Diffusion in Polymers and its Relevance to Anti-Corrosion Performance

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Abstract

This paper outlines the theory of diffusion of small molecules through polymer films and examines the effect of polymer type and pigmentation on the permeation of water vapour, oxygen and carbon dioxide through barrier coatings. The relevance of such data to anti-corrosion performance is discussed. Some new technologies for barrier property enhancement are described, including the use of nanofillers.

Keywords: Permeability, diffusion, paint, corrosion, nanofiller.

Introduction

Studies of the sorption and transport properties of small molecules in polymeric materials are of considerable importance in many industry sectors. These include diverse applications ranging from packaging materials for consumer products through to membranes with selective permeability for gas separation in large-scale industrial processes. In the polymer packaging industry, especially the food and beverage sector, the barrier properties of the polymer to oxygen, carbon dioxide and water vapour are key factors in determining performance.

In recent years a number of interesting new technologies have emerged to enhance the barrier properties of polymer films. One of these is the use of polymer nanocomposites. These novel materials contain relatively small amounts (typically less than 5 wt %) of nanometre-sized filler particles, which, if properly dispersed, are predicted to reduce gas and vapour permeability [1].

The aim of this paper is to outline the theory of diffusion of small molecules through polymer films and to review how polymer characteristics such as functional groups, crystallinity and cross-linked density affect the permeability of polymer films to water vapour, oxygen and carbon dioxide. The relevance of this data to the barrier properties of paint coatings is discussed, particularly with respect to corrosion protection of steel and the

carbonation of concrete. The applicability of new technologies, such as nanofillers, is also considered.

Theory and Definitions

Basic Principles

The permeation of a gas or vapour through a polymer film depends on both its solubility within the polymer and its ability to diffuse through it.

Diffusion in many systems can be represented by Fick's first and second laws, which are given below (respectively) for the one-dimensional case:

$$J = -D(c)\frac{dc}{dx} \dots\dots\dots\dots\dots\dots\dots(1)$$

and,

$$\frac{dc}{dt} = \frac{d}{dx}\left[D(c)\frac{dc}{dx}\right]\dots\dots\dots\dots\dots\dots\dots(2)$$

Where: J is the flux, i.e. the amount of permeant (i.e. the species that permeates) passing through unit area in unit time, D is the diffusion coefficient, c is the concentration and x is the coordinate in the direction of flux.

Under steady-state conditions with a linear concentration gradient, the flux is simply given by:

$$J = D\frac{(c_1 - c_2)}{l}\dots\dots\dots\dots\dots\dots(3)$$

Where: c_1 and c_2 are the concentrations of the gas at the two surfaces of the film and l is the thickness of the film.

For most barrier measurements it is far easier to determine the partial pressure of the gas on either side of the polymer film rather than its concentration in the surface of the film. It is therefore preferable to express equation (3) in terms of the vapour pressures, p_1 and p_2, on either side of the coating:

$$J = P\frac{(p_1 - p_2)}{l}\dots\dots\dots\dots\dots\dots(4)$$

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The constant P is the permeability coefficient, i.e. the rate per unit area at which gas passes through a film of unit thickness under one unit of pressure difference.

Assuming Henry's law is obeyed, the relationship between the concentration of gas in the surface of a polymer film and its vapour pressure in the gaseous phase is given by:

$$c = S.p .... (5)$$

Where: S is the solubility coefficient.

From equations (3), (4) and (5), it follows that the relationship between the permeability coefficient, diffusion coefficient and the solubility coefficient is given by:

$$P = D.S .... (6)$$

Hence permeability is the product of diffusivity and solubility. Equation (6) is the simplest case in which both D and S are constants that are independent of concentration and time. This simple relationship provides a good basis for a conceptual understanding of the general principles governing permeability. In practice, diffusion in many polymer systems is both concentration and time-dependent, and this considerably complicates both the mathematical treatment and the measurement of transport properties [2].

Ideal and Anomalous Behaviour

Diffusion behaviour is described as 'ideal' if it is Fickian and if Henry's law is obeyed, as in the simple case described above. This type of behaviour normally occurs if the penetrant is small compared with the monomer unit of a given polymer and there is only a weak thermodynamic interaction between them. Diffusion occurs by random jumps of the penetrant molecule between the polymer chains. Simple gases such as H_2, O_2 and CO_2 usually exhibit ideal diffusion behaviour, as does water in hydrophobic polymers.

If the penetrant molecules are comparable in size with or larger than the monomer unit of a polymer, then diffusion requires a co-operative movement of several monomer units (i.e. a polymer segment) to take place to create 'holes' of the appropriate size. Organic vapours, solvents and swelling agents come into this category. The diffusion coefficient, D, is usually strongly concentration dependent, but the kinetics are still Fickian if the system is above its glass transition temperature (Tg) value.

Below Tg, diffusion is more complex: glassy polymers have time-dependent responses and exhibit non-Fickian or 'anomalous' behaviour. Thus, it takes a finite time for the polymer

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molecules to arrange themselves to accommodate penetrant molecules and deviations from Fickian behaviour occur.

Alfrey et al. [3] have categorised diffusion behaviour according to the relative rates of penetrant mobility and polymer segmental relaxations as follows:

1. Case I (Fickian) – penetrant mobility is much less than polymer segmental relaxation rates.

2. Anomalous – penetrant mobility and polymer segmental relaxation rates are comparable

3. Case II – penetrant mobility is much greater than polymer segmental relaxation rates. This type of transport is characterised by a sharp boundary separating the inner glassy core from the outer swollen layer and the boundary advances at constant velocity. It occurs in systems where there is considerable swelling of the polymer by the penetrant. Simple gases do not exhibit such behaviour.

Case I (Fickian) and Case II can be viewed as the two limiting types of transport process, with anomalous behaviour in between. The amount , M, of penetrant absorbed per unit area at time, t, is often represented by:

$$M_t = K\, t^n$$

Where K and n are constants. For Fickian systems, $n = \frac{1}{2}$, for Case II transport, $n = 1$, and for 'anomalous' diffusion, $\frac{1}{2} < n < 1$.

The type of transport behaviour observed for any polymer–penetrant system will vary with both temperature and penetrant activity. Over a sufficiently wide range of temperature and/or penetrant activity, the transport behaviour of organic vapours and solvents in a polymer system may exhibit all the types of behaviour discussed above [4].

For transport of organic solvents in glassy polymers, the rate controlling process is diffusion of solvent down an activity gradient coupled with time-dependent mechanical deformation of the polymer glass in response to the swelling stress. It is possible to explain transport behaviour in terms of two basic parameters: the diffusivity of the penetrant, D, and the viscous flow rate of the glassy polymer, $1/\eta_0$. A theory has been proposed [5] that combines these two factors and is able to predict a wide range of observed transport phenomena, from Fickian diffusion at one extreme to Case II behaviour at the other. Further

anomalous effects have been observed in the transport of water in some polymer systems [6]. For example, clustering of water molecules in the polymer matrix can occur.

Units

The units of permeability are often a source of confusion and are therefore worth considering in some detail. The permeability coefficient, P, as defined in equation (4) has the following dimensions:

$$P = \frac{(amount\_of\_permeant)x(film\_thickness)}{(area)x(time)x(pressure\_drop\_across\_film)}$$

For the transport of gases such as H_2, He, N_2, O_2 and CO_2 through most polymer films, the permeability coefficient is characteristic of the polymer–penetrant system. However, the permeability of polymer films to water and organic penetrants may well vary as a function of film thickness and pressure drop. These data should be expressed as a transmission rate, Q, with the dimensions:

$$Q = \frac{(amount\_of\_permeant)x(film\_thickness)}{(area)x(time)}$$

quoting the vapour pressure of the penetrant applied across the film and the test temperature [7].

There are numerous units for expressing permeability and this causes difficulty when comparing data sets. For example, P can be expressed in:

$$\frac{cm^3.mm}{cm^2.s.cm(Hg)} \quad or \quad \frac{m^3.m}{m^2.day.PPa} \quad or \quad \frac{in^3.mil}{100in^2.day.atm} \quad etc$$

Fortunately tables of conversion factors do exist [7].

Permeability Data

General principles relating to the effect of polymer type in determining permeability will be discussed first: much of this information coming from research in the food packaging industry [8]. Application of these principles to organic coatings for anticorrosion performance will then follow [9].

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Polymer Films

Permeation of a gas or vapour through a polymer film is thought to involve the following stages: absorption of the permeating species into the polymer surface, solubility in the polymer matrix, diffusion through the film down a concentration gradient, and desorption from the opposite surface. Either of the middle two stages may be rate controlling and permeability is defined as the product of diffusivity, D, and solubility, S, as described in equation (6). It is instructive to investigate whether D or S is more likely to be the dominant factor controlling permeation.

The permeability of polymers to gases such as oxygen and carbon dioxide is more usually dominated by the diffusivity term, D. For example, Meares [10] has reported that the range of values covered by the diffusion coefficient of oxygen in a series of polymers at constant temperature is far broader than the corresponding range of values of solubility coefficient, S, as shown in Table 1 below.

Table 1: Solubility (S) and diffusion coefficient (D) of oxygen in several polymers at 43℃ [10].

Polymer	Oxygen: S x 10^2 cm³ at stp/cm³ polymer x atm	Oxygen: D x 10^7 cm²/sec
Natural Rubber	10.4	36
Polyisobutylene	10.8	2.4
Polybutadiene	9.7	30
Polydimethyl butadiene	11.7	4.1
Neoprene	7.8	10.0
Polyvinyl Acetate	6.0	1.7

In the case of water permeation in polymer films, permeability is more usually dominated by the solubility of water in the polymer. This is illustrated by the work of Muizebelt and Heuvelsland [11], whose data show that increases in water vapour permeability in a range of model coatings are due to increases in solubility rather than diffusivity (Table 2). The coatings examined were ester diols i.e. esters of tere- or isophthalic acid (T or I) with the

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diols glycol (G), butanediol (B) or neopentyl glycol (N), which were cross-linked with hexamethoxymethyl melamine (HMMM) or poly-functional isocyanate.

Table 2: Water Vapour Permeabilities (P) with Solubility (S) and Diffusion Coefficient (D) at 21°C [11].

Coating	$P \times 10^{11}$ g.cm/cm^2.(cm Hg).sec	$S \times 10^2$ g/cm^3.(cm Hg)	$D \times 10^9$ cm^2/sec
BIB/HMMM	5.0 ± 0.6	1.6	3.2
GTG/HMMM	4.6 ± 0.2	1.7	2.7
NIN/HMMM	4.4 ± 0.3	2.1	2.1
BIB/isocyanate	6.7 ± 0.5	4.8	1.4
B/isocyanate	21 ± 3	10	2.0
N/isocyanate	17 ± 4	11	1.5

The appreciation that the diffusivity term is predominant in gaseous permeation and the solubility term predominant in water permeation provides a useful framework for a conceptual understanding of the way that permeability is affected by polymer type. The permeability of polymers to gases decreases with increasing polymer polarity, largely due to the higher activation energy for diffusion in a polar polymer. Thus, highly polar polymers such as those containing many hydroxyl groups (e.g. polyvinyl alcohol) are excellent gas barriers. However, they are poor water barriers because water is very soluble in such polymers. In fact polyvinyl alcohol dissolves in water. Conversely, highly non-polar polymers, such as polyethylene, are impermeable to water due to the low solubility of water in hydrophobic materials. But polyethylene is a poor gas barrier because gaseous diffusion occurs much more readily in a non-polar polymer where inter-molecular attraction is relatively weak.

The diffusing species of interest to both the food technologist and the paint technologist are oxygen, carbon dioxide and water vapour. The permeabilities of these species in a range of different polymers are shown in Table 3. The data are collated from [8] and are listed in increasing order of oxygen permeability, which is also increasing order of carbon dioxide permeability. The effect of polymer structure in determining barrier properties is discussed below.

Table 3: Barrier Properties of Polymers [8].

Polymer	Oxygen, $\frac{cm^3.100\mu m}{m^2.day.atm}$ at 23℃, 0% RH	Carbon Dioxide, $\frac{cm^3.100\mu m}{m^2.day.atm}$ at 23℃, 0% RH	Water Vapour $\frac{cm^3.10\mu m}{m^2.day.atm}$ at 38℃, 100% RH
Poly (vinyl alcohol) dry	0.04	0.12	79,000
*Poly (vinylidene chloride)	0.4	1.2	7.9
Cellophane (dry)	0.5	1.2	14,000
*Epoxy (bisphenol A/amine)	12	35	160
*Nylon-6	20	35	700
* Poly (ethylene terephthalate)	20–39	47–79	80–160
*Poly (vinyl chloride)	31–59	79–157	80–120
*Poly (vinyl fluoride)	59	118	70
*Poly (methyl methacrylate)	67	157	470
Poly (vinyl acetate)	220	450	4,200
Cellulose Nitrate	390	1,180	3,150
High density Polyethylene	433	1,180	20
Polyurethane	530	1,380	4,800
Polypropylene	590	1,770	20
Poly (tetra fluoro ethylene)	866	2,360	10
Polycarbonate	890	2,165	550
Polystryrene	1,640	4,920	510
Low density PE	1,890	5,900	60
Polybutadiene	15,000	31,000	670

*Oxygen and carbon dioxide permeabilities measured at 100% RH.

Functional Groups

The chemical structure of a polymer film is the predominant factor controlling permeability: highly polar polymers are usually excellent gas barriers, whereas non-polar polymers are poor gas barriers. In Table 3 it is seen that the permeabilities of oxygen and carbon dioxide are about five orders of magnitude lower in dry polyvinyl alcohol than in polybutadiene. This is due to the much greater inter-molecular attraction in polyvinyl alcohol compared with polybutadiene.

Conversely, non-polar polymers are good barriers to water but highly polar polymers are very water sensitive. The water vapour permeability of polyethylene is at least three orders of magnitude less than that of polyvinyl alcohol.

For the best overall barrier properties, it is necessary to achieve a compromise between these two extremes. Some degree of polarity is required, but the absence of hydrophilic groups is a prerequisite for low water permeability. Polyvinylidene chloride is an example of an excellent all-round barrier polymer (Table 3). The chloride substituents on the skeletal carbon chain contribute some polarity but are not hydrophilic. These substituents are relatively small and regularly placed, which encourages good chain packing and crystallinity.

Chain Symmetry and Crystallinity

A comparison between polyvinylidene chloride (PVDC) and polyvinyl chloride (PVC) serves to illustrate the effects of chain symmetry and crystallinity on barrier properties (Table 3). PVDC has double the chlorine content of PVC: this of itself will contribute to the gas barrier through its effect on cohesive energy, as mentioned above. This apart, PVDC, i.e. ($-CH_2-CCl_2-$)n has far greater symmetry along the chain than atactic PVC. Chain symmetry gives rise to good chain packing and crystallinity, both of which decrease permeability to gases and water.

Another example of the effect of crystallinity is a comparison of high and low density polyethylene. HDPE with a degree of crystallinity of 80% is four times less permeable to gases and three times less permeable to water vapour than HDPE with a degree of crystallinity of 50% [8]. Crystallites act as inert fillers that are impermeable to both gas and liquid penetrants. Hence permeability decreases as crystallinity increases.

Orientation

Orientation of polymer molecules reduces permeability: the extent depending on the type of polymer and the degree of orientation. Polyethylene terephthalate (PET) is commonly used as biaxially oriented sheet. Orientation of up to 500% can reduce both gaseous and water permeability by a factor of two [8].

Cross-linking

Cross-linking should decrease permeability, especially in cases where the polymer is readily swollen by the penetrant. For example, polyvinyl alcohol will dissolve in water but this can be prevented by lightly cross-linking the polymer. In other systems, however, the effect may not be very noticeable. Muizebelt and Heuvelsland [11] found that permeation of water in ester diol systems was not much affected by the cross-link density of the films. More important was the effect of functional groups on water solubility.

Plasticisation and Tg

Large changes in permeability can occur either side of the glass transition temperature of a polymer. The increased segmental mobility above Tg gives rise to increased diffusivity and hence increased permeability. Addition of plasticisers to a polymer also causes increased segmental motion and effectively lowers the Tg, thus increasing permeability. For example, plasticisation of PVDC can cause an increase in oxygen permeability from 0.4 to 5.1 $cm^3.100\mu m/m^2.day.atm$ [8]. Highly polar polymers are particularly susceptible to plasticisation by moisture from the atmosphere and this can have a dramatic effect on their barrier properties. For example, dry cellophane has an oxygen permeability of 0.5 $cm^3.100\mu m/m^2.day.atm$ but this increases to a value of 787 at 100% relative humidity [8].

Data from Paints and Films

The oxygen and water vapour permeabilities of a number of resin and paint films are shown in Table 4 with data from [12]. These measurements were made on free films that had first been cast as a single coat onto glass and allowed to dry at room temperature for two weeks. Oxygen permeabilities were measured at 23°C and 85% RH with an oxygen pressure of 1 atmosphere. Water vapour permeability tests were carried out at 38°C and 95% RH.

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Table 4: Barrier Properties of Resin and Paint Films [12].

Polymer	Oxygen Permeability, $\dfrac{cm^3.100\mu m}{m^2.day.atm}$ at 23°C, 85% RH	Water Vapour Transmission, $\dfrac{g.10\mu m}{m^2.day}$ at 38°C, 95% RH
VC–VDC copolymer resin	22 ± 9	28 ± 10
Chloropolymer resin	82 ± 19	100 ± 20
Epoxy/polyamide resin	130 ± 33	155 ± 20
Chlorinated Rubber – plasticised Resin	183 ± 7	95 ± 5
Styrene acrylic latex	1464 ± 54	2300
VC–VDC copolymer paint	12 ± 5	68 ± 12
Chlorinated Rubber paint (unmodified)	30 ± 7	50 ± 8
Chloropolymer paint	33 ± 2	65 ± 12
Aluminium epoxy mastic	110 ± 37	105 ± 15
Coal tar epoxy paint	213 ± 28	75 ± 3
Acrylic water–borne paint	500	1800 ± 92
TiO$_2$ pigmented alkyd	595 ± 49	645 ± 15

From Table 4 it is clear that the choice of resin type is a key factor in determining the barrier properties of a paint system. Polymers with a high concentration of hydrophilic substituents are generally quite permeable to water, hence the high water vapour permeability of the acrylic–based films. Also alkyd systems, which have backbone ester groups, do not make good barrier paints. On the other hand, polymers with a skeletal chain of carbon atoms and non–polar substituents will be much less permeable. Thus, chlorinated polymers, such as chlorinated rubber, vinyl and vinylidene copolymers provide good barriers to both water vapour and oxygen. The epoxy–based systems have intermediate barrier properties, which can be improved with suitable choice of pigmentation.

The poor gas barrier properties of the hydrophilic systems may seem surprising in view of the general principles previously discussed. However, all measurements were carried out at 85% RH and the water sensitivity of these resins probably results in plasticisation and therefore increased oxygen permeability, as discussed for cellophane.

It is interesting to compare the permeabilities of the paint films with those of the polymers shown in Table 3. Note that the good barrier paints compare favourably with the good barrier polymers such as PET, PVC, PVF and epoxy (bisphenol A/ amine).

Oxygen and water vapour permeability measurements are a very useful guide to the barrier properties of paint films. However, it should be noted that measurements on free films might not always reflect the performance of films on coated substrates such as steel or wood [13], particularly if there is a reaction between the coating and the substrate. Also in some pigmented coatings there may be a discrepancy between the permeability of liquid water and water vapour [13]. This is because liquid water can accumulate at the pigment/ binder interface when adhesion is poor, or be transported by capillary flow through pores in the coating. Hence some paint films will be worse barriers to liquid water than to water vapour.

The Effect of Pigmentation

The incorporation of inorganic or metallic pigments into polymer films or paint coatings is a well-established method of reducing permeability [14]. There are three requirements for maximum effectiveness:

- The pigments should be impermeable.

- Plate-like pigments of high aspect ratio should be used and pigment particles should be aligned parallel to the paint/substrate interface.

- There must be good adhesion between the pigment and binder in both wet and dry conditions.

The level of pigment used is also very important because properties of a paint coating can vary dramatically depending on the pigment volume concentration (PVC).This was first shown by the work of Asbeck and Van Loo [15] who showed that above a critical pigment volume concentration (CPVC) a rapid deterioration in barrier properties and rust resistance will occur. They defined the term CPVC as that point in a pigment/binder system at which sufficient binder is just present to fill the voids between the pigment particles. Above the

CPVC there is insufficient binder to fill the space between the pigment particles and the coating will be porous and therefore much more permeable.

Although in principle it would appear that optimum barrier properties should be achieved at a PVC value at or just below the CPVC, in practice barrier coatings containing lamellar pigments are formulated at a range of PVC values considerably lower than the CPVC i.e. over the PVC/CPVC range of 0.2 to 0.7 [16]. One reason for this is that flexibility decreases as the PVC increases towards its critical value and, depending on the application, it may be necessary to formulate well below the CPVC to achieve a compromise between permeability and flexibility.

Examples of lamellar pigments used in paint systems are inorganic materials such as mica, micaceous iron oxide, glass flake, talc and graphite, and metallic flakes such as aluminium, stainless steel, nickel and cupro-nickel.

Aluminium flake is particularly successful as a barrier pigment in paint coatings. Primers pigmented with Al flake have been shown to give superior performance compared with conventionally pigmented systems in a range of different paints on both clean and rusted steel substrates [17].

It is interesting to assess the effect of pigmentation on barrier properties compared with the effect of changing the resin type. Such a comparison can be made from the data in Table 4. As discussed above, it is seen that large changes in permeability can be achieved by changing the resin type. For example, the water vapour permeability of the chlorinated rubber primer is only one tenth of that of the TiO_2 pigmented alkyd. Furthermore, the VC-VDC copolymer latex films were found to be nearly two orders of magnitude less permeable to water vapour than films of the styrene acrylic latex.

Such large reductions in permeability cannot be achieved from incorporation of barrier pigments alone. From Table 4 it is seen that the Al flake pigmented epoxy had moisture permeability about two-thirds of that of the unpigmented epoxy-polyamide system and their oxygen permeabilities are not significantly different. However, the more modest improvements that can be achieved by pigmentation do nevertheless have significant effects on performance: Al flake mastics give excellent performance as barrier systems particularly on difficult surfaces such as contaminated and corroded steel. The ability to be applied as a high-build coating, 150 µm per coat, doubtless makes an important contribution to the overall barrier effect [16], [17].

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Corrosion Protection of Steel

In principle, a paint coating should be effective in protecting steel from corrosion if it can exclude either water or oxygen or ions from the metal surface, or eliminate the conductive pathway between anodic and cathodic sites. Although this might seem quite straight-forward, in practice the mechanisms by which paint coatings protect against corrosion are very complex. They have been the subject of much study and controversy for many years [18].

Paint coatings can be divided into 3 types: barrier primers, inhibitive primers (that contain anti-corrosive pigments) and zinc rich primers (that operate by cathodic protection). Here we are interested in barrier primers, which protect by isolating the metal from its environ-ment. The original concept of a paint coating as an impermeable barrier to water and oxygen has been largely discredited by the work of Mayne [19]. He showed that the rate of transport of water vapour through paint films is at least an order of magnitude greater than that required to support corrosion even on unpainted steel. It was therefore concluded that the permeation of water vapour through paint films cannot be the rate determining process governing corrosion. This conclusion has been widely substantiated [18], [20]. Some results from Haagen and Funke [21] are shown in Table 5 and clearly indicate that more water can be supplied by permeation than is necessary for corrosion to occur.

Table 5: Water Vapour Permeability of Paint Films at 23–25°C [21]

Paint Film	Water Vapour Permeability for 100μm Coating, mg/cm^2/day
Alkyd Resin	2.3
Chlorinated Rubber	1.0
Polyurethane	1.4
Polyester Resin	1.3
Epoxy-coal tar	1.1
Phenolic Resin	1.1
Nitrocellulose	4.8
Water necessary for corrosion of unpainted steel	0.003–0.06 mg/cm^2/day

The permeation rate of oxygen through paint films was also examined by Mayne [19] and it was found to be much more comparable to the oxygen consumption rate during corrosion. Results varied from one tenth to a value greater than that consumed by unpainted steel specimens. However, because painted steel corrodes so much slower than unpainted steel, it was considered that oxygen permeation could not be a rate determining process for corrosion. Mayne concluded that barrier paints do not operate as impermeable membranes to water and oxygen but that they prevent corrosion by virtue of a high ionic resistance, which impedes the movement of ions and reduces the corrosion current to a low value.

Since this time, much work has been carried out to examine the ionic permeability of paint films and its relation to corrosion protection [18]. For example, Leidheiser, Mills and Bilder [22] have examined the permeability of polybutadiene coatings to water, oxygen and ions to establish which of these species is rate controlling for cathodic delamination. They compared the measured permeabilities with the rates calculated to sustain cathodic delamination. Their results are shown in Table 6. It can be seen that the water and oxygen permeation rates are far in excess of the calculated values required. However, the Na^+ ion transport differed only by a factor of 4 from the calculated rate and the charge transport rate is virtually identical to the calculated value. It was concluded that the cation transport through the coatings is the rate–determining step in the cathodic delamination of polybutadiene coatings from steel.

Table 6: Comparison of Measured Permeability and Calculated Rate to Sustain Cathodic Delamination [22]

Species	Measured Permeability mg/cm^2/day (25µm coating)	Calculated Rate to Sustain Cathodic Delamination mg/cm^2/day
Water	3	1.5×10^{-5}
Oxygen	2.5×10^{-3}	1.3×10^{-5}
Na^+ ion	1.4×10^{-3}	3.5×10^{-4}
Charge transport	1.3×10^{-6} coulombs/day	1.7×10^{-6} coulombs/day

Although the permeation rate of water through paint films is not rate limiting for the cathodic reaction, the role of water in the corrosion process should not be underestimated. Padget and Moreland [23] have pointed out that the conductivity and resistance of a coating

is highly dependent upon its water content because the latter strongly influences the solubilisation of ions and the ionic diffusion characteristics of the film. Furthermore, Leidheiser and Granata [24] have shown that ionic diffusion through a coating is preceded by water uptake and that cation transport occurs largely by means of aqueous pathways. In addition, the permeation of water through a coating can give rise to loss of adhesion and blistering. According to Funke [25], good wet adhesion between the coating and substrate is the single most important property governing good performance.

The question of whether oxygen permeation through paint films could be rate controlling for corrosion has been an issue of some debate. Guruviah [20] measured the permeation of oxygen and water through iron oxide pigmented paint films and coated these paints on to steel panels that were subsequently allowed to corrode. The weight loss calculated from the oxygen permeability data and the observed corrosion rate from the accelerated tests were in good agreement, indicating that the low corrosion rate could be due to the slow diffusion of oxygen through the paint films. This conclusion was supported by Haagen and Funke [21], who measured the oxygen permeability of several paint coatings. Their results were either below or within the calculated range of oxygen consumption rates necessary to maintain corrosion, as shown in Table 7. Furthermore, they found their paint films to be effectively impermeable to chloride, sulphate and hydroxyl ions and concluded that corrosion behaviour was controlled by the permeability of oxygen and water: the former through its polarization of the cathodic reaction and the latter due to its effect on loss of adhesion.

Table 7: Oxygen Permeability of Paint Films at 20℃ [21]

Paint Film	Oxygen Permeability for 100μm Coating, mg/cm^2/day
Alkyd Resin	0.0103
Chlorinated Rubber	0.0022
Epoxy Polyamide	0.0073
Vinyl Chloride/Vinyl Acetate Copolymer	0.0075
Nitrocellulose	0.106
Oxygen necessary for corrosion of unpainted steel	0.008 – 0.150 mg/cm^2/day

It is probable that different mechanisms will become rate controlling under different circumstances. This is illustrated by the work of Morcillo et al. [26], who studied the corrosion of steel beneath a thin varnish film when variable amounts of $FeSO_4$ and NaCl were present at the steel/varnish interface. It was found that corrosion depended on the surface concentration of contaminant. Corrosion significantly increased with increasing surface contamination, indicating that ionic conduction was the rate-controlling factor. However, above a critical level of contamination, ionic conduction was no longer rate controlling. Under these conditions, the corrosion rate was determined by the diffusion of oxygen through the varnish.

These studies are relevant to many practical situations where steel is exposed to industrial or marine environments before painting and may become contaminated with sulphate and/or chloride. Such contaminants are difficult to remove by grit blasting. Contamination by aggressive ions is the major problem in painting wire-brushed rusty steel: salts become concentrated in 'nests' at the steel/rust interface. In such situations ionic diffusion through the paint coating is no longer rate controlling for corrosion: the most effective paint coatings have been shown to be those with a low permeability to both water vapour and oxygen [27].

Coatings for Concrete

Concrete is normally regarded as maintenance-free, but there are several reasons why concrete structures may need to be coated: namely, for decoration, waterproofing, chemical resistance or weatherproofing. Corrosion of reinforcing bars in concrete has been a matter for concern for many years, and the application of coatings to concrete is one way of retarding the degradation of reinforced structures.

It may be questioned why rebar corrosion should occur at all, because a coating of good quality concrete should provide excellent protection against corrosion. Interstitial fluids in Portland cement usually have a pH in excess of 13 and at this pH steel should remain passive over a wide range of potentials.

There are two main factors responsible for rebar corrosion [28]. The first is the presence of chloride ion, which can cause depassivation of steel even in alkaline environments. Calcium chloride is the most effective, cheapest and most widely used accelerator of the hydration of Portland cement and was used extensively from 1960 until 1977 as an admixture in reinforced concrete. Even if not deliberately added, chloride ion can find its way into reinforced concrete from other sources: from marine environments, from the use of

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chloride-contaminated aggregate and chloride contamination from de-icing salts. The second factor is the carbonation of the alkaline components of cement by atmospheric carbon dioxide. Carbonation can cause a drop in pH to values below pH 9 and thereby remove the protection inherent in the concrete coating. Carbonation should not occur if the concrete is properly compacted and the amount of cover exceeds the minimum recommended for the design life of the structure: unfortunately, good practice has not always been observed.

One solution to this problem is to coat reinforced concrete in order to reduce the rate of carbonation. A successful coating will be alkali resistant, adherent and flexible. Obviously, it should have a low permeability to carbon dioxide. It should also prevent the ingress of liquid water but nevertheless be permeable to water vapour, thus allowing the concrete to 'breathe' so that moisture retained in the concrete can gradually diffuse out. These barrier properties are mutually incompatible, and coating design poses a problem for the paint technologist. In practice it is often necessary to achieve a compromise between the desired CO_2 and water vapour permeabilities [29] [30].

Recent Innovations in Barrier Property Enhancement

In recent years there has been an increasing trend to replace metal and glass containers with plastic-based packaging materials. This has stimulated the plastics packaging industry to consider new ways of improving barrier properties. The major innovations are in the following areas [31]: vacuum deposited coatings, new barrier polymers, blends of barrier polymers and nanocomposites. Doubtless these technologies will also be of value for corrosion protection and abrasion resistant coatings.

Vacuum Deposited Coatings

Physical vapour deposition or plasma-enhanced chemical vapour deposition can be used to produce thin, glassy barrier films of SiO_x on PET, polypropylene and nylon [32]. These films are transparent and have barrier properties equivalent to metallized films, although flexibility is a problem.

New Barrier Polymers

New barrier polymers include liquid crystalline polymers and thermoplastic epoxy resins [31]. Both these resin types can be co-extruded with common packaging polymers and are claimed to give reductions in oxygen permeability of around 50 times.

Blends

Blending of polymers can be successful in reducing permeability depending on the morphology of the resulting blend. The barrier polymer needs to be present in lamellar form to optimise the barrier effect. For example, ethylene vinyl alcohol (EVOH) has been blended with polypropylene [33].

Nanocomposites

Polymer nanocomposites are novel materials that contain relatively small amounts (typically less than 5 wt%) of nanometer-sized filler particles. The fillers may be natural or synthetic clays, fibres, tubes or sol-gel particles: all with at least one dimension in the nanometer range. These materials are of great scientific interest and are expected to find significant use in many technological applications.

Barrier packaging is an important application for polymer nanocomposites [1]. Nanofillers, when properly dispersed, will create a more tortuous diffusion path through a polymer film and hence reduce gas and vapour permeability. Such films are also transparent because the filler particle size is less than the wavelength of light.

There are four methods for the production of nanocomposites [34]: in-situ polymerisation, melt compounding, sol/gel technology and preparation from solution. Whichever method is employed, it is important that the nanofiller particles are well dispersed in the polymer to optimise the resulting properties.

Nanocomposites are still largely under development. However, there is intense interest in these materials from the polymer industry based on the perception that they will bring about a step change in performance.

Nanocomposites also offer great potential for coatings for corrosion protection and abrasion resistance. For example, montmorillonite nanoclay fillers have been successfully dispersed in epoxy resin and gave a significant improvement in oxygen barrier properties [35]. Also monodisperse silica particles in radiation-cured acrylic resins have shown a great enhancement of scratch and abrasion resistance [36]. Nanofillers also have the ability to control ion-transport through organic coatings [37] and hence the possibility of reducing corrosion currents.

Conclusions

The barrier properties of a paint coating are important in controlling its performance and hence suitability for use in a given environment. Through choice of both resin system, and type and loading of pigmentation, it is possible to design a system with the required gas and water barrier. For many applications, it is necessary to achieve a compromise between properties: for example, between permeability and flexibility. Furthermore, some coating systems are requited to prevent the ingress of gases and liquid water, but nevertheless be permeable to water vapour to allow the system to 'breathe'. Such demands clearly underline the need for good understanding of the basic principles governing permeation through paint coatings.

There has been some controversy over the role of paint barrier properties in controlling the corrosion rate on steel substrates. It is well established that the permeation of water through paint films is not rate limiting for the cathodic reaction. Barrier paints are thought to prevent corrosion because of a high ionic resistance, which impedes the movement of ions and reduces the corrosion current to a low value. However, water permeation through a coating is clearly deleterious, causing both blistering and loss of adhesion. Oxygen permeation is more likely to be rate determining for corrosion, especially on previously corroded or contaminated surfaces. Further reductions in both the oxygen and water barrier of paint films should result in improved performance and eventually produce coatings that are truly rate limiting for the cathodic reaction.

In recent years there has been considerable interest in nanocomposites from the packaging industry because nanofillers, when properly dispersed, will create a more tortuous diffusion path through a polymer film and hence reduce gas and vapour permeability. Nano-composites offer great potential for coatings for corrosion protection: they have been shown to give significant improvement in oxygen barrier properties and also have the ability to control ion-transport.

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