

Raman microscopic studies of the distribution of the fungicide fluorfolpet in plasticised PVC films

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Abstract

We have used Raman microscopy (in confocal mode to carry out depth profiling) to study the distribution and redistribution (by leaching) of the fungicide, Fluorfolpet, FF (5%) in PVC polymer films plasticised using various levels of dioctylphthalate [DOP]. Molecular distribution maps both in *X*-, *Y*- and *Z*-directions have been used to demonstrate that, although DOP is not lost on leaching, there was a quantifiable loss of the FF, selectively from the film surface. The loss varied between a few and 25% and reached a maximum at ~25% DOP content of the film. This maximum at 20–25% DOP also occurred for the difference in bulk and surface concentrations of DOP. This is considered to be related to a combination of molecular mobilities in the film, driven by the plasticisation (T_g) effects of DOP, and the mutual solubilities of the additives in water and PVC. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyvinyl chloride; Dioctylphthalate fungicides; Raman mapping

1. Introduction

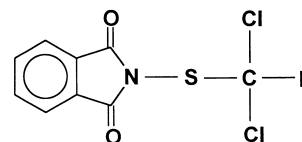
Plasticised polyvinyl chloride (pPVC) is used [1] in a wide range of applications including shower curtains, cable insulation, wall coverings and medical devices. The combination of the basic polymer $(\text{CH}_2\text{CHCl})_n$ with a wide range of additives including plasticisers, fillers, lubricants, stabilisers, and pigments yields an infinite number of PVC-based plastics with physical, chemical and electrical properties that can be tailored to almost any requirement by simply varying the choice of additives [2,3]. Nevertheless, pPVC films can be attacked by microorganisms, especially fungi [4–6]. Of the main PVC formulation components, those vulnerable to microbiological attack include most plasticisers, some stabilisers, lubricants and organic fillers such as wood flour [7]. To prevent biodeterioration special biocidal additives are used in PVC formulations [8,9].

The distribution and stability of these biocide molecules in the processed vinyl product determines, to a large extent, the useful lifetime of the functional article. It is therefore important to have a technique capable of monitoring the biocide incorporation into the polymer and any changes in the molecular distribution of the additives (biocide and others) as a consequence of leaching induced by the sorption

of water (or other solvents) into the polymer matrix. Raman micro-spectroscopy can be used to obtain structural information, conformation and crystallinity [10], to identify small inclusions in bulk materials [11–13] and to study the effect of stress and strain on materials [14–16]. Several relevant Raman microscopic techniques can be used; Raman imaging and mapping [17–21] and depth profiling [22–27] may all be used to measure the distribution (and redistribution) of small molecules in polymer matrices.

In this paper we present the results obtained from an investigation of the distribution of fluorfolpet (FF) (see below) and dioctylphthalate (DOP) molecules in PVC thin films cast with different degrees of plasticisation. We also report on the effect of water exposure on the redistribution of these additives. In both cases the data have been related to the expected and measured behaviour of the polymer matrix as a function of the additive content.

Fluorfolpet (*N*-dichlorofluoromethylthiophthalimide):



The film surface and bulk were probed using Raman mapping, and Raman depth profiling, respectively.

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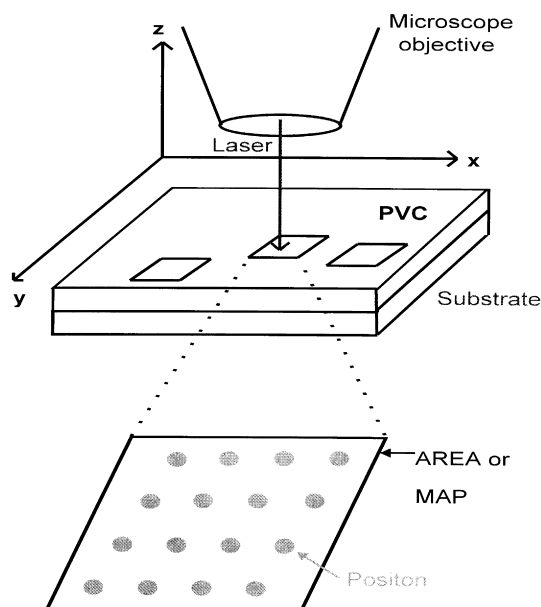


Fig. 1. Schematic diagram of arrangements made to perform Raman mapping.

2. Materials and sample preparation

The system studied was composed of DOP at concentrations ranging from 10 to 30% (w/w), and fluorfolpet (5%, w/w) in PVC. The polymer (polyvinyl chloride), plasticiser (dioctylphthalate) and solvent (dimethylformamide (DMF)) were obtained from Aldrich.

- Polyvinylchloride, secondary standard, typical M_w 85 000, typical M_n 40 000.
- *N-N*-dimethylformamide, HPLC grade, 99.9%.
- Dioctylphthalate, 99%.

The pure biocide, fluorfolpet, was supplied by Avecia Limited.

Polyvinyl chloride films with an average thickness of 15 μm , were cast from a DMF solution onto a ZnSe FTIR-ATR crystal (as the samples were also analysed using FTIR-ATR spectroscopy). The solutions were cast at 40°C, and the solvent was evaporated in the oven at 60°C for approximately 15–20 h. The solutions used for casting were prepared by first dissolving the PVC powder and the other additives in DMF, at room temperature. The solutions were then heated (with stirring) to 40°C for better dissolution of the materials. Optical microscopic analysis of films showed neither microvoids nor defects. It was concluded that good fusion of the plasticiser (and the biocide) with the polymer had taken place.

3. Instrument and techniques

The Raman spectrometer used was a Renishaw RamanScope 2000 system, equipped with a 633 nm laser. In this spectrometer the stigmatic single spectrograph was attached to an Olympus BH2 microscope which was equipped with a computer controlled stepping microscope stage. The system utilises the so-called, back scattering configuration in which the scattered light is collected using the same objective as is used to focus the laser onto the sample. The most important features of this system are: (i) the adjustable slit, together with the Peltier-cooled CCD detector, which are used to secure the confocal set-up; (ii) the plasma line rejection filters; (iii) the diffraction grating; and (iv) the notch filters (which prevent Rayleigh scattered laser light from entering the spectrograph). The instrument was used in the normal mode with a 50 \times objective for Raman mapping, and in confocal mode for depth profiling. The instrument was set-up in “confocal” mode using a 100 \times objective, a slit

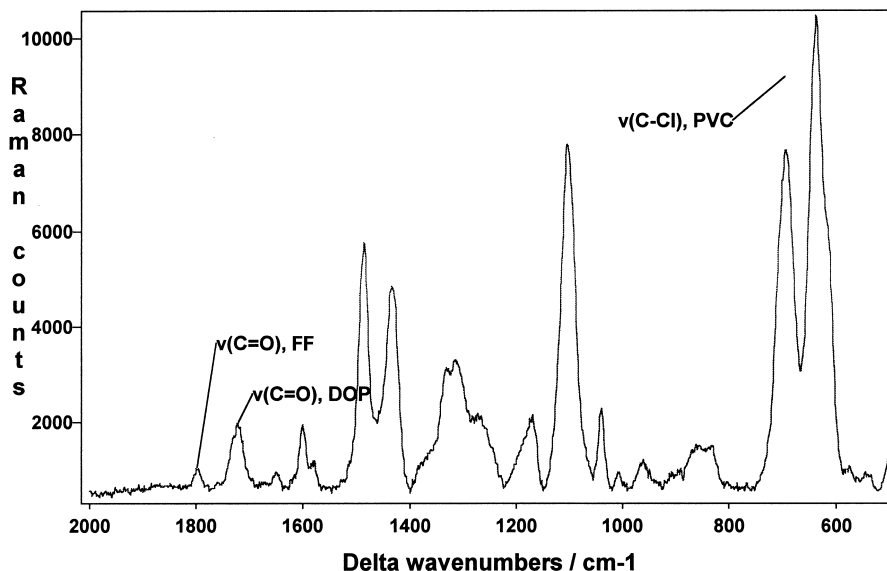


Fig. 2. A typical Raman spectrum of a filled PVD film (5% FF/20% DOP/PVC).

$$\text{PVC / DOP} = \frac{A_{(\text{PVC})}}{A_{(\text{DOP})}} \qquad \text{PVC / FF} = \frac{A_{(\text{PVC})}}{A_{(\text{FF})}}$$

Where $A_{(\text{PVC})}$ = the area under the $\nu(\text{C-Cl})$ stretching vibration of PVC between $590 - 750 \text{ cm}^{-1}$,

$A_{(\text{DOP})}$ = the area under the $\nu(\text{C=O})$ stretching vibration of DOP at 1726 cm^{-1} ,

$A_{(\text{FF})}$ = the area under the $\nu(\text{C=O})$ stretching vibration of FF at 1786 cm^{-1} .

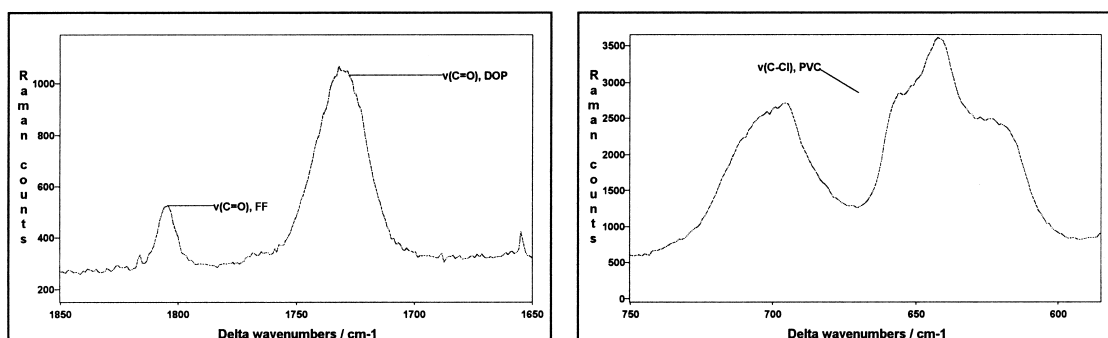


Fig. 3. Calculation of PVC/DOP and PVC/FF ratios.

width of about $10 \mu\text{m}$ and a CCD area of 5×576 pixels. A spatial resolution of about $2 \mu\text{m}^3$ was achievable with this arrangement, as described before [17–29]. Similar arrangements have been developed by other workers [30,31].

3.1. Raman mapping

The microscope was used to focus on a particular area of the sample, and within this particular area, we were able to examine the Raman spectra of the film. By detecting the Raman spectra at several positions at regular intervals across the film, we could assess the distribution of components in the xy direction. Fig. 1 shows how Raman microscopy was used to determine the distribution of small molecules in a polymer matrix.

The construction of a map involved four main steps:

1. Acquisition of a number of spectra, usually 49 per map, from a small area of the sample surface. The dimension of an area analysed was $3000 \times 3000 \mu\text{m}^2$. The interval between positions at which the spectra were taken was $500 \mu\text{m}$. An exposure time of $2 \times 20 \text{ s}$ over the range of $500\text{--}2000 \text{ cm}^{-1}$ was used. The Raman micro-spectrometer was run in the normal mode utilising the $50 \times$ objective, therefore yielding a laser spot of $5 \mu\text{m}^2$, and a penetration depth of $4\text{--}5 \mu\text{m}$. Three different areas (chosen at random) were mapped per sample.

2. Identification of component bands (see Fig. 2). The three bands marked on the spectrum, correspond to the $\nu(\text{C-Cl})$ stretching band of PVC between $590\text{--}750 \text{ cm}^{-1}$, the $\nu(\text{C=O})$ stretching band of DOP at 1726 cm^{-1} , and the $\nu(\text{C=O})$ stretching band of fluorfolpet at 1786 cm^{-1} .
3. Calculation of PVC/DOP and PVC/FF ratios (see Fig. 3). The calculation of these ratios offers the advantage of minimising errors due to the fluctuation of laser power over the duration of the experiment (mainly as a result of errors in focusing the laser, with a resulting rapid decrease in intensity with distance from the objective focal plane).
4. Construction of the map by plotting the value of PVC/DOP or PVC/FF ratio against position, thereby obtaining a molecular distribution map of the surface of the film for a particular component of the film. Typical examples are shown in Fig. 4.

3.2. Raman depth profiling

In the same way that Raman mapping was performed in the xy plane, it was possible, using confocal Raman microscopy, to obtain spectra of sections of a film at various depth (along the z -axis). The depth profiling experiment was started by taking a spectrum of the surface of the film, and then collecting spectra at steps of $2 \mu\text{m}$, moving down into

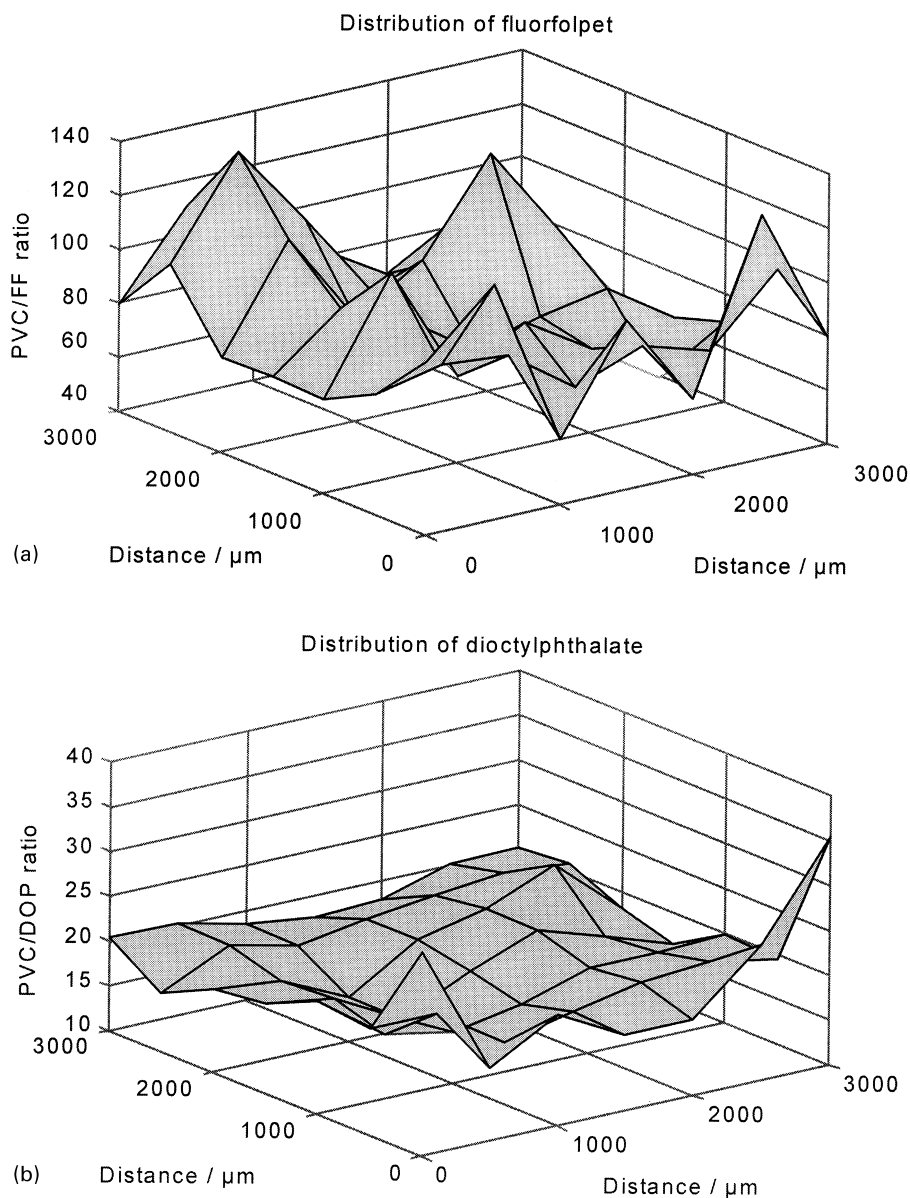


Fig. 4. (a) A typical map obtained for the distribution of fluorfolpet in a 20% DOP/FF/PVC film. (b) A typical map obtained for the distribution of DOP in a 20% DOP/5% FF/PVC film.

the bulk of the film, until the surface of the crystal was reached.

The data was analysed in the same way as the Raman mapping data, and yielded a depth profile consisting of a plot of the band area ratio (of PVC to the additive) as a function of depth. The results are shown in Figs. 5–8 where in each case, the zero on the distance scale corresponds to the polymer–substrate interface.

3.3. Quantitative analysis of the maps

A semi-quantitative analysis was achieved by calculating the mean and standard deviation of the PVC/DOP and PVC/FF ratios, thereby obtaining the overall level of component in the mapped area, and a measure of the heterogeneity of

the distribution on a micron scale. A comparison between these values for the distribution maps and the redistribution maps (after leaching) yielded a measure of loss of fluorfolpet from the film.

The comparison of average levels of component from all three maps for a given sample, allowed us to characterise the distribution of FF and DOP on a millimeter scale.

3.4. Calculation of errors

Error on the value of the PVC/FF and PVC/DOP ratios were obtained using the following approach: errors arise from the measurement of the band areas of the fluorfolpet, DOP and PVC bands. These errors were estimated by measuring the area of the same band repeatedly and the

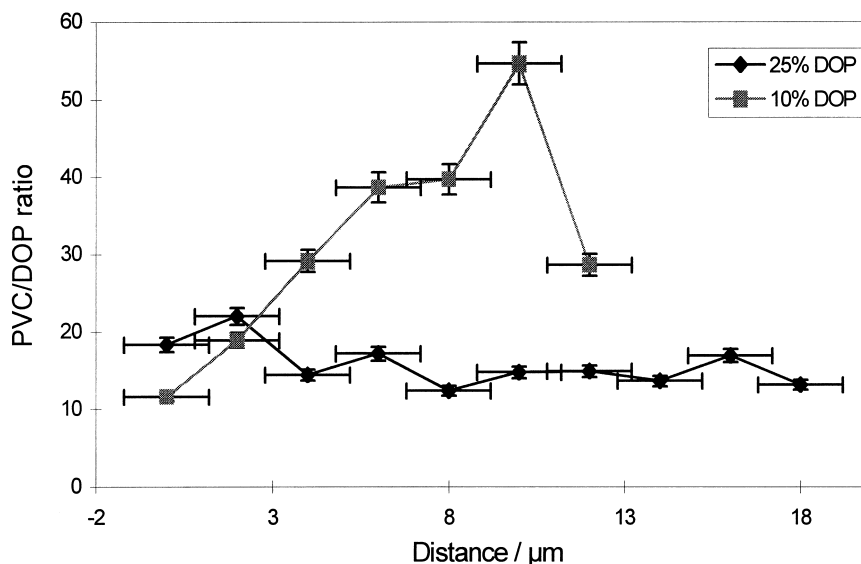


Fig. 5. Depth profile plots for the distribution of DOP in films containing 10 and 25% DOP (the first point in each graph; LHS, is at the polymer–substrate interface. The air–polymer interface is RHS).

difference in the measurement of this area constituted the error obtained in the measurements of the band area. The estimated errors on the measurement of the band area (expressed as %) were 12, 6 and 2% for FF, DOP and PVC band areas, respectively. The errors on the ratios PVC/FF and PVC/DOP therefore become 14 and 7%, respectively.

4. Results and discussions

4.1. Distribution and redistribution of DOP

4.1.1. Mapping of DOP

For each different DOP concentration, several (usually two or three) samples were analysed. The mapping results for the distribution and redistribution (due to leaching of fluorfolpet) of dioctylphthalate are presented in Table 1 and a typical set of maps is shown in Fig. 4.

The variation of concentration of DOP within a particular map (as shown by the values of the standard deviation from the mean PVC/DOP ratio value within each map) demonstrated the heterogeneity of the distribution of DOP on a micron scale. Concentration differences between two positions of up to 35% have been observed for films containing 10% dioctylphthalate. Generally, the variation from one position to another (at 500 μm intervals) is much smaller; of the order of 15–25%. This was true both for the distribution and the redistribution processes.

On the contrary, comparison of the overall mean concentration of DOP of each of the three mapped areas, reveals only minor differences, of the order of 4%, suggesting a homogeneous distribution of DOP and no evidence for significant fluctuation of DOP levels across the film. This

applied to data for both the distribution and the redistribution processes.

Comparison of the overall levels of DOP after leaching of FF (in the redistribution) with those before, shows that there are only small differences, which are all within the experimental error. This strongly suggests that little or no DOP was lost during the period in which the films were in contact with water. Generally plasticisers and other additives are well known to migrate from the films into the media with which the films are in contact [32–36]. Murase et al. [37] and Fayad et al. [38] found that plasticisers (such as dioctylphthalate) leached into water when the plastic film was exposed to high temperature ($\approx 120^\circ\text{C}$), or left outdoor for long periods (25 days), or exposed to sunlight (UV) and water. This also showed that degradation of PVC films was accompanied by the leaching of the plasticiser.

However, other experiments by Messadi and Vergnaud [33] showed that there was no transfer of DOP into liquid mixtures of ethanol and water having less than 8% ethanol, i.e. no migration of DOP into pure water at 30°C . As DOP is insoluble in water, but quite soluble in ethanol, the experiments by Messadi and Vergnaud suggested that the driving force for the migration was strongly related to solubility; as the amount of ethanol in the mixture decreased, so did the leaching of DOP into the solution.

4.1.2. Depth profiling of DOP

The depth profiling results for the distribution and redistribution (due to leaching of fluorfolpet) of dioctylphthalate are presented in Table 2.

The standard deviation of the mean concentration of DOP within a single depth profile demonstrates, on the micron scale, the heterogeneous characteristics of the distribution of DOP in the bulk. The approximate standard deviation of a given set of data (Table 2) varied between 2 and 45%

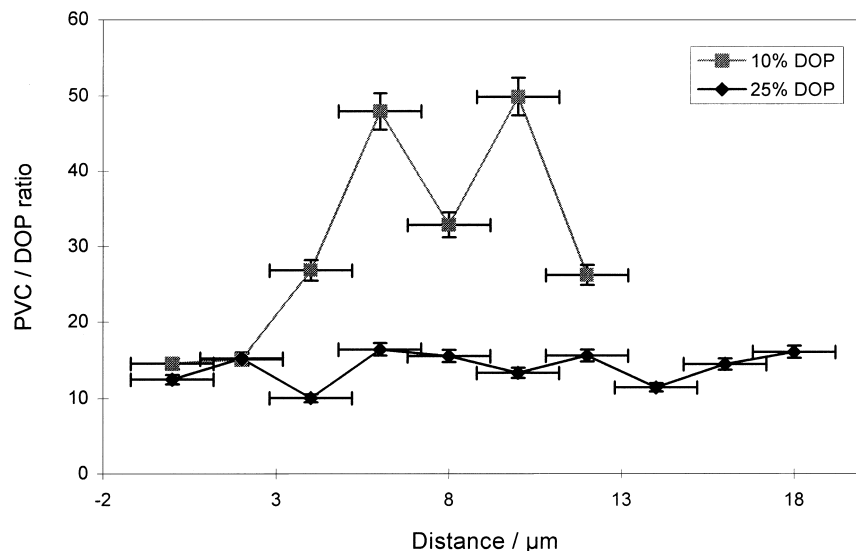


Fig. 6. Depth profile plots for the redistribution of DOP in films containing 10 and 25% DOP.

(at intervals of 2 μm), but variations of more than 25% were unusual. This is true for both the initial distribution and the redistribution processes.

The comparison of the overall concentration of DOP for each depth profile (represented by the mean value of PVC/DOP ratios per depth profile) shows that the level of DOP in the bulk is relatively invariant over the entire film both before and after leaching.

By comparing the mean values of PVC/DOP ratios obtained from Raman mapping with the values obtained from depth profiling (Tables 1 and 2), it can be seen that the level of plasticiser in the bulk was marginally smaller than that on the surface of the films, except for the samples containing only 10% plasticiser where the level of plasticiser is higher in the bulk than on the surface. Indeed, this is also apparent from the depth profile plots in Fig. 5.

The difference of DOP concentration between the bulk and the surface decreased as the plasticiser concentration increased to 25%. At 30% DOP in the film, it increased again. Fig. 9 shows a plot of the difference in DOP concentration (expressed as percentage) between the bulk and the surface of the film, as a function of total DOP concentration in the film. This shows there was an increase in the homogeneity of the film (between bulk and surface) as the plasticiser content increases to 25%, at which concentration the solubility limit of DOP in PVC is reached [39].

After leaching (in the redistribution of DOP), results confirm the mapping result; i.e. that there was no leaching of DOP. Furthermore, there was very little difference in DOP concentration (about 5–7% which is of the order of the estimated experimental error) between the bulk and the surface in the majority of the films (see Fig. 6). Films

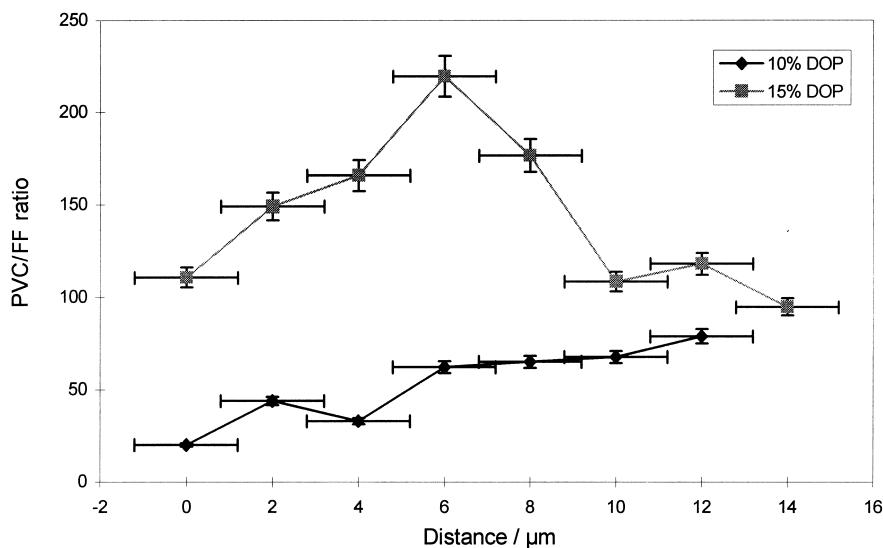


Fig. 7. Depth profile plots for the distribution of FF in films containing 10 and 15% DOP.

Table 1
Mapping results for the distribution and redistribution (due to leaching of fluorfolpet) of DOP in PVC films

DOP (%)	Distribution of DOP		Redistribution of DOP	
	PVC/DOP ratio	Mean value for PVC/DOP ratio	PVC/DOP ratio	Mean value for PVC/DOP ratio
10	44 ± 16	44	53 ± 21	50
	43 ± 13		48 ± 20	
	46 ± 10		48 ± 20	
10	50 ± 12	51	45 ± 9	47
	47 ± 12		49 ± 12	
	55 ± 20		48 ± 16	
15	17 ± 3	18	18 ± 2	19
	18 ± 3		18 ± 2	
	19 ± 3		20 ± 3	
15	20 ± 2	19	20 ± 3	20
	19 ± 3		20 ± 3	
	20 ± 2			
20	20 ± 4	19	21 ± 3	20
	19 ± 2		20 ± 3	
	20 ± 4		20 ± 5	
25	13 ± 2	13	13 ± 2	13
	13 ± 2		13 ± 2	
	12 ± 1		13 ± 2	
25	13 ± 1	13	14 ± 3	13
	13 ± 2		13 ± 2	
	13 ± 2		13 ± 2	
25	14 ± 2	14	15 ± 2	15
	14 ± 2		15 ± 2	
	14 ± 2		15 ± 2	
30	12 ± 1	12	11 ± 1	10
	12 ± 1		10 ± 2	
	11 ± 1			
30	11 ± 2	11	12 ± 1	12
	11 ± 2		12 ± 1	
	11 ± 1		12 ± 2	

Table 2
Depth profiling results for the distribution and redistribution (due to leaching of fluorfolpet) of DOP in PVC films

DOP (%)	Distribution of DOP		Redistribution of DOP	
	PVC/DOP ratio from	Mean value of PVC/DOP ratio	PVC/DOP ratio from	Mean value of PVC/DOP ratio
10	26 ± 8	32	38 ± 3	35
	32 ± 13		33 ± 13	
	39 ± 8			
10	33 ± 5	34	34 ± 8	36
	35 ± 6		38 ± 7	
15	22 ± 2	22	16 ± 3	16
15	22 ± 4	22	20 ± 5	20
20	23 ± 8	21	25 ± 1	21
	19 ± 12		18 ± 3	
25	14 ± 1	14	13 ± 2	13
	14 ± 1		13 ± 2	
25	15 ± 3	14	15 ± 1	14
	14 ± 2		14 ± 2	
25	13 ± 1	14	14 ± 2	13
	16 ± 2		11 ± 2	
30	13 ± 2	14	10 ± 2	10.5
	15 ± 3		11 ± 2	
30	14 ± 1	14	13 ± 2	12.5
	15 ± 2		12 ± 2	

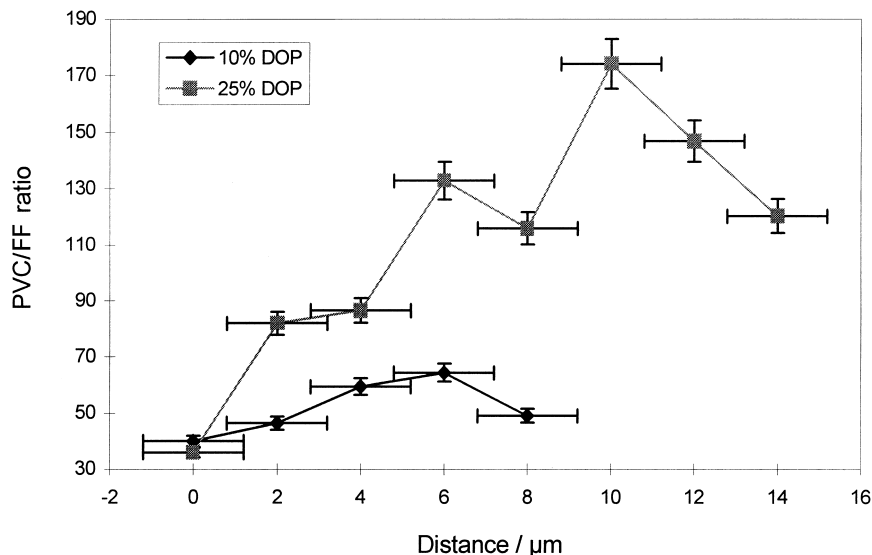


Fig. 8. Depth profile plots for the redistribution of FF containing 10 and 25% DOP.

containing 10% DOP still showed a large difference between the bulk and the surface concentration, of the order of 25%; the amount of plasticiser was higher in the bulk than on the surface (see Fig. 6).

For films containing more than 10% (w/w) DOP, we can see that a redistribution of the molecules took place during ingress and removal of water; we observed a more homogeneous distribution of DOP between the surface and the bulk of the film. As water diffuses into the films and creates additional free volume and chain mobility, by swelling and plasticisation of the polymer matrix, small molecules were able to move more freely inside the matrix. Also, leaching of fluorfolpet from the films provides extra voids (or void space) for the plasticiser.

All the experiments were carried out at ambient temperature (20–26°C). The glass transition temperatures of these films

(at 10% DOP) was 32.6°C, and therefore the polymer films were in their “glassy” state. For the films containing 15% (or more) DOP however, the glass transition temperature was below 22°C (Table 4) and at room temperature films were in the “rubbery” state. Flexibility and chain mobility is greater in the rubbery state compared to the glassy state. For films containing more than 10% DOP, i.e. in their rubbery state, redistribution of the DOP molecules occurred, in such a way that segregation noticed in the distribution of DOP between the bulk and the surface before leaching disappeared. However, in films containing 10% DOP, i.e. in films in their glassy state, the segregation of DOP distribution between the bulk and the surface persisted. Therefore it is plausible to suggest that the heterogeneity of the distribution of DOP between the bulk and the surface is a consequence of the lack of mobility of the molecules in the polymeric matrix.

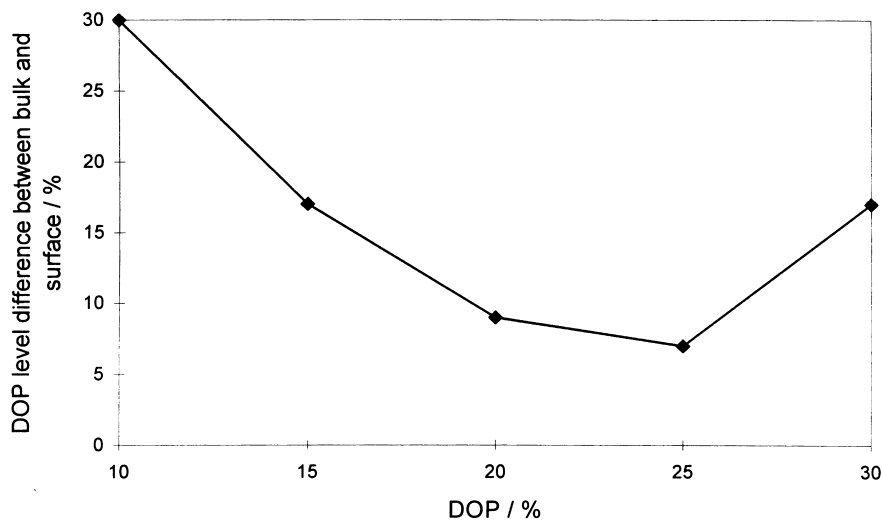


Fig. 9. Difference of DOP concentration between bulk and the surface as a function of DOP content.

Table 3
Mapping results for the distribution and redistribution of fluorfolpet in PVC films

DOP (%)	Distribution of FF		Redistribution of FF		Difference in FF level
	PVC/FF ratio	Mean value for PVC/FF ratio	PVC/FF ratio	Mean value for PVC/FF ratio	
10	64 ± 17	64	71 ± 21	68	-6
	62 ± 12		68 ± 17		
	64 ± 13		64 ± 14		
10	79 ± 26	70	71 ± 18	72	-3
	58 ± 13		62 ± 15		
	74 ± 32		82 ± 22		
15 ^b	217 ± 63	195	248 ± 62	238	-18
	212 ± 67		212 ± 61		
	156 ± 49		253 ± 53		
15 ^b	122 ± 46	121	150 ± 76	145	-16
	115 ± 41		141 ± 51		
	127 ± 51				
20	86 ± 20	82	119 ± 57	108	-24
	77 ± 20		108 ± 53		
	82 ± 17		97 ± 26		
25	67 ± 24	65	74 ± 16	84	-23
	68 ± 19		93 ± 33		
	61 ± 14		85 ± 21		
25	56 ± 14	57	79 ± 18	73	-22
	57 ± 14		71 ± 23		
	58 ± 11		68 ± 18		
25 ^b	110 ± 48	107	116 ± 40	119	-10
	113 ± 30		135 ± 35		
	97 ± 26		106 ± 26		
30 ^a	21 ± 1	21	23 ± 3	24	-12.5
	22 ± 2		25 ± 3		
	20 ± 2				
30 ^a	38 ± 7	38	42 ± 6	42	-10
	37 ± 7		43 ± 6		
	40 ± 3		42 ± 6		

4.2. Distribution and redistribution of fluorfolpet

4.2.1. Mapping of fluorfolpet

For each different DOP concentration, several (usually two) samples were analysed. The mapping results for the distribution and redistribution (due to leaching) of fluorfolpet

are presented in Table 3. The difference in overall level of fluorfolpet in the films between before and after leaching is given as a percentage.

As for DOP, the distribution of fluorfolpet inside the area mapped is heterogeneous, indeed the level of fluorfolpet varies between 20 and 35% (and occasionally 45%) from

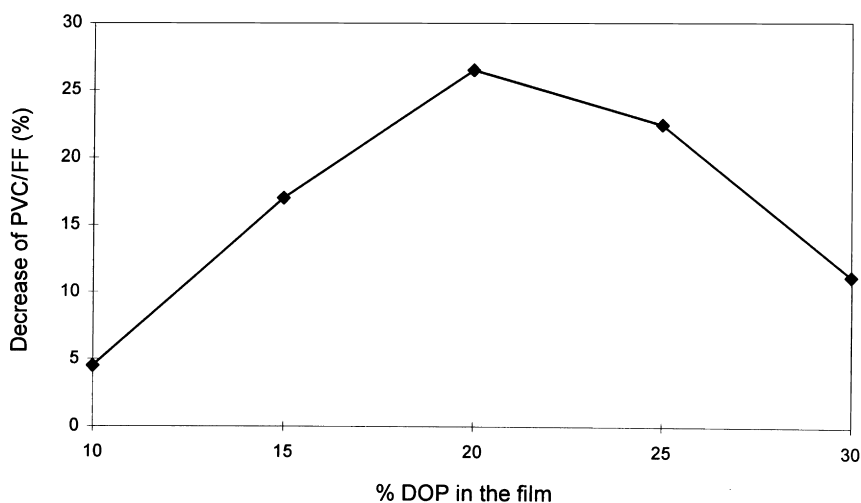


Fig. 10. Loss of fluorfolpet from the film surface as a function of DOP content.

Table 4
Glass transition temperatures as a function of DOP content

DOP (%)	T_g (°C)
10	32.6
15	22.5
20	12.3
25	1.8
30	-8.5

the mean values from point to point. It appears, however, that such local (micron scale) heterogeneity was not function of the plasticiser content.

It can also be seen that the standard deviations in individual maps were generally higher for the distribution of fluorfolpet than for the distribution of DOP. This is an indication of a more heterogeneous distribution of fluorfolpet molecules, both before and after leaching. A comparison of the mean values of all three maps for any particular sample, on the other hand, indicates that the overall level of fluorfolpet throughout the whole sample only varies very slightly, about 2–5%, (with two exception, due to a slightly higher level of fluorfolpet in one of the maps). This denotes homogeneous macroscopic distribution of fluorfolpet over the whole sample. More importantly, the data in Table 3. shows a decrease in the overall concentration of fluorfolpet on the film surface. The proportion of fluorfolpet removed from the surface, was dependent upon the degree of plasticisation of the film. Indeed, the amount of fluorfolpet displaced from the surface of the film reached a maximum for films containing 20% plasticiser. This is more clearly illustrated in Fig. 10, which shows a plot of the percentage of fluorfolpet lost (from the initial 5% loading) against the plasticiser concentration.

Vergnaud and Messadi [34,36,37,40] have postulated that when a plasticised poly(vinyl chloride) film is in contact with a liquid, some matter transfer may take place, the liquid entering the polymer while the plasticiser or any other additive present in the formulation leaves the polymer. These two mass transfers are controlled by transient diffusion and are connected with each other. Elsewhere (details in Ref. [41]), we show that the diffusion rates of water entering the polymer (as well as the total water content of the film) show an identical dependence on DOP concentration as does the leaching detected here by Raman mapping. This demonstrates

Table 5
Solubility of fluorfolpet and phthalate esters in water [47]

Compounds	Solubility in water	Solubility in DOP
Fluorfolpet	15 ppm	~2% by wt
Dimethylphthalate	0.43% by wt	–
Diethylphthalate	0.09% by wt	–
Dipropylphthalate	0.015% by wt	–
Dibutylphthalate	0.001% by wt	–
Diethylphthalate	Insoluble	–

clearly the interdependence between leaching and solvent penetration. Thus the leaching of fluorfolpet can be connected to the “free volume” and chain mobility in the films. As the concentration of plasticiser in the film increases, the mean free volume increases accordingly [42,43], as does the chain mobility, as demonstrated by the decreasing T_g (see Table 4).

The degree of leaching of fluorfolpet from the film is also probably related to its solubility in water (15 ppm) because, as more water penetrates the film, a larger amount of FF dissolves in the penetrant and leaches. We have also shown [41] that the water content at equilibrium is strongly dependent upon the level of plasticiser in the film. Riquet et al. [44], in their study of the diffusion of fatty and aqueous liquids into rigid PVC proposed that penetrant diffusion activates the migration of the additives by mobilising the small molecules which then rapidly diffuse out of the polymer matrix. Of the two additives, only fluorfolpet leaches out of the film. This most likely to be explained by their different solubility in water. Solubility data for fluorfolpet in water and DOP, as well as DOP and other phthalate esters in water, are presented in Table 5. These show that fluorfolpet is only slightly soluble, but that DOP is totally insoluble. Nevertheless, although fluorfolpet is more soluble in DOP than in water, leaching has occurred. At 5% of total weight concentration, the concentration of FF in the film exceeds its solubility value in DOP. Further, at high concentration of DOP (30%), precipitation and agglomeration of fluorfolpet was (visibly) observed, in one sample within 7 days from the sample preparation. This suggests that the fluorfolpet molecules in the film are not just dissolved in the plasticiser, but dispersed in the polymer matrix.

The decrease in fluorfolpet leaching at $\geq 25\%$ DOP concentration may be explained by one or all of the following:

1. decrease in “free volume” brought about by the occupation of the free volume sites by a plasticiser excess;
2. ‘antiplasticisation’ of the films [45–49], decreasing water content of the films.

However it is unlikely that “antiplasticisation” is relevant here since it usually is a phenomenon occurring at low ($\sim 5\%$) plasticiser content.

4.2.2. Depth profiling of fluorfolpet

The depth profiling results for the distribution and redistribution (due to leaching) of fluorfolpet are presented below (Table 6).

The standard deviation of the mean concentration of fluorfolpet within single depth profiles demonstrates the heterogeneous characteristic of the distribution of the biocide in the bulk on a micrometer scale. The level of fluorfolpet may vary between 4 and 60% at intervals of 500 μm , but a typical variation from position to position is of the order of 20%.

The comparison of the overall concentration of fluorfolpet

Table 6
Depth profiling results for the distribution and redistribution of fluorfolpet in pPVC films

DOP (%)	Distribution of FF		Redistribution of FF		Difference in FF level between before and after (%)
	PVC/FF ratio	Mean value of PVC/FF ratio	PVC/FF ratio	Mean value of PVC/FF ratio	
10	46 ± 18 53 ± 19 58 ± 8	52	49 ± 13	49	+6
10	68 ± 14 63 ± 6	65	54 ± 9 74 ± 18	64	+2
15	143 ± 40	143	146 ± 37	146	-2
20	86 ± 43 72 ± 50	79	106 ± 35 103 ± 46	104	-24
25	70 ± 11 56 ± 23	63	72 ± 14	72	-14
25	54 ± 13 71 ± 10	62	69 ± 22 61 ± 10	65	-4
30	45 ± 14 41 ± 3	43	45 ± 13 42 ± 9	43	0

per sample (represented by the mean value of PVC/FF ratios per depth profile) shows that the level of FF in the bulk is similar over the entire film. This highlighted the homogeneous characteristic of the macroscopic distribution of fluorfolpet in PVC.

Comparison between the average fluorfolpet level on the surface and in the bulk (i.e. between mapping and depth profiling) showed that there were two types of films:

1. When DOP concentration was $\leq 15\%$, there was a difference of about 15% in the biocide (FF) loading between the surface region and the bulk of the film. At 10% DOP loading there was more FF in the bulk than on the surface, whereas at 15% DOP loading, the opposite was true (see Fig. 7).
2. When DOP concentration was $\geq 20\%$, there was no noticeable difference between the level of fluorfolpet in

the bulk and on the surface (i.e. no segregation between the two regions).

The difference in distribution of fluorfolpet between films containing 10 or 15% DOP, and the ones containing 20, 25 and 30% DOP may be explained by the increase of FF solubility in the polymer matrix as the T_g is lowered and more “free volume” introduced, or by the difference in polymer state (i.e. glassy or rubbery). In the glassy polymer the ratio of crystalline to amorphous ratio is larger than in the rubbery polymer. Plasticisation and diffusion are phenomenon taking place in the amorphous region only [50,51]. As the amorphous regions surround the crystalline regions a higher extent of crystalline morphology will lead to greater microscopic heterogeneity.

Table 6 shows that the fluorfolpet was removed from the films containing 20 and 25% DOP, but at 10, 15 and 30%

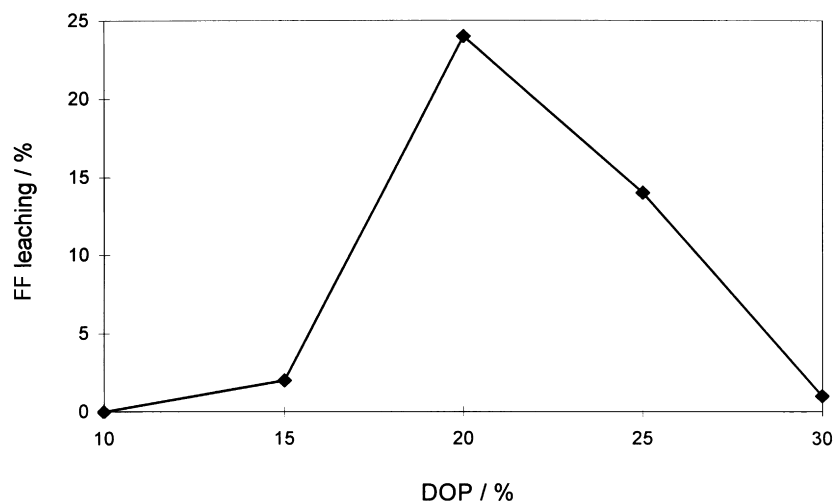


Fig. 11. A plot of percentage fluorfolpet leached versus DOP.

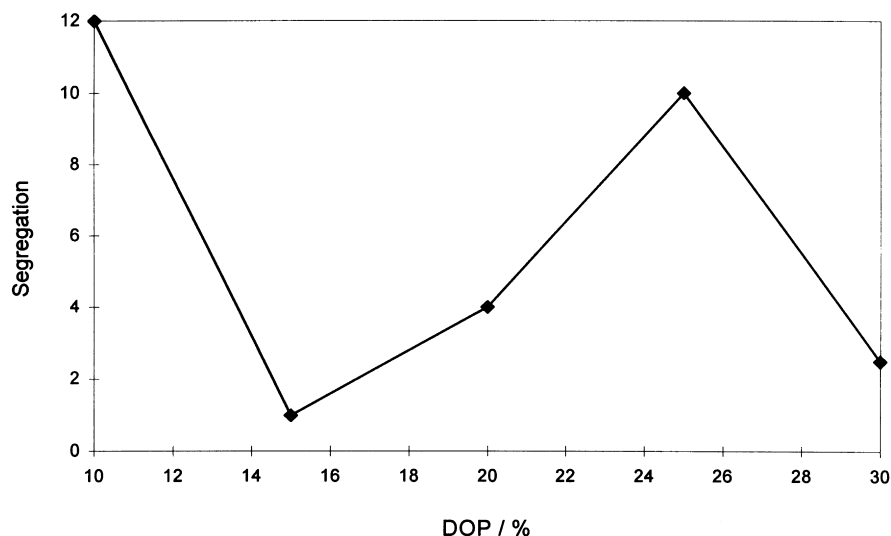


Fig. 12. A plot showing the difference of FF concentration between film and bulk surface (i.e. the degree of segregation due to leaching of fluorfolpet).

DOP content the experiment does not allow us to conclude that leaching has occurred. Variations observed were smaller than the estimated experimental error. The positive difference in FF content after the leaching at 10% DOP concentration suggests that some redistribution (without leaching) had occurred.

Fig. 11 shows a plot of percentage fluorfolpet leached versus DOP concentration in the film.

This confirms the results obtained from mapping. A more detailed study of the individual profiles would be needed to determine whether leaching was a surface or bulk phenomenon.

After leaching, when comparing the average amount of fluorfolpet present in the bulk and on the surface (i.e. PVC/FF ratios from depth profiling and mapping, see Table 6 and Fig. 12), one can see at once that the concentration of fluorfolpet was higher in the bulk than on the surface. Fig. 8 shows two depth profile plots of plasticised films with 10 and 25% DOP concentration. These plots show that the region from which the fluorfolpet was removed was the surface region. It was also apparent from the profiles that the amount of fluorfolpet removed decreases with depth. We can therefore conclude that leaching first occurred on the surface at the film–liquid interface. At longer times the FF molecules either moved towards the surface, or were directly removed from lower depths in the film. These findings are in close agreement with Murase et al. [37] on the migration of plasticiser from heat degraded PVC films.

Samples with 15% DOP showed a quite different behaviour one from the other. One sample shows an important segregation between the bulk and the surface, whereas the other one demonstrates no significant difference in concentration throughout the film. At 15% DOP concentration the films have at T_g at 22.5°C. Therefore, depending on the ambient temperature on the day of the experiment, the film might have been in the glassy or rubbery state. On

comparison with films containing 10% DOP, it is clear that the film showing a high concentration difference between the bulk and the surface, was in the glassy state when the experiment was performed.

Segregation was high at 20 and 25% DOP and low at 30% DOP concentration. Segregation is more important at concentrations at which leaching is more important, showing that leaching is more rapid than the migration of fluorfolpet inside the film [37].

5. Summary and conclusions

The results have demonstrated the potential of Raman depth profiling and Raman mapping as tool for the study of molecular distribution and leaching. The following information on the distribution and leaching of DOP and fluorfolpet have been drawn from the above results:

1. The distribution of both dioctylphthalate and fluorfolpet were found to be uneven (or ‘heterogeneous’) on a micron scale. There was no evidence however, for inhomogeneity of either component distribution on the larger macroscopic scale. (Fig. 2 and Tables 1 and 2).
2. There was little or no leaching of DOP from the films into water (Tables 1 and 2).
3. Leaching of fluorfolpet from the films was observed (Tables 3 and 6) and the measured redistribution of fluorfolpet molecules (via mapping and depth profiling) showed that leaching was strongly dependent upon the plasticiser concentration or amount of water penetrating the film (Fig. 10). It was demonstrated that leaching could be a consequence of:
 - excess number of fluorfolpet molecules in the film;
 - solubility of fluorfolpet in water;
 - chain mobility and free volume parameters of the film. Indeed leaching was more important in those

films where chain mobility and free volume were the highest (and T_g was lowest).

4. There was some segregation of the DOP distribution (i.e. concentration) between the bulk and the surface of the film before leaching of fluorfolpet (Fig. 12)
5. Redistribution of the DOP molecules in the films occurred after leaching of fluorfolpet molecules: but no difference in segregation between the distribution of DOP in the bulk and on the surface was noticed after leaching (Fig. 6 and Tables 1 and 2).
6. No segregation between bulk and surface distribution was noticed for fluorfolpet before leaching. (Tables 3 and 6). However leaching led strong differences of fluorfolpet concentration between the bulk and the surface of the sample, the surface showing a much lower concentration of FF (Figs. 8 and 12). This clearly demonstrated that leaching occurred from the surface, i.e. from the film–solvent interface.

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