fig. 4. Stylized picture of a typical two-stage absorption curve. The relative weight gain $M(t)/M_\infty$ is plotted as a function of the square root of time. $M(t)/M_\infty = 1$ for the (fictitious) Fickian saturation level.

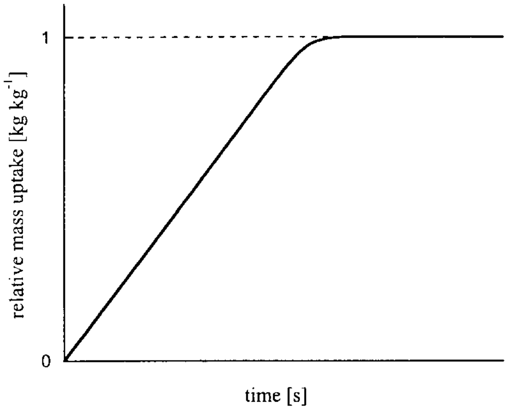

Fig. 6. Stylized picture of a typical Case II absorption curve. The relative weight gain $M(t)/M_\infty$ is plotted as a function of time.

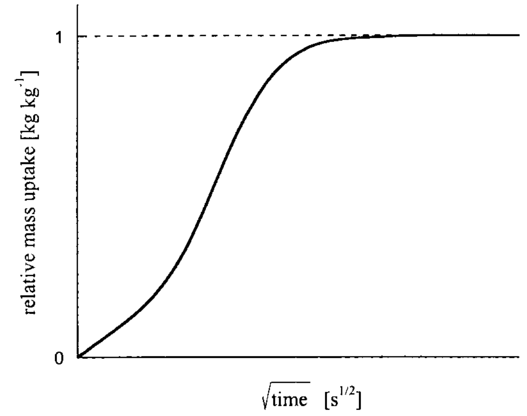

Fig. 5. Stylized picture of a typical sigmoidal (S-shaped) absorption curve. The relative weight gain $M(t)/M_\infty$ is plotted as a function of the square root of time.

$M_F(t)$ is given by solutions of the diffusion Eq. (1). It is assumed that more than one independent relaxation process is possible, so $M_R(t)$ is given by

$$M_R(t) = \sum_i M_{\infty,i}[1-e^{-k_i t}], \tag{4}$$

where $M_{\infty,i}$ represents the equilibrium absorption due to the ith relaxation process, and k_i is the first-order relaxation constant of the ith relaxation process. Originally, the model has been developed for diffusion in spherical particles, but it has also been applied to diffusion in polymer films, e.g. [27].

2.3.1.3. Sigmoidal sorption. Sigmoidal sorption is another typical non-Fickian behaviour (Fig. 5). Curves are S-shaped, showing a point of inflection. In the early 1960s, Long and Richman [28] proposed the "variable surface concentration" (VCS) model, giving a satisfying description of the experimental data. They assumed that the transport process in the film is Fickian, but due to slow establishment of equilibrium at the surface of the film, kinetics appear anomalous. Initial sigmoidal effects may be followed by subsequent two-stage effects. See e.g. de Wilde and Shopov [29] who combined the diffusion–relaxation model and the VCS model to describe their kinetics adequately.

2.3.1.4. Case II sorption. An apparently totally different form of non-Fickian kinetics is named Case II sorption (Fig. 6). It was noticed that some systems of polymer sheets and liquid penetrant showed linear kinetics, i.e. mass uptake proportional to time. This was accompanied by a considerable amount of swelling. Optical density scans of absorption of methanol by a sheet of PMMA revealed "step-type" concentration profiles, showing negligible concentration gradient behind sharp fronts [30]. As Case II sorption principally requires a sharp diffusion front, and a constant progress of that front in time, overall linear kinetics will not occur in case of a geometry other than a unidimensional sheet (e.g. a sphere) [31].

Many models have been proposed to account for the features of Case II diffusion. Crank [32] and Petropoulos and Roussis [33,34] developed a theory which included a history-dependent diffusion coefficient. Peterlin [35] rewrote the diffusion Eq. (1), incorporating a term to describe the constant velocity movement of a penetrant front. Van Westing et al. [36], who studied an epoxy coating system with impedance measurements, reported one of the few examples of Case II sorption with liquid water as the penetrant. They observed linear kinetics, preceded by a Fickian-like induction period. They suggested that initially, water molecules do not interact with polarizable groups of the coating, but only fill up pores and interstitial sites without disturbing the polymer. Next, swelling occurs, ascribed to interaction of the coating polymer and the water molecules. In order to account for the swelling, they simply added a swelling coefficient (S_c) to the analytical solution of

Eq. (1) given by Crank [24] for Fickian kinetics with a constant D. The swelling coefficient was taken to be linear in time and the swelling is consequently given by $S_c t$. It seems to us that a constant diffusion coefficient is not expected in the first place when swelling (involving local water storage) is concerned, so the use of the solution of Crank is principally unacceptable. It goes without saying that addition of a swelling coefficient that is linear in time results in linear kinetics, provided that the contribution is large enough compared to the Fickian contribution.

Opposite to these empirical methods, Thomas and Windle [37] developed a theory with physical foundation. They studied the absorption of liquid methanol in PMMA extensively; their experimental data for methanol sorption in PMMA sheets of 1 mm thickness at 24°C agreed well with calculated concentration profiles and sorption plots.

Their basic assumption is that the diffusion of the penetrant is much faster in a swollen element than in a glassy element. When initially penetrant molecules enter the element, they "clear the way" for successive molecules; the plasticizing effect causes next molecules to enter more rapidly and so on. Accumulation is at least initially much faster than transport to the next element. This condition results in a sharp front. For a sheet of polymer that is immersed in a bath of penetrant, this will continue until the fronts have met in the centre of the sample. At that point, the polymer sample is totally plasticized. In terms of penetrant activity, the mechanism described above results in the following diffusion equation for filling of an initially glassy element [31]:

$$\left(\frac{\partial\phi}{\partial t}\right)_X = \frac{\partial}{\partial X}\left[D(\phi)\left(\frac{\phi}{a}\right)\frac{\partial a}{\partial X}\right] \tag{5}$$

Here ϕ is $\phi(X,t)$ (–), the ratio of actual and saturation concentration of the Xth element as a function of time, and a (–) is the penetrant activity.

Recently, Samus and Rossi [38] questioned the tendency to describe any deviation from the "Fickian" curve as "anomalous" or "non-Fickian". In that case, the "Fickian" curve refers to the curve commonly considered Fickian. In line with that, they criticized the common practice of fitting Fick's law to kinetic data by means of (often vaguely defined) relaxation parameters. They reason that apparent non-Fickian curves may actually result from Fick's law (1) if geometrical constraints on swelling behaviour are taken into account properly. For instance, solvent uptake in a polymer film or slab causes a sharp front, separating the glassy from the plasticized region, and swelling is only possible in the direction perpendicular to the film surface. The rigid inner region restricts swelling in the other two directions, and consequently, the concentration of solvent in the overall swollen state is limited to a lower level than the final equilibrium concentration. The constraint from the rigid core is released when the solvent reaches the central region of the film and the material in this region becomes entirely plasticized. Only at this point, the polymer can swell in the other two directions and the solvent concentration grows to the final equilibrium value in the entire material. They believe that the regime of accelerated uptake, leading to two-stage absorption curves, originates from this effect of hindered swelling. On the other hand, for spherical samples constraint release is gradual, since swelling can take place isotropically from the start. For this geometry, no dramatic signature of accelerated uptake in the sorption curves is expected. Processes of the kind just described play a role even in the absence of a sharp concentration front between the glassy and plasticized region. If sorption experiments are carried out just above the nominal T_g, the elastic moduli can still experience significant changes as the concentration of solvent within the sample increases.

2.3.2. *Typical permeation kinetics*

Permeation experiments offer a different approach to characterize transport kinetics. In a permeation experiment, the penetrant activity at both sides of the film is different. Consequently, the driving force for diffusion is directed from the high activity side of the film towards the low activity side and the penetrant migrates through the film from one side to the other.

In Fig. 7, a typical permeation plot is shown. Here Q (kg m^{-2}) is the total amount of penetrant, which has passed through the film during a period of time t from the start. Initially, penetrant also accumulates in the film, which is essentially a sorption process and shows up as an induction period. When steady-state conditions occur, a diffusion coefficient can be extracted from the slope of the linear part:

$$F = -D\frac{\partial C}{\partial x} \tag{6}$$

actually being Fick's first law of diffusion. Here F (kg m^{-2} s^{-1}) is the rate of transfer through the film — i.e. the flux, $\Delta Q/\Delta t$ — which is constant in the steady state. This diffusion coefficient principally differs from the one derived

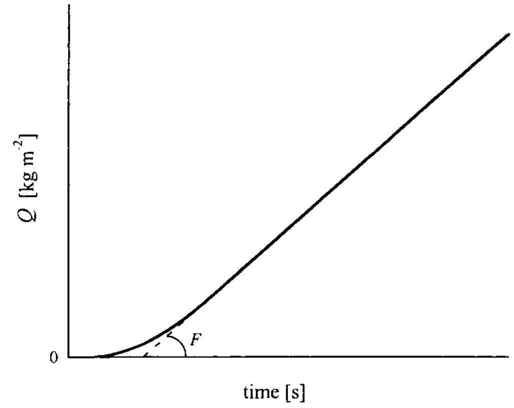

Fig. 7. Stylized picture of a typical permeation curve. The total amount of penetrant Q, which has passed through the film in time t, is plotted as a function of time. The slope F of the linear part is the penetrant flux.

from sorption experiments, since the underlying differential equation does not include a time parameter t.

Therefore, the rate of permeation is generally expressed by the permeability (P) ($\mathrm{m}^3\ (\mathrm{m\ s})^{-1}$) rather than by a diffusion coefficient. The permeability is dependent on both the (steady state) diffusion coefficient derived from Eq. (6) and the solubility (S) ($\mathrm{m}^3\ \mathrm{m}^{-3}$) of the penetrant in the film [3]:

$$P = DS \tag{7}$$

The solubility S is the slope of the sorption isotherm, and is constant for the linear sorption isotherm, which obeys Henry's law (see Section 2.4). This equation apparently is similar to the relationship between the isothermal vapour diffusivity $D(\varphi)$, the slope of the sorption isotherm ($\partial\varphi/\partial a$), and vapour permeability δ in rigid porous materials [5].

As in that case the vapour permeability is a function of the penetrant activity a (or concentration C), a functional relationship between D and a (or C) may be estimated. However, considering inaccuracies in determination of both the permeability and sorption isotherm, such approach may lead to considerable mistakes [5]. Apart from this, in the case of polymer systems, transport may be highly affected by glassy–rubbery state transitions, and by volume effects in each state. As both the permeability P and solubility S are in fact steady-state quantities, not taking account of such effects, the $D(C)$ relationship may not be estimated on the basis of Eq. (7).

Although the permeation experiments discussed above do not reflect kinetics, closer examination of the induction period should give information about kinetic behaviour. Performing differential permeation experiments — i.e. measurements of the rate of transfer F as a function of time — may offer more insight in the period before reaching steady state. Experiments of Nguyen et al. [39] suggest that for permeation anomalous features may be distinguished similar to those of absorption, related to volume changes of the film during the experiment.

2.4. *Equilibrium sorption*

Section 2.3 dealt with diffusion, this section deals with equilibrium. Within the field of polymer physics, the term usually refers to any equilibrium uptake of vapour or liquid. Brunauer et al. [40,41] developed a still leading classification (the so-called "BET classification") on equilibrium sorption behaviour of porous materials, as reflected by their sorption isotherms. Sorption isotherms describe equilibrium sorption of porous materials in the non-saturated region as a function of the penetrant activity, including adsorption (i.e. formation of multilayers) and capillary condensation. In the saturated region, equilibrium sorption is described by the so-called capillary pressure curve. The BET classification originally distinguished five types of sorption isotherm (Fig. 8) [41]. Type I is the well-known Langmuir isotherm, which is applicable to microporous solids. Type II and Type III isotherms describe adsorption of gases on macroporous or non-porous solids, and Type IV and Type V isotherms are applicable to both mesoporous or microporous solids. The presence of hysteresis loops is characteristic for Type IV and Type V, but may also appear in the other isotherms. Brunauer et al. [40] originally stated their theory at least to be valid for gases which do not possess considerable dipole moments. Water molecules possess a large dipole moment. Nevertheless, the BET classification has been adopted without much doubt for water in polymers, e.g. by Barrie [10] in his classic review. Polymers may show a widely varying appear-

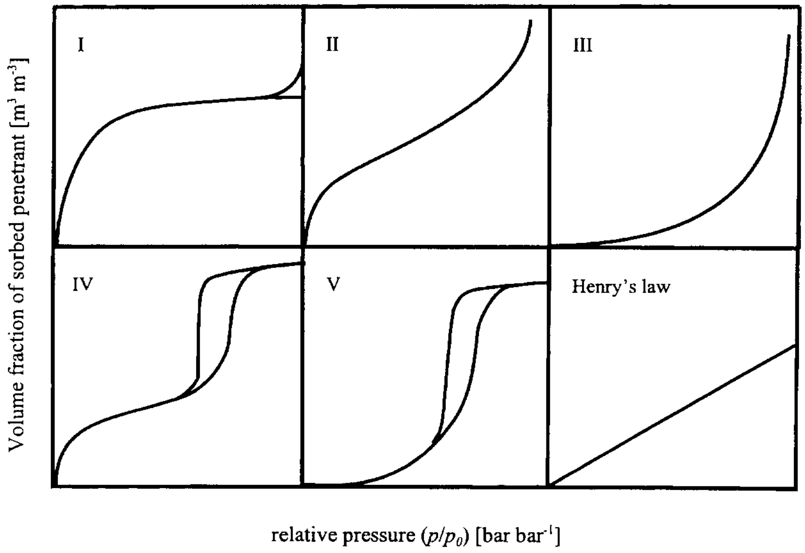

Fig. 8. Stylized picture of the five types of sorption isotherm according to the BET-classification [40], and the linear isotherm according to Henry's law. The volume fraction of sorbed penetrant is plotted as a function of the relative pressure (p/p_0).

ance of water sorption isotherms. Type II isotherms are commonly encountered with hydrophilic polymers such as wool, silk and cellulose acetate. For less hydrophilic ones (ethylcellulose, polydimethyl siloxane) Type III isotherms are observed. Linear isotherms are found for hydrophobic polymers (polystyrene, polyethylene). These findings justify the assumption that these types of polymers may be considered non-porous. Linear isotherms imply that Henry's law is valid over the entire range of penetrant activities. Since Henry's law expresses ideality of dissolution, this also implies insignificance of penetrant–polymer interactions, which is plausible for water sorption in hydrophobic polymers. Non-linear isotherms consequently indicate that the sorption process deviates from ideality, i.e. they reflect interactions between water molecules and polymer structure. The nature of these interactions will be discussed in Section 2.5.

2.4.1. *Localized sorption theories*

Brunauer et al. [41] proposed a model to describe features of five different types of sorption isotherm. Starting point of their model is the presence of a dynamic equilibrium, in which condensation of molecules onto bare sites equals the evaporation from occupied sites. As polymers are commonly regarded as non-porous the classical BET model is normally used in a linearized two-parameter form (see e.g. [3]), assuming the number of adsorbed molecular layers to be infinite:

$$\frac{a}{\varphi(1-a)}=\frac{1}{\varphi_{\mathrm{m}}c_{\mathrm{BET}}}+\left(\frac{c_{\mathrm{BET}}-1}{\varphi_{\mathrm{m}}c_{\mathrm{BET}}}\right)a \tag{8}$$

where φ is the volume fraction of penetrant as related to the total volume ($\mathrm{m}^3\ \mathrm{m}^{-3}$), a the penetrant activity ($a=p/p_0$, p (bar) is the vapour pressure, p_0 (bar) is the saturation vapour pressure), φ_{m} (–) is the volume fraction of a complete penetrant monolayer, c_{BET} (–) is a parameter of the BET model, reflecting the partitioning of higher sorption layers. This parameter can be calculated approximately by

$$c_{\mathrm{BET}}=\mathrm{e}^{(\phi_1-\phi_{\mathrm{L}})/(RT)} \tag{9}$$

where ϕ_1 is the heat of adsorption of the first penetrant layer, and ϕ_{L} is the heat of liquefaction. Although c_{BET} can be calculated, it is normally used as a fitting parameter for polymers, thereby actually casting doubt on the theoretical basis. In addition, a three-parameter form, assuming a limited built-up of molecular layers, was presented in the original paper [40]. It has not been commonly applied for polymers, according to Jonquières and Fane [42] because it required an — in that time difficult — non-linear mathematical treatment. A better explanation would be that finiteness of the number of layers is only important for porous materials, and polymers are generally characterized as non-porous. The BET model is considered to give good agreement with experimental values for water activities between 0 and 0.5 in hydrophilic glassy polymers [42], thus being better than originally reported by Brunauer et al. [41] for porous materials. In contrast to non-porous polymers, for porous materials the application of BET is limited at activities above 0.3 due to capillary condensation effects.

Anderson [43] discussed a modification to the BET model by assuming that the heat of adsorption in the multilayer system is less than the heat of liquefaction. Together with work of Guggenheim [44] and de Boer [45], this led to the three-parameter Guggenheim–Anderson–de Boer (GAB) equation. A slightly modified form is given by Jonquières et al. [42]:

$$\varphi=\frac{\varphi_{\mathrm{m}}c_{\mathrm{GAB}}ka}{(1-ka)}\frac{1}{1+(c_{\mathrm{GAB}}-1)ka} \tag{10}$$

The parameters in this equation are the same as for the BET model, except for c_{GAB} (–) and k ($\mathrm{J\ J}^{-1}$), being a fitting parameter of the GAB model, and the ratio of heat of adsorption and the heat of liquefaction, respectively. k is assumed to be less than 1. Jonquières and Fane [42] recently showed that the GAB equation is effective for fitting data of non-ideal water sorption in polymers (Type II or III) over activity ranging from 0 to 0.95, which is not the case for the classic BET model.

Another localized sorption model is the so-called "dual sorption model", which is developed by Vieth et al. [46]. The model is a combination of the linear isotherm according to Henry's law, accounting for normal dissolution, and the Langmuir isotherm, which is included in the BET model and accounts for immobilization of penetrant at fixed sites within the medium (microvoids or holes in the glassy polymer structure). Still, the GAB model fits Type III isotherms better than the dual sorption model [42].

2.4.2. *Dissolution theories*

In localized sorption theories, penetrant is considered to bind at specific sites in the polymeric structure, e.g. in cracks, pores, or at specific polar groups which are capable of interaction with polar penetrants like water. The so-called dissolution theory offers another — macroscopic — approach to penetrant sorption. A number of models have been proposed assuming homogeneous dissolution of penetrant in polymers. Flory [47] discussed the entropy of mixing small molecules and high polymers. The starting point of his theory was that for polymer–penetrant systems that do not display strong interactions observed deviations from ideal behaviour should be attributed to incompatibility of their molecule sizes. This basic concept was evolved by Huggins [48] and Flory [49], leading to the following "Flory–Huggins" relation:

$$\ln(a)=1-\varphi+\ln(\varphi)+\chi\,(1-\varphi)^2 \tag{11}$$

In this model, φ ($\mathrm{m}^3\ \mathrm{m}^{-3}$) is the volume fraction of dissolved penetrant, and a is the penetrant activity. The compatibility of polymer and penetrant is expressed by a dimensionless interaction parameter χ [50]. According to Flory [49] the theory is limited to relatively apolar systems, interacting only weakly. In contrast to that starting point, the

Flory–Huggins relation is also used for fitting water sorption. Barrie [10] notes that the relation tends to be useful for water in relatively hydrophobic polymers for activities larger than 0.5. Perrin et al. [51] showed for the Type III isotherms of water vapour sorption in hydrophilic cellulose acetate good agreement for low and intermediate activities ($a_w < 0.7$), which is a totally different range than was indicated by Barrie. It may be concluded that the application of the Flory–Huggins relation with respect to the type of polymer–penetrant system as well as to the penetrant activity range is still questioned.

The assumption that clustering of penetrant may cause the sorption isotherm to depart from the Flory–Huggins relation for higher penetrant activities [52], led to another approach of Perrin and Favre [51,53] by taking penetrant–polymer as well as penetrant–penetrant interactions into account. A second interaction parameter k_s was introduced to account for these mutual penetrant interactions. In this model the interactions between polymer and penetrant are reflected by the parameter k_p, comparable to the Flory–Huggins interaction parameter χ. The following relation was empirically derived for the solvent fraction as a function of the penetrant activity (a):

$$\varphi = \frac{e^{(k_s-k_p)a}-1}{(k_s-k_p)/k_p} \tag{12}$$

This two-parameter model, named after the ENSIC laboratory, may describe some Type III isotherms over nearly the entire activity range, whereas Flory–Huggins fails at higher activities.

2.5. *Interactions of water in polymers*

Water molecules are highly dipolar. This character is due to the high electronegativity of oxygen compared to hydrogen. Partial electrostatic charges due to this difference in electronegativity result in strong interactions of water and other charged or polar groups and between water molecules mutually in polymers. Both the types of interaction as well as the degree of interaction depend strongly on polymeric structure. It is generally accepted that for sorbed water molecules at least three different states are possible:

1. *Single water molecules*, which neither show significant interactions with other water molecules nor with their environment.
2. *Aggregated water molecules*. These are water molecules, which interact with other water molecules to form agglomerates or clusters. Usually, such clusters are not large enough to resemble bulk water properties.
3. *Localized interactions* of water molecules and polymer groups.

It is suggested that for highly hydrophilic polymers, such as polyvinyl alcohol, (3) is even subdivided into two states [54,55]:

(3a) Non-freezing water, i.e. water that is strongly bound to polar groups in the polymer.
(3b) Freezable bound water, i.e. water that is weakly bound to the polymer or to the non-freezing water.

It may be suggested that for porous polymers, similar to other porous materials also bulk water is present.

Transport of water in hydrophobic systems is normally by single water molecules (1), especially at low water activities. Interactions of water molecules and hydrophobic polymers are minimal, since the polarizability of water is small, and dispersion forces only weakly contribute to interaction with non-polar materials. As indicated in the previous paragraph, linear sorption isotherms are found, indicating ideal dissolution of water molecules in the matrix.

It is already mentioned that clustering of water molecules (2) may cause a marked deviation from Henry's law. Water clusters stem from a high mutual affinity of water molecules combined with a relatively low affinity of water molecules for the polymeric matrix. Consequently, clustering of water is expected primarily in hydrophobic polymers for high water activities [10]. On the other hand, also for hydrophilic polymers clustering may be expected if the amount of water molecules in the polymer is higher than the quantity that can be bound to the polymer. For weak penetrant–polymer interactions (e.g. water–hydrophobic polymer), Zimm [56] and Zimm and Lundberg [57] developed a statistical analysis to determine the extent of clustering from measured sorption isotherms. For an amorphous polymer, they arrive at the following expression:

$$\frac{G_{ww}}{V_w} = -(1-\varphi_w)\left[\frac{\partial(a_w/\varphi_w)}{\partial a_w}\right]_{PT} - 1 \tag{13}$$

G_{ww} is the so-called cluster integral, V_w and a_w are the partial volume and activity of water molecules in the polymer, respectively, and φ_w is the volume fraction of water in the polymer.

The cluster integral indicates whether clustering takes place or not. For ideal solutions, it follows from Eq. (13) that $G_{ww}/V_w = -1$, indicating that a particular water molecule does not affect the distribution of other water molecules. If $G_{ww}/V_w > -1$, there is a tendency to cluster. In this case, the concentration of water molecules in the neighbourhood of a given water molecule is higher than would be the case for random distribution. The relation can only be applied for comparative purpose.

Whereas the cluster integral is suited for weakly interacting penetrant–polymer systems, a model for clustering of water in hydrophilic polymers is given by the group of Favre and Perrin [51,53]. They characterize in their previously described ENSIC model clustering in terms of a 'mean cluster size' (MCS) (–) as a function of penetrant volume fraction:

$$\mathrm{MCS} = \frac{(1-\varphi)(k_2\varphi+1)\ln(k_2\varphi+1)}{k_2\varphi} + \varphi \tag{14}$$

In this relation, $k_2 = (k_s - k_p)/k_p$. In the case of water, the quantity MCS is interpreted as the number of water molecules in the vicinity of another absorbed water molecule. The advantage of the MCS is that an interpretation in quantitative terms is provided, whereas the Zimm–Lundberg cluster integral is mainly qualitative. However, the starting points for the models are different and suitability of the model depends mainly on the hydrophobicity of the polymer.

The overall solubility of water in the polymer is determined by the amount and nature of polar groups in the polymer. Hydroxyl, carboxyl and peptide groups were found to bind water molecules strongly [58]. Furthermore, equilibrium sorption depends also on the position of the polar group at the polymer chain. For example, some polyamides show low equilibrium sorption values, although the amide group is highly polar. This notion has been attributed to interchain hydrogen bonds sufficiently strong to resist interactions with water molecules [10].

Hodge et al. [55] suggested that the non-freezing type of bound water (3a) is an important plasticizer in highly hydrophilic polymers, i.e. this type of water binding causes a transition from glass to rubber to occur upon water absorption. It is discussed that polar groups facilitate equilibrium sorption of water, both by the localized binding in itself, and by plasticization effects. However, for diffusion the two factors are contradictory [3]. Plasticization tends to facilitate diffusion, since rubbery polymers entail higher diffusion coefficients than glassy polymers. On the other hand, immobilization of water molecules at polar binding sites causes the diffusion coefficient to decrease for low water concentrations.

3. Coatings

3.1. General aspects

3.1.1. Solvent-borne and water-borne paints

Solvent-borne paints are generally cross-linking coating systems. In the wet state, the binder is usually present as low molecular weight polymer. Upon curing cross-linking takes place, resulting in a polymer network. Consequently, the dry film is not soluble anymore. Polyesters, alkyds, and epoxies are typical binders. For interior applications (especially wood) alkyds are frequently used, since they are cheap and cure easily with oxygen from the air at room temperature. A problem with alkyds is their low durability, and for white paints, their tendency to turn yellow.

The current expansion of water-borne dispersion (latex) paints is a result of the pressure to reduce volatile organic compounds and the industrial trend towards friendlier products with low toxicity to the product formulation. Typical binder polymers are acrylics and vinyl acetate copolymers. The first step in the process of film formation is evaporation of water from the film. Secondly, coalescence (particle deformation) starts to take place when the polymer particles come into contact, resulting in a polyhydric structure once the water has evaporated from the film. Deformation mechanisms have been reviewed by Visschers et al. [59]. The final stage is interfacial diffusion of polymeric chains that should result in a continuous and homogeneous film [60]. However, doubt is cast whether the formation of a completely homogeneous film actually takes place. Dried latex films should be considered cellular [61], which is clearly shown in electron micrographs of Zosel [62]. Richard [63] concluded on the basis of experiments that water vapour is mainly transported via the interfaces of the latex particles, without entering the more hydrophobic core of the particle.

3.1.2. Pigments and fillers [64]

Pigments are insoluble substances, which are suspended into the coating formulation mainly for colouring, but also with other objectives such as corrosion inhibition. They are usually dense inorganic compounds, but also insoluble organic compounds may be used. Common pigments are titanium dioxide, iron oxide, and aluminium flakes.

Most fillers are cheap natural minerals, and typically include talc, clay, chalk and quartz. Their major role is lowering the paint price, but they also contribute to the hiding power, and affect coating properties such as hardness.

The amount of pigments and fillers relative to the amount of binder is usually expressed as the pigment volume concentration (PVC). The PVC is the volume fraction of pigment in the dry coating film (normally expressed as a percentage). When the amount of binder is such that the total pigment volume is just completely wetted, the PVC equals the so-called critical PVC (CPVC). The CPVC is considered a transition point, playing a pivotal role in many coating properties.

Pigments are generally obtained from the manufacturer with particle sizes much larger than the size of the pigment crystal. The process of breaking up these so-called "agglomerates" is called pigment "dispersion". Firstly, a pigment dispersion concentrate is prepared by grinding pigment in a mill, together with a minimum of solvent and resin. Additives like dispersion agents facilitate this process. The performance of the paint depends clearly on the quality of the pigment dispersion concentrate. Furthermore, stabilization of the pigment dispersion may be critical, since flocculation, i.e. pigment agglomeration in the paint due to insufficient stabilization of the pigment particles may take place.

3.1.3. Additives [65]

Additives are generally applied to coatings to improve their performance. Some of them are essential, such as stabilizers. Many of them contain hydrophilic parts, therefore also contributing to the moisture affinity of the film. The most important additives usually are pigment dispersants, rheology modifiers, leveling additives, and antifoams. Pigment dispersants facilitate agglomerates of pigment particles to break up in the dispersion process; rheology modifiers or thickeners are used to obtain the right paint viscosity. They are usually hydrophilic polymers, but also hydrophobe-modified forms (associative thickeners) are used. Leveling agents, such as higher boiling alcohols, facilitate spreading of the paint over the substrate surface and homogeneous film formation. Antifoams prevent foam formation and typically are oils, silica and surfactants.

3.1.4. Homogeneity of a coating

Although coatings are clearly heterogeneous in a microscopic sense, they are usually considered homogeneous from a macroscopic point of view. Bear and Bachmat [66] introduced the so-called representative elementary volume (REV) to assess whether macroscopic homogeneity can be supposed. The REV is defined as the minimum volume for which statistically meaningful averages can be obtained. Although the concept was developed for porous media, it should also be suitable to other micro-heterogeneous systems such as polymeric coatings. Besides defects that are difficult to prevent, such as capillaries resulting from coating application, the size of coating constituents determine the REV of the coating. Pigment particles are usually the most sizeable coating constituents, having typical dimensions of 0.1–0.4 μm. For a 60 μm dry coating thickness, the film thickness is about 150–600 times larger than the typical size of pigment crystals, and consequently, well-dispersed coatings without defects are clearly homogeneous in a macroscopic sense.

3.2. Effects of pigments and fillers

3.2.1. Ideal pigmentation

Pigments are generally dense inorganic compounds, with little or no water solubility. Ideally, these pigments are non-hydrophilic, well dispersed, and uniformly distributed through the film, and there are no flocculates within the film. Furthermore, the pigments are strongly bound to the binder polymer, and as a result the interface will allow only minimal penetration. In such an ideal system, water can only permeate by circumnavigation of the pigment particles, increasing the effective path length for diffusion and therefore lowering the permeability [64]. This is a combined effect including: (1) a correction of the diffusion coefficient D for increased path length; (2) a decrease of water solubility in the film resulting from an increasing volume fraction φ_p ($m^3\ m^{-3}$) of impermeable pigment [3]. The first correction is expressed as

$$D_s = KD_b. \tag{15}$$

Here D_s is the overall unidimensional diffusion coefficient in the coating, and D_b is the diffusion coefficient in the binder fraction. The correction factor K (–) in fact is a sort of 'tortuosity' and $K = K(\varphi_p)$. The effect of overall solubility in the film is described as

$$S_s = (1-\varphi_p)S_b, \tag{16}$$

where S_s is the overall solubility in the coating, and S_b is the solubility in the binder fraction. Using Eq. (7), consequently, the relationship between permeability of coating (P_s) and binder (P_b) is given by

$$P_s = K(1-\varphi_p)P_b. \tag{17}$$

According to Nielsen [67], the dependence of K on φ_p can be estimated as

$$K = \frac{1}{1 + (l_p/2w_p)\varphi_p}, \tag{18}$$

where l_p/w_p is the ratio between the length and width of the pigment particles assuming ellipsoid particle shape ($l_p/w_p = 1$ for a sphere). Basically, this equation assumes a random distribution of particle orientation. For a non-spherical geometry, the estimated and actual permeability may differ strongly if the particle orientation is not random. Especially platy pigments with large l_p/w_p ratios may show a large decrease of permeability due to orientation of pigment particles parallel to the substrate.

Even for ideal pigmentation, the volume fraction of pigment φ_p cannot be increased unrestrictedly. Above the CPVC the binder is not able to wet the pigment particles completely, resulting in a porous coating. With increasing pigment volume concentrations above CPVC, the permeability rises steeply (Fig. 9), corresponding with enhanced transport through the pores of the film. Therefore, the CPVC is observed to coincide with the minimum in permeability.

3.2.2. Non-ideal pigmentation

Many pigmented coatings do not show the ideal behaviour described above. Non-ideal behaviour includes hydrophilic

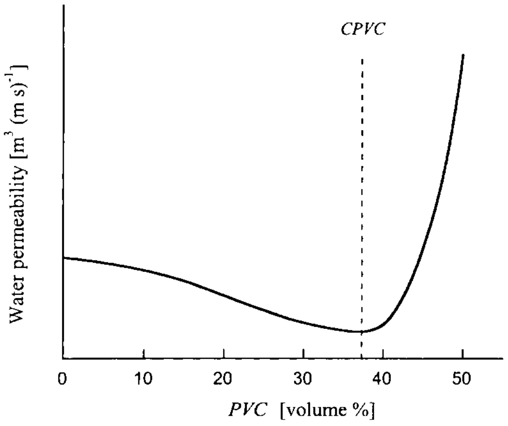

Fig. 9. Stylized picture of the water permeability (P) as a function of the pigment volume concentration (PVC) for ideal pigmentation. The dotted line represents the critical PVC.

and not fully dispersed pigments, including irregular distribution through the film and particle flocculation.

Due to hydrophilicity of pigment particles, pigments may be bound insufficiently to the binder, resulting in "vulnerable" interfaces. Water accumulation — i.e. water layer formation — around pigments causes expansion of the overall volume of pigment and adsorbed water. Within these interspaces liquid transport takes place, which is faster than diffusion through the binder matrix [64]. According to Michaels [68], water permeation through the interfaces between pigment and binder is important for hydrophilic pigments, since these pigments facilitate water solubility in the film.

Pigment agglomeration, caused by incomplete dispersion or flocculation, affects water transport. Pigment particles in the agglomerates are not completely wetted, and may therefore contain empty volume, facilitating water transfer. Furthermore, circumnavigation is hindered less by agglomerates than by the individual pigment particles [64].

In conclusion, pigmentation can significantly lower moisture transport in coatings. However, factors like incomplete dispersion, flocculation, and poor binding between pigment and resin may diminish this effect substantially and may even lead to an overall rise in moisture transport compared to non-pigmented films.

3.3. Effects of additives

Since most additives attract water, they increase both the solubility and equilibrium absorption of coatings. Despite general knowledge, little is really known in detail about their influence. Recently, Shay et al. [69] found marked differences with respect to water absorption properties of different types of thickener. However, their research only covered pure thickeners, and not their effect on coating performance. Furthermore, most additives leach out of the coating because of their (slight) solubility in water. Consequently, the actual coating performance may vary in time, since the hygroscopicity decreases and empty volume in the film increases. Furthermore, more coating free space may also result from degradation of binder and additives.

Roulstone et al. [70] studied effects of surfactants on the water vapour permeability of polybutyl methacrylate latex films. They found that the cationic surfactant dodecylethyldimethyl ammonium bromide (DEDAB) significantly increased water vapour permeability. This effect was attributed to incompatibility of the surfactant with the binder. On the other hand, small quantities of the more compatible anionic surfactant sodium dodecyl sulphate (SDS) were found to lower permeability due to formation of denser films.

4. Discussion and conclusions

The distinction between Fickian and non-Fickian effects is usually based on the appearance of kinetic curves, inherently including effects of boundary conditions and/or experimental circumstances. Such distinction does not take account of mechanistic aspects. Actually, any kinetic curve governed by Fick's law should be designated as Fickian by definition. In this respect, it is curious that the 'variable surface concentration' model of Long and Richman [28] is treated as a model for non-Fickian effects, considering the determinative role of boundary conditions.

Samus and Rossi [38] support this view towards Fickian behaviour, suggesting that geometrical constraints on swelling behaviour may cause anomalies in the overall kinetic curve, however, still responding to Fick's law.

Transport of penetrant in a polymer is at least a function of both penetrant concentration and temperature. Essentially two views towards this complicated relationship are recognized. The concept of Hopfenberg and Frisch [8] assumes concentration-independent transport at very low temperatures, as well as at very low concentrations. On the other hand, the Deborah theory of Vrentas et al. [11–13] introduces three zones in the temperature–concentration plane, each showing different transport features corresponding to Fickian or non-Fickian behaviour. It may be said that those concepts appear not compatible. The Deborah plot shows that especially near the boundary lines characterized by the so-called threshold temperatures T_V and T_E, respectively, a transition takes place from Fickian towards non-Fickian (or reversely), corresponding to a change in diffusion coefficient. As the Deborah theory deals with temperature effects on diffusion more soundly, application of this concept appears more realistic.

The concentration dependence of diffusion coefficients in polymers and coatings has never been fairly determined due to insufficient spatial resolution of measuring techniques. Determination of such relationship requires measuring of time-dependent penetrant concentration profiles in the thin polymer film or coating. Recently, the successful application of new techniques in the area of moisture transport in porous materials has been demonstrated (Pel et al. [71]). However, the spatial resolution of those techniques still does not allow monitoring of profiles in polymer films and coatings.

In order to derive the dependence of the diffusion coefficient D on penetrant concentration, a functional relationship between these parameters is therefore assumed in advance. Even more generally, a constant (or concentration independent) diffusion coefficient is adopted, probably since it addresses the analytical solution of Crank [24].

After entering the relationship in the model, the sorption curve can be calculated from the solution of the transport equation for given boundary conditions. Provided that the experimental conditions correspond to the boundary conditions in the model, the diffusion coefficient can be deduced from adjustment of the chosen relationship to obtain the best fit of calculations with measurements. A major drawback of this method is the assumption of the functional description of D. Actually, obtaining such a relationship is the main objective of the experiments.

No theoretical difference exists between absorption of water vapour and liquid water in polymers in case polymeric films and coatings are considered non-porous [10]. Obviously, in such systems water cannot be connected to a state of liquid or vapour. In porous media, diffusion mechanisms are different for vapour and liquid water, but both are usually assimilated into one overall diffusion coefficient [14]. Consequently, diffusion in coatings with pigment volumes above the CPVC, which are considered porous, should be mechanistically different from polymers and coatings below their CPVC.

It is questionable when polymeric films should be considered porous media. Polymeric films may contain a large amount of free space, especially rubbery polymers. However, such free volume is not generally related to pores. It is rather considered an enlargement of the volume in which a polymer segment statistically can be present because of an increase in temperature. Of course, the latter process is accompanied by swelling of the film.

The glass transition is critical in this respect, since in glassy polymers free volume can be 'frozen' in the polymer below T_g. In conclusion, however, a consistent definition of the glass transition is still lacking. To quote Bondi [20]:

"*None of the attempts that have been made to define T_g in terms of free-volume theory or in terms of thermodynamic arguments or in terms of mechanical properties has been entirely successful. A general theory of glass transition may not be developed until its phenomenological definition has been clarified. Conversely, we may well find that the sharp rise in viscosity, characteristic of or even the cause of glass transition, cannot be tied consistently to any equilibrium argument. In that case, there will be no clear-cut definition and no general theory*".

For equilibrium sorption, different models have been considered. Two basic types are recognized, localized sorption (adsorption) models and dissolution models. Originally, adsorption models have been developed to account for equilibrium surface adsorption at the walls of pores in porous materials. It is not clear beforehand that these models are also applicable to polymer films and coatings since most polymeric materials are still considered non-porous. Furthermore, localized binding stemming from polar–polar interactions of water and hydrophilic groups in the polymer is mechanistically clearly distinct from classical adsorption, and may give rise to similar descriptions. Neither the traditional localized sorption model (BET) nor the traditional dissolution model (Flory–Huggins) describes sorption isotherms well over the entire range of activities. Numerous 'improvements' to the theories have been proposed, introducing an increasing number of fitting parameters. It is obscure to what extent such curve fitting originates from mechanistic considerations. The same doubts can be cast on the kinetic models.

Pigments and fillers as well as additives may clearly affect diffusion kinetic parameters (D, P), as well as equilibrium parameters (S, φ). Actually, the critical pigment concentration (CPVC) is a transition point with respect to moisture transport.

Most additives seriously enlarge solubility and equilibrium absorption values of water in the coating, thereby increasing permeability. Furthermore, leaching of soluble additives may affect water permeation. Water-borne coatings are most prone to this, sometimes intensified by imperfect film formation due to the process of coalescence. These effects are, however, more qualitatively than quantitatively known.

In conclusion, a profound understanding of transport mechanisms in organic polymers and coatings is still missing. Firstly, the concentration dependence of diffusion in many polymer–penetrant systems is hardly understood, partly due to the lack of adequate measuring techniques. Secondly, free volume and porosity in polymers and coatings is still a subject of discussion.

Acknowledgements

Prof. E.L.J. Bancken is thanked for useful comments.

References

[1] G.K. van der Wel, O.C.G. Adan, E.L.J. Bancken, Towards an ecofriendlier control of fungal growth on coated plasters?, XXIV FATIPEC Kongress, vol. C, 1998, p. 15.
[2] G.K. van der Wel, O.C.G. Adan, E.L.J. Bancken, Prog. Org. Coat., in press.
[3] R. Blahník, Prog. Org. Coat. 11 (1983) 353.
[4] M. Huldén, C.M. Hansen, Prog. Org. Coat. 13 (1985) 171.
[5] O.C.G. Adan, On the fungal defacement of interior finishes, Ph.D. Thesis, Eindhoven University of Technology, 1994.
[6] W.R. Vieth, Diffusion in and through Polymers: Principles and Applications, Hansér, Munich, 1991.
[7] P. Neogi (Ed.), Diffusion in Polymers, Marcel Dekker, New York, 1996.
[8] H.B. Hopfenberg, H.L. Frisch, J. Polym. Sci. B 7 (1969) 405.
[9] G. Challa, Polymer Chemistry: An Introduction, Prentice-Hall, Englewood Cliffs, NJ, 1993.
[10] J.A. Barrie, in: J. Crank, G.S. Park (Eds.), Diffusion in Polymers, Ch. 8, Academic Press, London, 1968.
[11] J.S. Vrentas, C.M. Jarzebski, J.L. Duda, AIChE J. 215 (1975) 894.
[12] J.S. Vrentas, J.L. Duda, J. Polym. Sci. 15 (1977) 441.
[13] J.S. Vrentas, C.M. Vrentas, W.J. Huang, J. Appl. Polym. Sci. 64 (1997) 2007.
[14] J.R. Philip, D.A. de Vries, Trans. Am. Geophys. Union 38 (1957) 222.
[15] O.C.G. Adan, HERON 40 (1995) 201.
[16] J.S. Vrentas, J.L. Duda, H.-C. Ling, Macromolecules 21 (1988) 1470.
[17] J.S. Vrentas, C.M. Vrentas, Macromolecules 22 (1989) 2264.
[18] J.S. Vrentas, C.M. Vrentas, J. Polym. Sci. 28 (1990) 241.
[19] J.L. Duda, J.M. Zielinski, in: P. Neogi (Ed.), Diffusion in Polymers, Ch. 3, Marcel Dekker, New York, 1996.
[20] A. Bondi, Physical Properties of Molecular Crystals, Liquids, and Glasses, Wiley, New York, 1968.
[21] J. Crank, G.S. Park, in: J. Crank, G.S. Park (Eds.), Diffusion in Polymers, Ch. 1, Academic Press, London, 1968.
[22] H. Corti, R. Fernandez-Prini, D. Gómez, Prog. Org. Coat. 10 (1982) 5.

[23] A. Kishimoto, Prog. Org. Coat. 1 (1972) 91.
[24] J. Crank, The Mathematics of Diffusion, Ch. 1, Clarendon Press, London, 1975.
[25] C.M. Balik, Macromolecules 29 (1996) 3025.
[26] A.R. Berens, H.B. Hopfenberg, Polymer 19 (1978) 489.
[27] Y.-M. Sun, H.-L. Lee, Polymer 37 (1996) 3921.
[28] F.A. Long, D. Richman, J. Am. Chem. Soc. 82 (1960) 513.
[29] W.P. de Wilde, P.J. Shopov, Composite Structures 27 (1994) 243.
[30] N.L. Thomas, A.H. Windle, J. Membr. Sci. 3 (1978) 337.
[31] A.H. Windle, in: J. Comyn (Ed.), Polymer Permeability, Ch. 3, Elsevier, London, 1985.
[32] J. Crank, J. Polym. Sci. 11 (1953) 151.
[33] J.H. Petropoulos, P.P. Roussis, J. Chem. Phys. 47 (1967) 1491.
[34] J.H. Petropoulos, P.P. Roussis, J. Polym. Sci. C22 (1969) 917.
[35] A. Peterlin, J. Polym. Sci. B3 (1965) 1083.
[36] E.P.M. van Westing, G.M. Ferrari, J.H.W. de Wit, Corros. Sci. 36 (1994) 957.
[37] N.L. Thomas,A.H. Windle, Polymer 23 (1982) 529, and references cited herein.
[38] M.A. Samus, G. Rossi, Macromolecules 29 (1996) 2275.
[39] X.Q. Nguyen, M. Šípek, Q.T. Nguyen, V. Hynek, Macromol. Chem. Phys. 197 (1996) 715.
[40] S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309.
[41] S. Brunauer, L.S. Deming, W.E. Deming, E. Teller, J. Am. Chem. Soc. 62 (1940) 1723.
[42] A. Jonquières, A. Fane, J. Appl. Polym. Sci. 67 (1998) 1415.
[43] R.B. Anderson, J. Am. Chem. Soc. 68 (1946) 686.
[44] E.A. Guggenheim, Applications of Statistical Mechanics, Clarendon Press, Oxford, 1966, p. 186.
[45] J.H. de Boer, The Dynamical Character of Adsorption, 2nd ed., Clarendon Press, Oxford, 1968.
[46] W.R. Vieth, J.M. Howell, J.H. Shieh, J. Membr. Sci. 1 (1976) 177.
[47] P.J. Flory, J. Chem. Phys. 10 (1942) 51.
[48] M.L. Huggins, Ann. NY Acad. Sci. 42 (1942) 9.
[49] P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, New York, 1953.
[50] G. Gee, Q. Rev. Chem. Soc. 1 (1947) 293.
[51] L. Perrin, Q.T. Nguyen, D. Sacco, P. Lochon, Polym. Int. 42 (1997) 9.
[52] M.I. Beck, I. Tomka, J. Macromol. Sci. Phys. B36 (1997) 19.
[53] E. Favre, R. Clément, Q.T. Nguyen, P. Schaetzel, J. Néel, J. Chem. Soc., Faraday Trans. 89 (1993) 4347.
[54] K. Nakamura, T. Hatakeyama, H. Hatakeyama, Polymer 24 (1983) 871.
[55] R.M. Hodge, T.J. Bastow, G.H. Edward, G.P. Simon, A.J. Hill, Macromolecules 29 (1996) 8137.
[56] B.H. Zimm, J. Chem. Phys. 21 (1953) 934.
[57] B.H. Zimm, J.L. Lundberg, J. Phys. Chem. 60 (1956) 425.
[58] A.D. McLaren, J.W. Rowen, J. Polym. Sci. 7 (1951) 289.
[59] M. Visschers, J. Laven, A.L. German, Prog. Org. Coat. 30 (1997) 39.
[60] C. Gauthier, A. Guyot, J. Perez, O. Sindt, in: T. Provder, M.A. Winnik, M.W. Urban (Eds.), Film Formation in Water-borne Coatings, Ch. 10, ACS Symposium Series, Washington, DC, 1996.
[61] J. Richard, in: T. Provder, M.A. Winnik, M.W. Urban (Eds.), Film Formation in Water-borne Coatings, Ch. 8, ACS Symposium Series, Washington, DC, 1996.
[62] A. Zosel, Polym. Adv. Technol. 6 (1995) 263.
[63] J. Richard, Polym. Adv. Technol. 6 (1995) 270.
[64] C.H. Hare, J. Protective Coatings and Linings 1410 (1997) 77.
[65] L.J. Calbo (Ed.), Handbook of Coatings Additives, Marcel Dekker, New York, 1987.
[66] J. Bear, Y. Bachmat, Introduction to Modeling of Transport Phenomena in Porous Media, vol. 4, Kluwer Academic Publishers, Dordrecht, 1990.
[67] L.E. Nielsen, J. Macromol. Sci. (Chem.) A1 5 (1967) 929.
[68] A.S. Michaels, Official Digest, June 1967, p. 942.
[69] G.D. Shay, K.R. Olesen, J.L. Stallings, J. Coat. Technol. 68 (1996) 51.
[70] B.J. Roulstone, M.C. Wilkinson, J. Hearn, Polym. Int. 27 (1992) 43.
[71] L. Pel, H. Brocken, K. Kopinga, Int. J. Heat Mass Transfer 39 (1996) 1273.