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Polymer 42 (2001) 4141–4152

polymer

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Infrared-ATR studies of the hydration and dehydration of formulated PVC films

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Received 24 July 2000; accepted 11 September 2000

Abstract

We have used FTIR-ATR spectroscopy to measure the water uptake, the rates of diffusion, swelling and dehydration of formulated PVC films containing different levels (10–30%) of dioctylphthalate (DOP) plasticiser and 5% of a fungicide, *N*-(fluorodichloromethylthio)-phthalimide, fluorfolpet. The diffusion rates and swelling levels are well correlated, implying that the mobility of water (measured using either simple Fickian or dual-mode models) is strongly dependent on the 'free volume' created by changing chain microstructure and flexibility as the polymer swells and becomes more rubbery. Both diffusion rates and degrees of film swelling show a maximum at 20–25% DOP concentration. However, T_g falls monotonically as the polymer is plasticised. Thus the water dynamics (and the previously discovered leaching of fluorfolpet) depends not only on the chain mobility but also on the degree to which 'free volume' is created in the presence of increasing amounts of DOP. Mutual solubility of the formulation components is likely to play a role, and the presence of phase separation at ~20% DOP cannot be ruled out. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyvinyl chloride; Fungicide; Water; Diffusion

1. Introduction

Although the diffusion of organic solvents and vapours [1–14] and food-based fluids [15–24] into rigid and plasticised PVC has been widely studied, relatively little attention [22,24–33] has been paid to the sorption and desorption of water into PVC films. Nevertheless, many important uses of PVC for example, in shower curtains, domestic tiles, water distribution systems, storage vessels, food wrapping, children's toys and separation membranes, all involve intimate contact with either water vapour or the liquid (or both). In almost all applications PVC materials are plasticised (usually using a phthalate ester) and in many instances they contain a fungicide to help prevent the growth of bacteria when exposed to ambient environments. It is thus important to quantify the formulated PVC/water interface in terms of the hydration/diffusion, leaching [34] and dehydration processes, and to attempt to correlate hydration behaviour with formulation details.

The ATR-FTIR method [35–39] presents an ideal choice of technique for the study of hydration and dehydration processes in thin polymer films. The advantages of this technique include high surface sensitivity, the direct monitoring of molecular-level interactions and perturbations and the ability to examine different molecular components simultaneously in a complex (i.e. formulated) mixture. The technique also allows a molecular-based assessment of polymeric swelling to be made in real time during the hydration process.

In this paper we report measured hydration diffusion coefficients and rates of dehydration for different levels of plasticiser (DOP) at a fixed level (5%) of the fungicide, fluorfolpet (see below). Although this is a complex 'matrix' we show that the measured transport data show useful correlations with formulation levels, which in turn aid the understanding of formulated polymer behaviour in aqueous environments.

2. Materials and sample preparation

The PVC polymeric system studied contained DOP at concentrations ranging from 10 to 30% w/w, and fluorfolpet. The polymer, plasticiser (dioctylphthalate) and solvent (dimethylformamide) were obtained from Aldrich as follows

- Polyvinylchloride, secondary standard, typical M_w 85 000, typical M_n 40 000;

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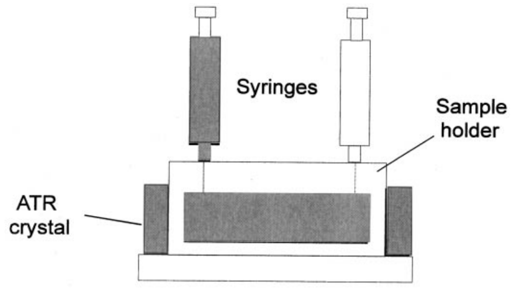
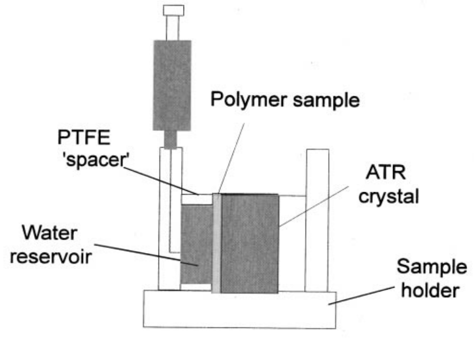
PII: S0032-3861(00)00688-1



Liquid cell - front view.



Liquid cell - side view.

Fig. 1. The FTIR-ATR cell used in this work.

- *N*-*N*-dimethylformamide, HPLC grade, 99.9%;
- Dioctylphthalate, DOP 99%.

The pure biocide, fluorfolpet, was supplied by Zeneca Specialties (now Avecia). Polyvinyl chloride films or formulated mixtures, with an average thickness of 15 μm, were cast at 40°C from a DMF solution onto a ZnSe FTIR-ATR crystal followed by solvent evaporation in an oven at 60°C for approximately 15–20 h. Optical microscopic analysis of the films showed no obvious microvoids or defects. It was concluded that good fusion of the plasticiser (and the biocide) with the polymer had taken place.

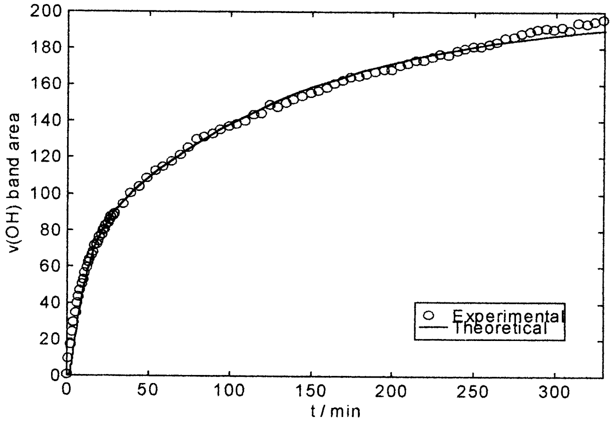


Fig. 3. A plot of the diffusion curve of water diffusing into a 20% DOP/5% fluorfolpet/PVC film (with typical dual-mode 'fit').

3. Experimental technique

All experiments were carried out in a liquid-holding ATR cell (Graseby-Specac Plc) at ambient temperature, 25 ± 2°C (see Fig. 1). The data were taken as a function of time, using a FIRST or WINFIRST macro program. The data collection protocol was as follows:

1. First, a spectrum of dry film was taken. This served as background for the subsequent data analysis. The liquid was then introduced into the cell.
2. Acquisition of a spectrum every minute for 30 min.
3. Acquisition of a spectrum every 5 min for 5 h.

All spectra (25 scans) were collected using a Mattson Polaris FTIR instrument operating at 4 cm^{-1} resolution with an MCT detector.

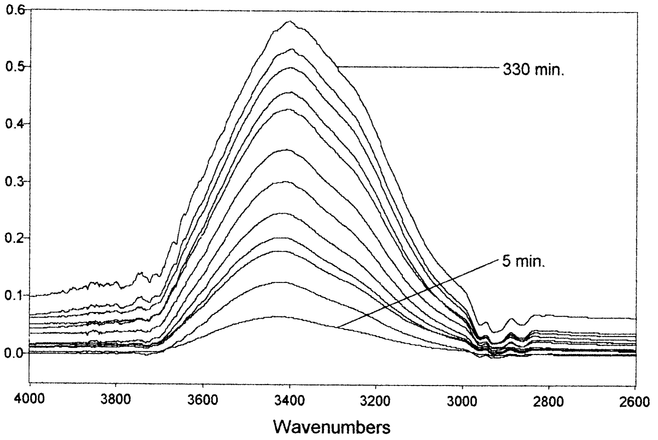


Fig. 2. Infrared spectra for water diffusing into a 20% DOP/5% fluorfolpet/PVC film (overlaid).

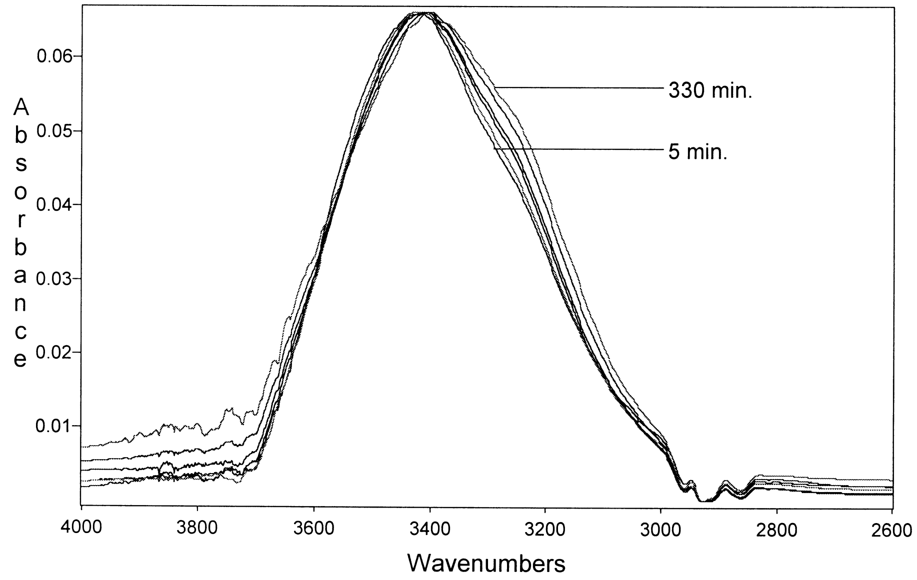


Fig. 4. Infrared spectra for water diffusing into a 20% DOP/5% fluorfolpet/PVC film (superimposed).

The diffusion data were obtained by integrating the increasing ν(OH) band of water between 2950 and 3700 cm^{-1} (Fig. 2). A plot of these integrated intensities versus time yielded the diffusion curve (Fig. 3). The normalised data of Fig. 4 shows that there is perturbation of the water 'clusters' within the polymer as shown previously by Sammon et al. [35].

By comparing the spectra of water as it diffuses into the polymer it is obvious that: (a) the shape of the water spectrum in the 3000–3600 cm^{-1} region varies as a function of time, the shoulder at 3200 cm^{-1} growing more quickly than the main band at 3400 cm^{-1}; and (b) there is a small shift of the band position, with time, towards the lower wavenumbers, indicating a strengthening of the water hydrogen bond network.

Two methods were explored here to describe the diffusion of water into the formulated PVC film; the dual-mode sorption model [40–42] and simple sorption kinetics, coupled to Fick's second law.

Okuno and co-workers [1,2] and Li and co-workers [29–31] previously found that the absorption of water (liquid or vapour) into PVC was well described by the dual-mode sorption model. A dual-mode sorption model was therefore used to determine the diffusion coefficients D_1 and D_2 of water diffusing into the PVC samples. A full description of the mathematical model of dual-mode sorption is given by Crank [40,41] and Vieth et al. [42], and the application of FTIR-ATR spectroscopy to the dual-mode sorption mode is described in detail by Fieldson and Barbari [36]. We have previously applied it to the study of diffusion in

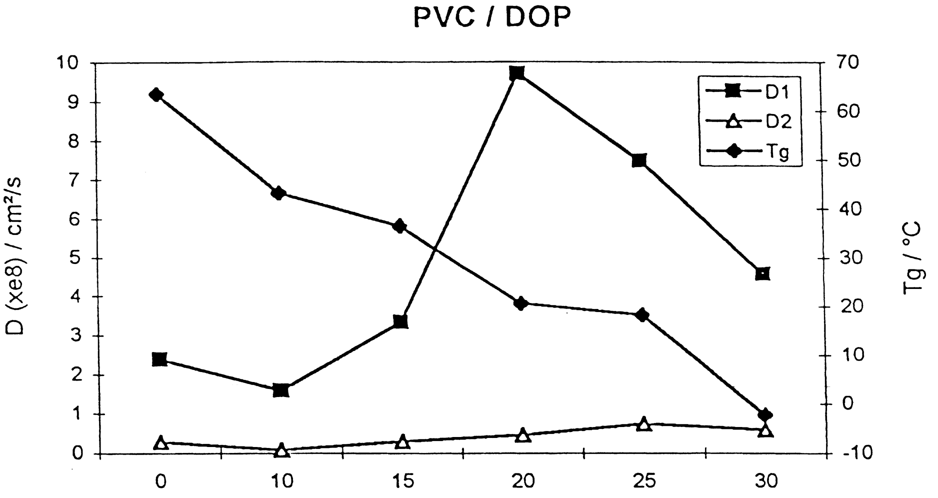


Fig. 5. A plot of diffusion rates and T_g versus DOP concentration for DOP/PVC films.

Table 1
Diffusion coefficients for water into DOP/PVC films

% DOP	T_g (°C)	D_1 (cm^2/s)	D_2(cm^2/s)
0	63.6	2.2×10^{-8}	2.6×10^{-9}
0	63.6	2.84×10^{-8}	2.51×10^{-9}
0	63.6	2.09×10^{-8}	3.30×10^{-9}
10	43.2	1.59×10^{-8}	9.03×10^{-10}
15	36.5	4.16×10^{-8}	3.63×10^{-9}
15	36.5	2.54×10^{-8}	2.36×10^{-9}
20	20.4	9.7×10^{-8}	4.6×10^{-9}
25	18.2	8.62×10^{-8}	8.09×10^{-9}
25	18.2	6.35×10^{-8}	6.48×10^{-9}
30	−2.3	4.59×10^{-8}	3.25×10^{-9}
30	−2.3	9.12×10^{-8}	8.59×10^{-9}

polyelectrolyte films [43]. Only a summary is necessary here. The dual-mode equations are;

$$\frac{A_1 - x_1A_0}{x_1(A_\infty - A_0)} = 1 - \frac{8\gamma}{\pi[1-\exp(-2L\gamma)]}\sum_{n=0}^{\infty}\left[\frac{\exp\left(\frac{-D_1(2n+1)^2\pi^2 t}{4L^2}\right)\left[\frac{(2n+1)\pi}{2L}\exp(-\gamma 2L) + (-1)^n(2\gamma)\right]}{(2n+1)\left(4\gamma^2 + \left(\frac{(2n+1)\pi}{2L}\right)^2\right)}\right] \tag{1}$$

for the first sorption mode and (partially mobile species)

$$\frac{A_2 - x_2A_0}{x_2(A_\infty - A_0)} = 1 - \frac{8\gamma}{\pi[1-\exp(-2L\gamma)]}\sum_{n=0}^{\infty}\left[\frac{\exp\left(\frac{-D_2(2n+1)^2\pi^2 t}{4L^2}\right)\left[\frac{(2n+1)\pi}{2L}\exp(-\gamma 2L) + (-1)^n(2\gamma)\right]}{(2n+1)\left(4\gamma^2 + \left(\frac{(2n+1)\pi}{2L}\right)^2\right)}\right] \tag{2}$$

for the second sorption mode (totally mobile species).

D_1 and D_2 are the two (Fickian) diffusion coefficients and the values of x_1 and x_2 are related, respectively, to the proportion of the partially and totally mobile molecules ($x_1 + x_2 = 1$). A is used to denote infrared absorbance at time t (zero, t or equilibrium, ∞), L is the film thickness and γ is the ATR field decay constant [37–39]. A procedure which uses the Levenberg–Marquardt algorithm for least squares fitting was written by Periera [34]. A typical result of fitting to our experimental data is given in Fig. 3 (solid line) and the diffusion parameters obtained, for the films studied here, are given in Tables 1 and 2 along with the glass transition temperatures (measured using DSC). These data agree broadly with those in the literature (Table 3). However, it is clear [43] that D_1 and D_2 are simply parameters which give a reasonable fit to the experimental data. Their relationship with the two diffusion processes (on which the model is based [40–42]) is necessarily tenuous. For this reason we also explored the quality of fitting to the Fickian diffusion equations (Eqs. (3) and (4); with a single transport coefficient D) as modified to apply to the ATR experiment by Fieldson and Barbari [36].

Table 2
Diffusion coefficients for water into DOP/5% fluorfolpet/PVC films

% DOP	T_g (°C)	D_1 (cm^2/s)	D_2 (cm^2/s)
10	32.8	5.05×10^{-8}	2.95×10^{-9}
10	32.8	3.91×10^{-8}	3.87×10^{-9}
10	32.8	5.54×10^{-8}	3.69×10^{-9}
15	22.5	3.92×10^{-8}	3.25×10^{-9}
15	22.5	4.88×10^{-8}	3.82×10^{-9}
20	12.3	1.19×10^{-7}	8.7×10^{-9}
20	12.3	1.93×10^{-7}	1.42×10^{-8}
20	12.3	1.30×10^{-7}	9.3×10^{-9}
20	12.3	1.87×10^{-7}	1.55×10^{-8}
25	1.8	5.10×10^{-8}	4.42×10^{-9}
25	1.8	6.37×10^{-8}	6.00×10^{-9}
30	−8.5	1.11×10^{-7}	8.9×10^{-9}
30	−8.5	9.24×10^{-8}	8.45×10^{-9}
30	−8.5	2.32×10^{-8}	2.05×10^{-8}

At short times:

$$\frac{A_t}{A_\infty} = \frac{2}{L}\left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \tag{3}$$

At long times:

$$\ln\left(1 - \frac{A_t}{A_\infty}\right) = \ln\left(\frac{4}{\pi}\right) - \frac{D\pi^2 t}{4L^2} \tag{4}$$

where A_t and A_∞ are the absorbances at time t and at saturation and L is the film thickness. It is assumed [36] that the ATR depth of penetration d_p is small compared with the film thickness (i.e. $\exp(-2L/d_p \ll 1)$.

4. Results and discussion

4.1. Transport coefficients

Tables 1 and 2 show that the rate of diffusion of water into pPVC films is dependent upon the amount of plasticiser in

Table 3
Previously published diffusion data by other workers (D_D, D_H, D_i and D_2 refer to D due to concentration gradients in Henry mode and Langmuir mode, D initial and in the second stage, respectively. DOA = dioctyl adipate, PNS = polyneopentyl glycol succinate, PAS = dibutyl ester of polyethylene glycol adipate sebacenate)

Solvent	Plasticiser	Plasticiser content (% wt)	Diffusion coefficients (cm^2/s)	T (°C)	Authors
Water vapour	0		$D_D = 2.75 \times 10^{-8}$ $D_H = 6.51 \times 10^{-9}$	40	Okuno et al., 1995 [1,2]
Ethanol vapour	0		$D_D = 1.37 \times 10^{-9}$ $D_H = 4.99 \times 10^{-10}$	40	Okuno et al., 1995 [1,2]
Desorption of liquid water	DOA	66	$D_1 = (1–3) \times 10^{-6}$ $D_2 = 10^{-9}–10^{-8}$	22	Chan et al., 1992 [31]
Liquid water	DOA	66	$D_1 = 3 \pm 0.3 \times 10^{-6}$ $D_2 = (1–6) \times 10^{-9}$	–	Li et al., 1996 [29]
Water vapour	PNS	16	4.02×10^{-8}	25	Chalykh and Belokurova, 1982 [48]
		29	2.80×10^{-8}		
		38	2.26×10^{-8}		
		44	2.56×10^{-8}		
Water vapour	PDEA	23	11.3×10^{-8}	25	Chalykh and Belokurova, 1982 [48]
		29	13.5×10^{-8}		
		38	12.6×10^{-8}		
Water vapour	PPA	29	20.7×10^{-8}	25	Chalykh and Belokurova, 1982 [48]
		38	32.2×10^{-8}		
		44	24.6×10^{-8}		
Water vapour	PAS	29	3.31×10^{-8}	25	Chalykh and Belokurova, 1982 [48]
		33	6.61×10^{-8}		
		38	6.90×10^{-8}		

the film, as found by Taverdet and co-workers [13] for the diffusion of alkanes into pPVC. Indeed, the rates of diffusion (D_1 and D_2) reach a maximum at 20% DOP content for both DOP/PVC and DOP/fluorfolpet/PVC films as shown in Figs. 5 and 6. The single mode Fickian diffusion coefficients D_1 (see below, Fig. 7) are very similar to those quoted in Tables 1 and 2 and do not give a statistically better representation of the data (for further discussion see Section 4).

Of course, the addition of placticiser to the PVC membranes lowers the T_g of the membrane; the chain mobility is enhanced, and this leads to an increase in the so called 'free volume'. One measure of this parameter may be obtained using positron annihilation spectroscopy (PAS, [44,46]). Borek and Osoba [45] showed, for example, that the amount of free volume increases linearly as the concentration of dioctylphthalate increases. Hence, permeation rates should increase with increasing level of plasticiser (0–20% in wt), as observed by Shailaja and Yaseen [33]

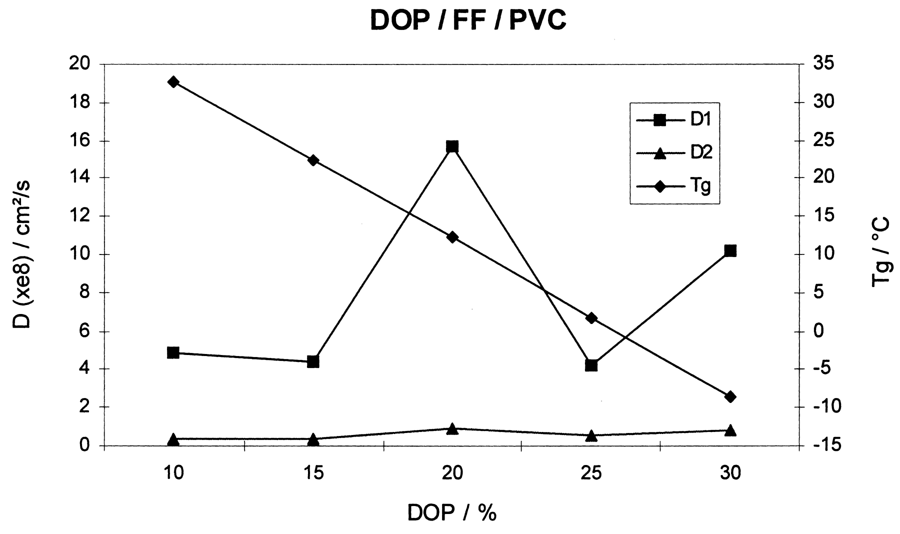


Fig. 6. A plot of diffusion rates and T_g against DOP concentration for DOP/fluorfolpet/PVC films.

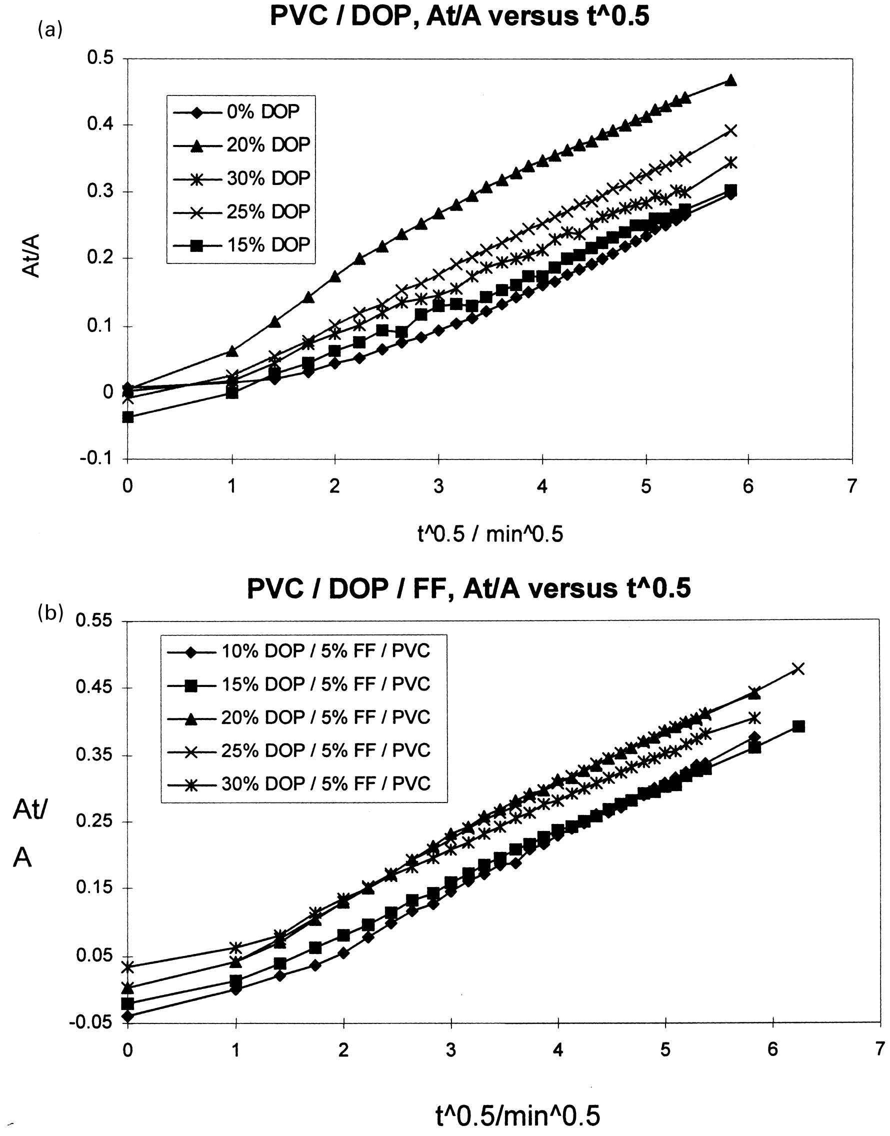


Fig. 7. Plots of: (A) (A_t/A_∞) versus $t^{1/2}$ for a PVC/DOP film; and (B) (A_t/A_∞) versus $t^{1/2}$ for a PVC/DOP/fluorfolpet film.

for the permeation of water vapour through PVC membranes. However, others have shown that for higher alkyl group phthalates in PVC [47] the ‘free volume’ increases up to medium concentrations and then decreases again (as found here). Similarly, for pPVC films plactisiced with PDEA and PPA, Chalykh and Belokurova [48] observed an increase in diffusion rates of water up to 30–38% plasticiser levels followed by a decrease in diffusion rate. Indeed, they observed a transition from a one-phase to a two-phase system near 30% (for PDEA, PAS, PPA and PNS) and 20% (for DOP) plasticiser concentration, using electron microscopy. The two-phase system would consist of: (i) plasticiser dissolved in PVC; and (ii) pure plasticiser. This transition was attributed to reaching the solubility limit of the plasticiser in the polymer. We believe that it may be this process of separation which leads to the non-monotonic behaviour in our system, although we have found no evidence [34] of loss of DOP or of segregation on a micron scale.

The reason for the maximum in D_1 and D_2 at ~20% plasticiser level is not entirely clear. It is tempting to invoke the ‘antiplasticisation’ phenomenon [45,49–51] but, as far as we are aware, this has only been observed at low plasticiser levels. It is more likely here that the observed maximum is associated with chain mobility changes as T_g changes. It is clear from Figs. 5 and 6 that the maximum in diffusion coefficient (especially D_1) occurs in the plasticiser regime where the polymer matrix is converted from a glassy material (below T_g) to a rubbery material above T_g (for measurements near 20°C). It thus seems possible to maximise water mobility in formulated polymer films using T_g information. However, the reasons why D drops again as the T_g drops further is still an open question and serves to emphasise the complexity of the system under

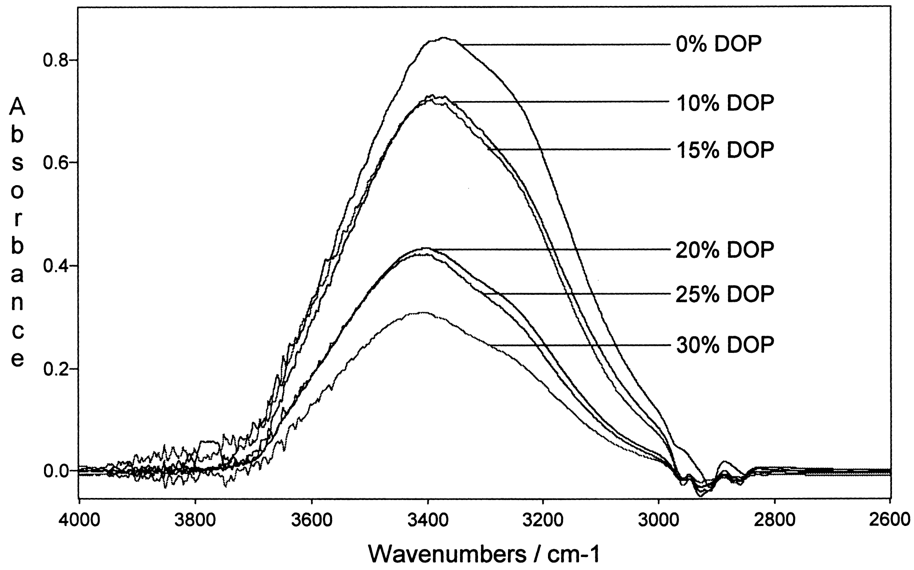


Fig. 8. The ν(O–H) stretching band of water (at equilibrium) between 3000 and 3700 cm^{-1} at various DOP concentrations for PVC/DOP films.

study. On changing from a glassy polymer to a rubbery polymer the diffusion process should become more (Fickian). This is shown clearly by Fig. 7 for which the data have been analysed at short times using Eq. (3). For pure PVC (Fig. 7A) the data have a 'concave' shape reminiscent of a Case II diffusion process [38,40,41]. Much more linear, Fickian plots are obtained at higher DOP concentrations (Fig. 7A and B). It is interesting to note that diffusion coefficients are also affected by the fungicide (fluorfolpet) incorporation. This appears to result from a more rapid drop in T_g as the plasticiser level is increased for formulated films.

4.2. Equilibrium water content of PVC films

PVC discs (2 cm diameter) with varying amounts of DOP were immersed in distilled water, and weighed at regular intervals to record the gain in weight due to water sorption. These gravimetric data show that the amount of water penetrating the films (between 1 and 0.3% by weight) decreases with increase of plasticiser content. This is confirmed by the infrared spectra of the films taken at equilibrium and shown in Fig. 8. The ν(O–H) stretching band intensity shows a gradual and systematic decrease with increasing DOP concentration. This could be due to either:

1. polymer–water interactions or water–DOP interactions, creating site exclusion, and thereby preventing sorption of water, or
2. decrease in solubility of water in the polymer as the

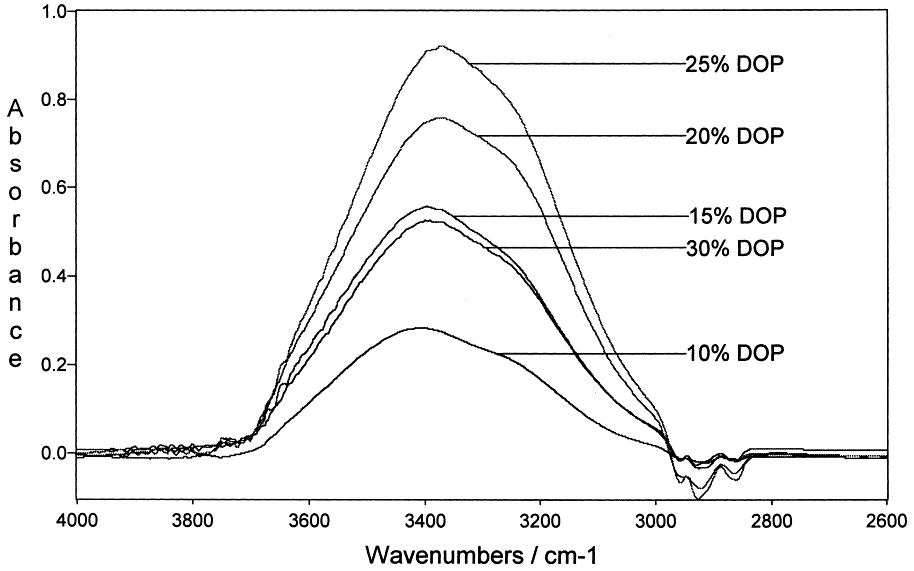


Fig. 9. The infrared spectra of the ν(O–H) stretching region of water at equilibrium for PVC/DOP/fluorfolpet films.

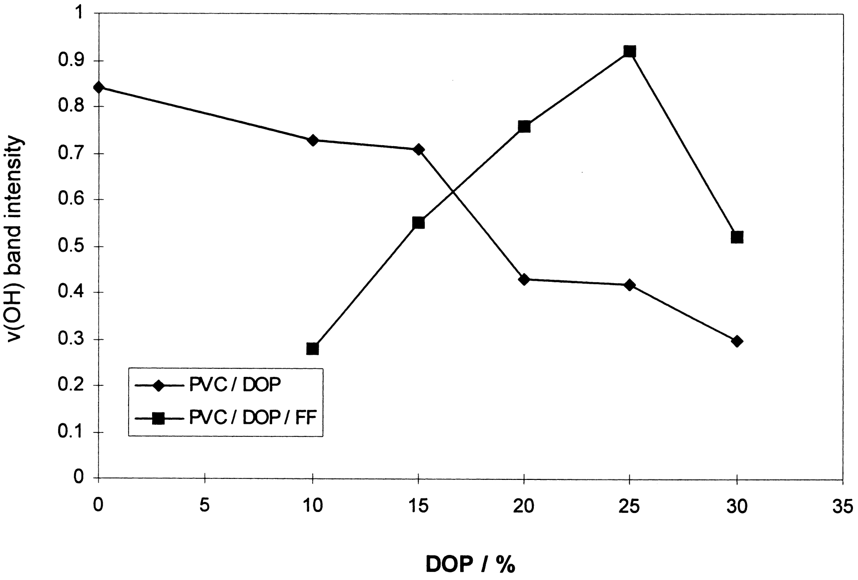


Fig. 10. A plot of equilibrium band intensity against DOP concentration for PVC/DOP films and PVC/DOP/fluorfolpet films.

relatively hydrophobic(?) plasticiser concentration increases.

Similar, although slightly higher, values were obtained by Chan and co-workers [31] who estimated the apparent equilibrium water content at 0.6% for 66% DOA (dioctyladipate) plasticised PVC membranes. These values are also comparable with those obtained by Berens [4] for similar molecules in rigid PVC (see Table 3).

For the films containing fluorfolpet, the amount of water in the polymer matrix increases with plasticiser content and reaches a maximum at 25% DOP concentrations (see Figs. 9 and 10). In this case, profiles of equilibrium water content and diffusion coefficient are clearly very similar. In both cases the entry of water into a polymer film is likely to act as a plasticiser (itself) causing cavity size to be increased and disrupting hydrogen bonding [52,53]. However, the difference in sorption between the two types of film indicates the significant effect of adding fluorfolpet on the properties of the film, by possibly;

- creating additional chain mobility
- adding new interactions between plasticiser–biocide, biocide–polymer and biocide–water molecules, thereby reducing the number of interactions between the plasticiser or polymer molecules and water. This could change the hydrophilic/hydrophobic balance at the molecular surface and affect the water take up and diffusion rate.

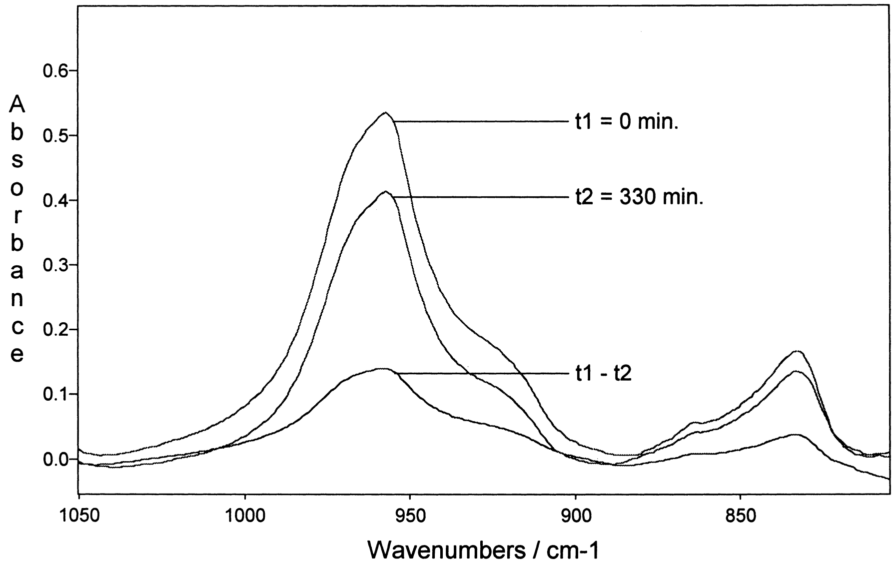


Fig. 11. The r(CH_2) rocking band at $t = 0$ and 330 min, and the difference spectrum for a DOP/PVC film.

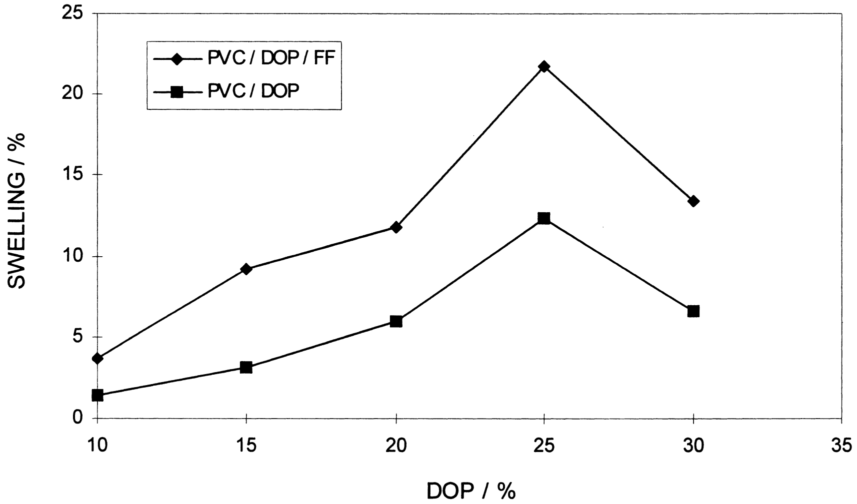


Fig. 12. Plot of swelling against DOP concentration for PVC/DOP and PVC/DOP/fluorfolpet films.

The decrease of equilibrium water content and diffusion coefficient above 20–25% DOP concentration could be explained by an overall decrease of 'free volume' due to sites being occupied by the additional DOP molecules.

4.3. Swelling of the matrix

FTIR-ATR spectroscopy can be used to determine swelling in a polymer matrix, by following the intensity loss of ν(C–H) bands as water diffuses into the film. This method was used by Balik and Xu [54] to simultaneously study the diffusion of water, swelling and calcium carbonate removal in a latex paint. We applied a similar method to measure swelling of the PVC matrix during water sorption. The CH_2 rocking band at 950 cm^{-1} was used. Fig. 11 shows the r(CH_2) band at $t = 0$ and $t = 330$ min, and the difference spectrum for a DOP/PVC film, thereby establishing that swelling has occurred.

The percentage swelling of the matrix is obtained by comparing the area of the band in the dry film and at equilibrium water content. Fig. 12 shows a plot of swelling against DOP concentration for PVC/DOP and PVC/DOP/fluorfolpet films. Swelling is more important in the films containing fluorfolpet, but the behaviour pattern is similar in both cases, increasing with plasticiser content to reach a maximum at 25% DOP concentration. Swelling clearly induces an increase of effective 'free volume' [55] presumably separating the polymer chains and creating larger micro-voids. Comparison of the diffusion coefficients and swelling (Figs. 6 and 12) show that their evolution with DOP is very similar, confirming the dependence of diffusion rate upon swelling.

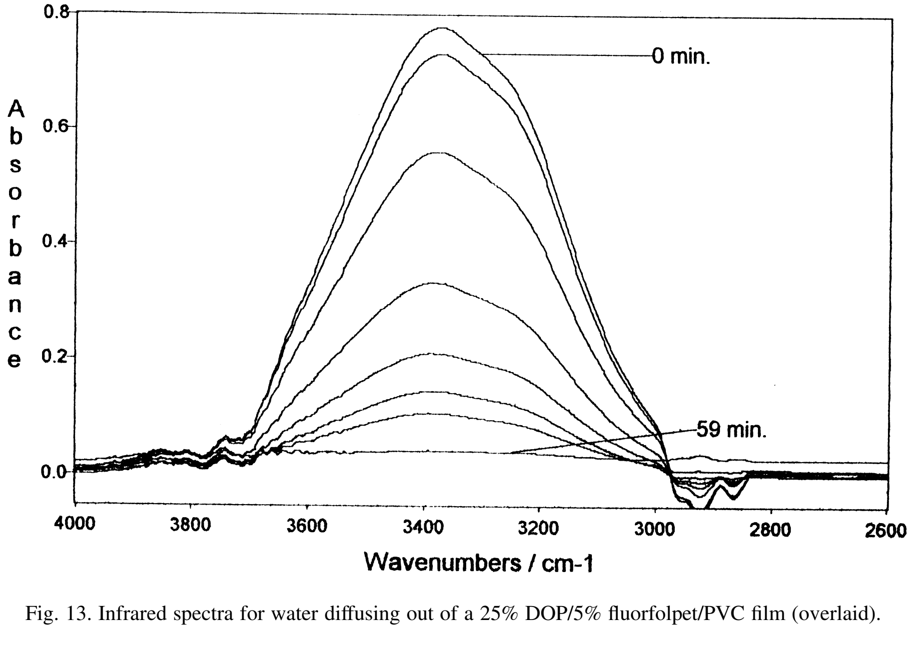


Fig. 13. Infrared spectra for water diffusing out of a 25% DOP/5% fluorfolpet/PVC film (overlaid).

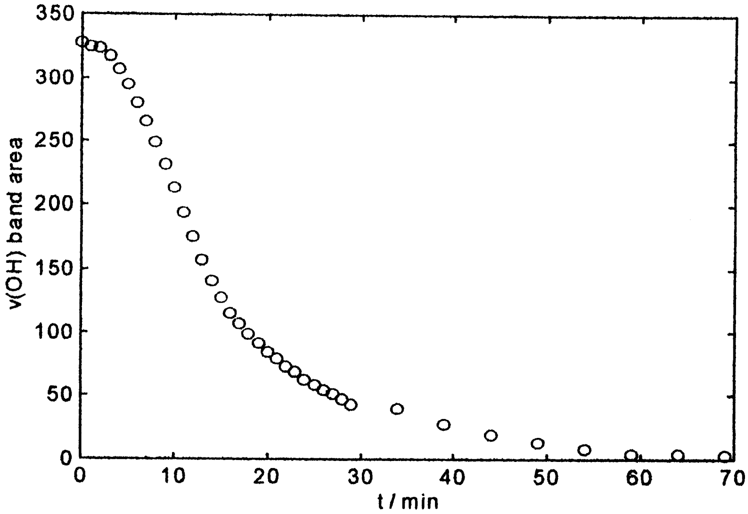


Fig. 14. A typical dehydration curve obtained from data in Fig. 13.

4.4. *Dehydration of plasticised PVC film*

By blowing dry nitrogen gas through the ATR liquid cell, at a pressure of 0.5 bar, we were able to remove the water from the polymer film, and follow the desorption process. The desorption of water from the polymer film was monitored using the ν(O–H) stretching band of water between 2950 and 3700 cm^{-1}. As the water was removed from the film, the ν(O–H) stretching band decreased as can be seen in Fig. 13, and the desorption curve was obtained by plotting the integrated area under the ν(O–H) stretching band against time (see Fig. 14). These data were obtained by ratioing the spectra of the wet polymer against those of the dry polymer.

In order to determine the type of diffusion involved, and the dynamics of the desorption, the data were plotted as (A_t/A_∞) versus $t^{1/2}$ and Eq. (3) was used to determine the diffusion coefficient. The diffusion coefficients thereby obtained are presented in Fig. 15. A similar equation was used by Chan et al. [31] to determine the rate of desorption of water from PVC-based ion-selection electrode membranes. The desorption of water from PVC films is a very rapid process compared with that of sorption, even though the nitrogen flow was very low. The desorption process also appears to be non-Fickian. At 20% DOP content the desorption is much quicker than at any other plasticiser concentration, as demonstrated by Fig. 15. The desorption rates therefore follow the same trends as the sorption rates, i.e. diffusion rates are higher in the films containing fluorfolpet and reach a maximum at 20% DOP concentration.

5. Summary and conclusions

This study has led to the following conclusions.

- The diffusion of water into PVC is a bimodal process,

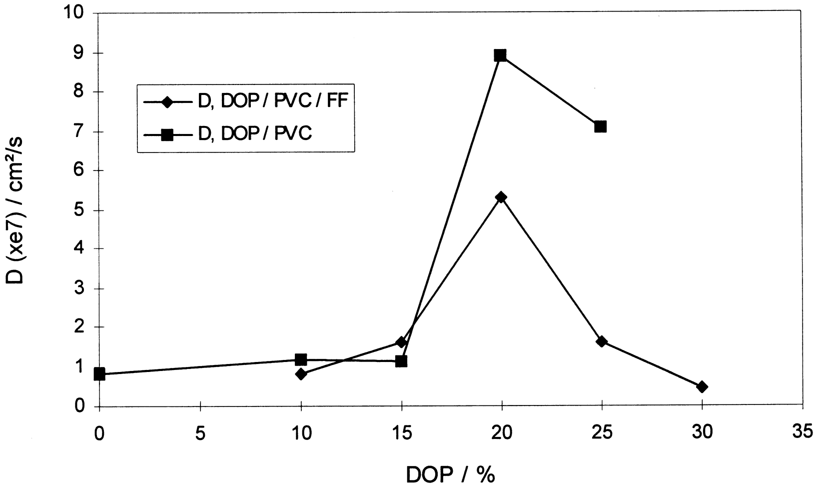


Fig. 15. Plot of the diffusion rates against DOP concentration for the removal of water from PVC films.

there being two different solute mobilities, one 100 times faster than the other (Tables 1 and 2). Both 'modes' appear to be pseudo-Fickian in the films studied. The dual-mode model therefore fits the data reasonably well, and we may deduce that some water molecules are much more mobile than others.
- The diffusion rates and swelling are both higher in the films containing fluorfolpet
- The glass transition temperatures are lower for films containing fluorfolpet.
- Sorption of water from the two types of film is very different. PVC/DOP films show a net decrease of water content at equilibrium as the concentration of DOP increases, whereas for PVC/DOP/fluorfolpet films, the water content depends on the same evolution with plasticiser concentration as degrees of swelling or diffusion coefficient.
- The diffusion rates and swelling profiles are similar for both formulations. In particular, they have a non-monotonic evolution with plasticiser concentration, and a maximum at 20–25% DOP concentration showing that diffusion rates are well correlated with the swelling.

The formulated polymer is obviously a complex system and it is clear that diffusion rates in these films may be affected be some or all of the following factors:

- the chain mobility;
- the effective 'free volume' or void density in the polymer;
- the number of sites available for 'binding' of water molecules and their relative hydrophibicity;
- the solubility of water and DOP in the polymer matrix.

Above T_g the molecular structure of the polymer is relatively mobile. As the concentration of DOP is increased, the T_g value is lowered, and chain mobility increases. Furthermore, frequent local conformational transitions can create transient 'pockets' or 'voids' which are then available for the penetrant to move through the polymer matrix. But, changes in T_g alone cannot account for the behaviour of the diffusion coefficient at DOP concentrations of 25 and 30%. We should expect a monotonic increase with DOP content increase. When fluorfolpet is introduced in the formulation, the T_g is lowered further, suggesting that the fluorfolpet molecules further increase the chain mobility. Certainly, the 'void density' increases considerably since water swells the PVC matrix.

It has been shown here that the swelling increased with DOP content (for both PVC/DOP and PVC/DOP/fluorfolpet films) to reach a maximum at 20–25% DOP content. As the plasticiser concentration became higher than 25%, the swelling diffusion rates and water sorption levels diminished. As swelling increases the water content at equilibrium is expected to do so too. Although this was found to be the case for films containing fluorfolpet, it was not the case for PVC/DOP films. The water content at equilibrium decreases substantially as the DOP concentration (and the swelling) increases. This may reflect the dependence of water sorption capacity on the number and type of adsorption site as well as on the chain microstructure and mobility. It strongly suggests the importance of interactions between water and the PVC (and the fluorfolpet molecules), presumably through the chlorine groups. The desorption process shows similar characteristics to the water uptake; especially in the sense that the diffusion coefficients behave in the same way with respect to the DOP concentration and the type of film.

The rates of dehydration diffusion are faster due to the fact that the removal is 'forced' by a nitrogen gas flow. Although the rate of diffusion is different, removal of water from PVC film appears to follow the same, pseudo-Fickian dual mode, so it is reasonable to suggest that the sorption and desorption dynamics are controlled by the similar factors.

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