



Migration of dioctylphthalate and dioctyladipate plasticizers from food-grade PVC films into ground-meat products

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The migration of dioctylphthalate (DOP) and dioctyladipate (DOA) plasticizers from polyvinyl chloride (PVC) films into ground meat of varying fat contents was studied at 4°C and –20°C. The amount of migrating plasticizer was determined indirectly after the extraction, saponification and quantification of the alcoholic constituent of the ester plasticizer using gas chromatography. The amount that had migrated ranged from approximately 2 to 80 mg per kilogram of meat (0.12–4.8 mg/dm²) after 8 days at 4°C and from 2 to 60 mg (0.13–4 mg/dm²) after 2½ months at –20°C. The amount of migrating DOA was (under similar experimental conditions) higher than the respective amount of DOP. The migration to samples of lower fat content was proportionally lower. Mathematical treatment of the migration of both DOA and DOP showed that the rate-determining step in the migration process is that of the diffusion of the plasticizer from the bulk of the PVC film to its surface.

INTRODUCTION

Polyvinyl chloride (PVC) films have found wide applications over the past several years in the packaging of a large variety of foodstuffs, such as fresh meat, fruits and vegetables, and cheeses (Castle *et al.*, 1987). These commercial films, in addition to the polymeric component, contain a number of plastic additives to improve the physical and, mainly, the mechanical properties of the film. Among these additives, the one used in the highest proportion is the plasticizer (Crompton, 1979).

Plasticizers are low-melting solids or high-boiling organic liquids added to plastic polymers in order to aid flow and processing, to extend and modify the natural properties of the resin and to develop new, technologically important properties not present in the resin itself. Chemically, plasticizers are related to solvents, but they are far less volatile (Sears & Darby, 1982). The most commonly used plasticizers are esters of dibasic or tribasic acids, with di-2-ethylhexylphthalate (DOP) and

di-2-ethylhexyladipate (DOA) being used in large volumes today in food packaging applications (Sears *et al.*, 1985).

Plasticizers, due to their significantly lower molecular weight as compared to the polymeric component of the plastic, possess a high mobility, resulting in their migration into foods with which they come into contact (Crompton, 1979). The tendency for migration of such compounds, in combination with their potential toxicity, has recently raised the question of consumer safety when used in applications such as food and drug packaging.

Several studies on laboratory animals fed with diets containing DOP reported symptoms such as reduced weight gain, enlargement of the liver, neuromuscular and skeletal abnormalities, and reduction in incidence of pregnancies (Baker, 1978; Lawrence, 1978; Pollack *et al.*, 1985). It has also been reported that the metabolite of DOP, mono-2-ethylhexyl-phthalate (MEHP), causes inhibition of growth as well as mutagenesis in several microorganism cultures (Ruuska *et al.*, 1987).

The determination of plasticizers in foodstuffs is often a difficult task, partly due to the complexity of the food system into which the plasticizer migrates so that its direct determination is not possible. Also, only

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minute quantities actually migrate, requiring analytical techniques of high sensitivity.

There are several methods reported in the literature for the determination of plasticizers in food systems, such as radiolabelling (Kampouris, 1976; Figge, 1980), gas chromatography (Daun & Gilbert, 1977), gas chromatography/mass spectrometry (Startin *et al.*, 1987), high-pressure liquid chromatography (Mori, 1976) and spectrophotometric methods (Wildbrett *et al.*, 1968).

The migration of DOA and DOP plasticizers from food-grade PVC films into olive oil has been studied previously (Kondyli *et al.*, 1990). In the present study, the migration of the above plasticizers was extended to solid foodstuffs such as ground meat with a fat content ranging from 3 to 55%. The experiments were carried out at 4°C (corresponding to commercial refrigerator temperature) and -20°C (corresponding to deep-freezing temperature).

MATERIALS AND METHODS

Materials

Two types of PVC film were used in all experiments: RMF-61 containing 31.5% DOA and VF-71 containing 29.5% DOP of 13 μm (5×10^{-4} in) thickness. Both films were supplied by Borden Chem. Division (N. Andover, MA, USA). Analytical-grade DOA and DOP were purchased from Fluka AG (Buchs, Switzerland). Meat was purchased locally and ground in a laboratory meat grinder.

Migration experiment

Circular ground-beef samples (1.1 cm thick) were wrapped in the PVC films and placed between glass plates, which were compressed by adding an appropriate weight to ensure complete contact between the film and the meat sample. The total contact area was 0.85 dm². The weight of the sample was 50 ± 2 g. The samples were then placed in the refrigerator (4°C) and the freezer (-20°C), respectively, and were analysed for plasticizer content at predetermined time periods.

Method for plasticizer analysis

The method for plasticizer analysis used was that of Daun and Gilbert (1977), modified accordingly. The samples were mixed with anhydrous sodium sulphate of the same weight and were extracted with hexane in a Soxhlet apparatus for 6 h. Thus, the fat and plasticizer were transferred to the hexane phase. The hexane was evaporated and the residue was saponified with 2M potassium hydroxide in methanol for 3 h. Thus, dioctylphthalate and dioctyladipate were decomposed to phthalic and adipic acid, respectively, and 2-ethyl-

hexanol. Potassium hydroxide solutions of 8 ml per 1 g of fat saponified were used. Upon completion of the saponification, methanol was evaporated and the residue was acidified and steam distilled until 200 ml of distillate had been collected. The distillate was extracted four times with 50 ml of diethyl ether. The combined ether extracts were evaporated and the residue was redissolved in carbon disulphide. In the resulting solution, 2-ethylhexanol was determined by gas chromatography using a standard curve. A VARIAN 3700 GC equipped with a flame ionization detector was used. Chromatographic conditions were as follows: column—SE-30, 10% on Chromosorb of dimensions 1.8 m \times 6.3 mm o.d. made of aluminium; column temperature—165°C; injection-port temperature—220°C; detector temperature—220°C.

All experiments were carried out in triplicate. The recovery factor of the above method was obtained by preparing meat samples with known amounts of DOA and DOP, respectively, and determining the plasticizer content following the same course as for experimental samples. Recovery factors of 74.5% for DOA and 68.1% for DOP were obtained.

RESULTS AND DISCUSSION

The amounts of DOP and DOA plasticizers migrated from the PVC films into ground meat at 4°C as a function of time are given in Fig. 1.

It is observed that the amount of migrating DOA, under the same experimental conditions, is higher than the respective amount of DOP. This difference becomes more pronounced at higher fat contents. For example, in the case of the meat sample with 55% fat content, a migration of 81.8 mg per kilogram (corresponding to

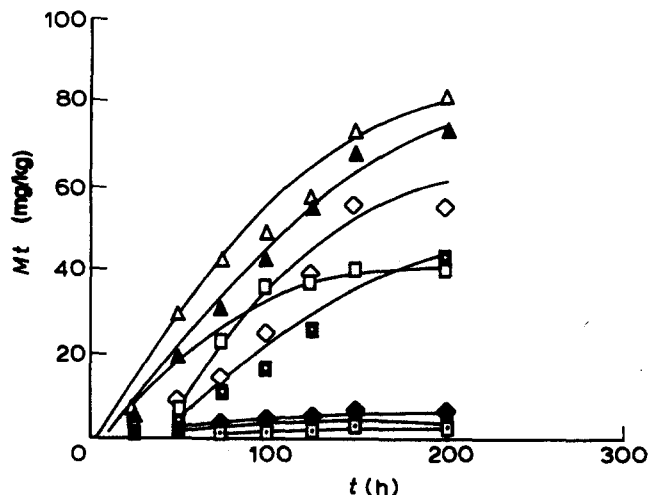


Fig. 1. Migration of DOP into ground-meat samples of 3% (□), 12% (◇), 30% (◻) and 55% (◊) fat contents and of DOA into ground-meat samples of 3% (■), 12% (□), 30% (▲) and 55% (△) fat contents at 4°C.

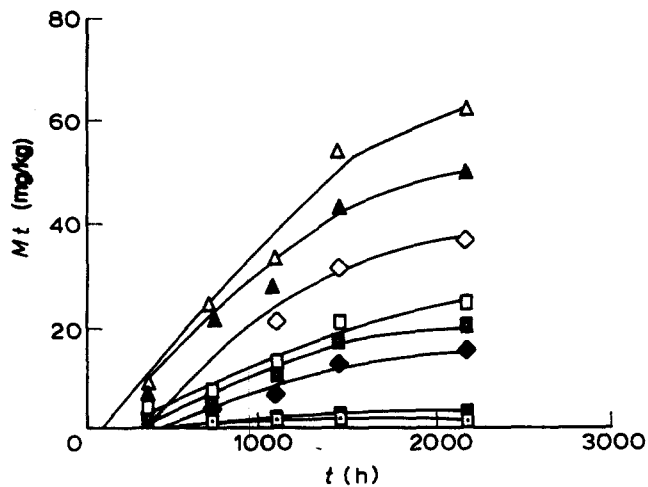


Fig. 2. Migration of DOP into ground-meat samples of 3% (\square), 12% (\blacklozenge), 30% (\blacksquare) and 55% (\diamond) fat contents and of DOA into ground-meat samples of 3% (\blacksquare), 12% (\square), 30% (\blacktriangle) and 55% (\triangle) fat contents at -20°C .

4.8 mg per 1 dm^2 of film) of food for DOA and 55.8 mg (3.3 mg/dm^2) for DOP was observed. This difference can be attributed to the lower molecular weight of DOA (a fact that enhances mobility of the plasticizer toward the film surface and into the food contacting phase) as well as to a relatively higher solubility of DOA in fat. It should also be mentioned that the initial content of DOA in the film was slightly higher than that of DOP (31.5% versus 29.5%).

It is also clear that the amount of migrating plasticizer increased with increasing fat content in the meat sample. This is expected, since the plasticizers are highly soluble in the fatty phase as compared to the muscle phase of the meat samples.

The amounts of DOP and DOA plasticizers migrated from PVC films into ground meat at -20°C as a function of time are given in Fig. 2.

The same trend regarding amount of migrating plasticizer at 4°C is also observed at -20°C . The explanation for this is similar to that given above. It is also clear that, for a given plasticizer and sample fat content, a significantly lower amount of plasticizer migrated into the meat sample at -20°C as compared to that at 4°C . It is obvious that the mobility of the plasticizer molecules increased with increasing temperature.

The values of migrating dioctyladipate plasticizer determined in the present study (3.75 mg/dm^2) are lower than those found in the literature (Daun & Gilbert, 1977; Till *et al.*, 1982; Startin *et al.*, 1987). These authors reported values of 5.5, 12 and 15 mg/dm^2 , respectively. On the other hand, the present values are higher than those found by Castle *et al.* (1987), who reported a value of 0.8 mg/dm^2 . This comparison concerns the migration of DOA from PVC film with an initial DOA concentration of approximately 25% (w/w) into fresh

meat after 1 week at 4°C . The differences reported above can be attributed to a variation in the contact surface of film/unit-weight of food used in each case. That is, the higher this ratio in the experimental design, the higher the amount of plasticizer migration that is expected. For instance, in the Castle *et al.* migration experiments the film-surface/food ratio was $5.6\text{ dm}^2/\text{kg}$ (corresponding to 0.8 mg of DOA per 1 dm^2 of film); in the present experiments, the respective ratio was $16.9\text{ dm}^2/\text{kg}$ (3.75 mg/dm^2).

Comparison of DOP values determined in the present work was not possible, due to lack of respective values in the literature.

In reference to the frozen-meat-migration experiment, our value of 21.6 mg of DOA per kilogram of beef (1.28 mg/dm^2) determined after 30 days at -20°C is in excellent agreement with that of Startin *et al.* (1987), who reported a value of 23 mg/kg (1.8 mg/dm^2) after 30 days at -18°C .

Furthermore, an attempt to present a simple mathematical treatment of the phenomenon of DOA and DOP migration from a PVC film into a solid foodstuff such as ground meat was made.

The migration of a low-molecular-weight compound such as a plasticizer from a polymeric matrix into a food matrix can be considered as a two-stage process. During the first stage, diffusion of the compound from the bulk of the polymer to the surface takes place. The mechanism of such a transfer depends on the nature and properties of the contacting phase (i.e. solid versus liquid, etc.) (Till *et al.*, 1982; Papaspyrides, 1986).

If the amount of plasticizer migrated at time t is Mt and M is the respective amount at equilibrium, then Mt will be given by

$$\frac{M-Mt}{M} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp -D \frac{(2n+1)^2 \pi^2}{4L^2} t \quad (1)$$

where D is the diffusion coefficient and L is the film thickness. Assuming long migration times and a diffusion coefficient independent of concentration, eqn (1) can be reduced to (Papaspyrides, 1986):

$$\frac{Mt}{M} = 1 - \left(\frac{8}{\pi^2} \right) \exp (-\pi^2 Dt/L^2) \quad (2)$$

Eqn (3) can be used instead of eqn (2) for the initial stages of migration:

$$Mt = 2C_{po}(Dt/\pi)^{1/2} \quad (3)$$

where Mt is expressed in milligrams per square centimetre and C_{po} (initial concentration of plasticizer in the film) is expressed in milligrams per cubic centimetre.

Under these conditions, the rate-determining step is that of the diffusion of the plasticizer from the bulk of the PVC film to the surface. Equation (3) indicates that migration is proportional to the square root of the elapsed time, and this relationship has been noted

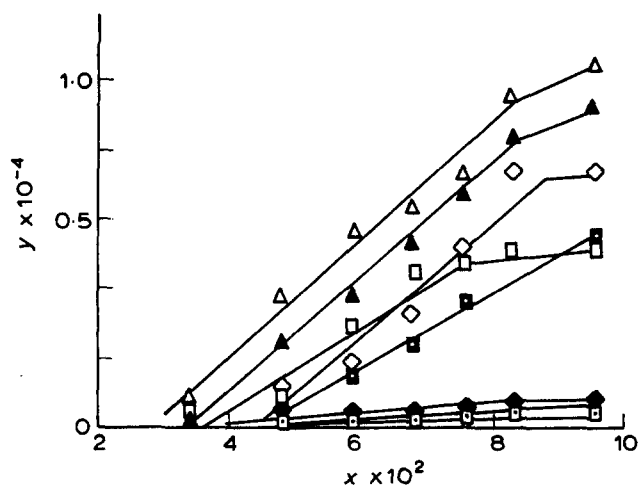


Fig. 3. Plot of $x = 2(t/\pi)^{1/2}$ versus $y = Mt/C_{po}$ for DOP into ground-meat samples of 3% (\square), 12% (\diamond), 30% (\blacksquare) and 55% (\diamond) fat contents and for DOA into ground-meat samples of 3% (\blacksquare), 12% (\square), 30% (\blacktriangle) and 55% (\triangle) fat contents at 4°C.

earlier (Pfab, 1973; Papaspyrides, 1986). One of the principal criticisms directed towards this simple model is that the diffusion coefficient of the plasticizer most probably varies with plasticizer concentration and, thus, is likely to be applicable in cases where only small amounts of plasticizer are removed or when solvents

penetrate the film and simulate the plasticizer that has been extracted (Pfab, 1973).

A completely different boundary condition must be used when the external phase is so poorly mixed that a stagnant layer forms adjacent to the polymer. Migrant leaving the polymer must then diffuse through the so-called boundary layer before it becomes mixed into the bulk of the external phase by convection. Mathematical treatment of this situation involves defining a mass transfer coefficient (k), which takes into account the rate of migrant diffusion through the layer and the apparent thickness of the layer. This case is described (Crank, 1975) by

$$Mt = 2C_{po}(Dt/\pi)^{1/2}[1 + (\sqrt{\pi/2Y})(\exp Y^2 \operatorname{erfc} Y - 1)] \quad (4)$$

The parameter Y is defined as

$$Y = kK(t/D)^{1/2} \quad (5)$$

where K is the partition coefficient and represents the ratio of plasticizer concentration in the food-contacting phase to that in the PVC film at equilibrium. When Y is large (large k , large K , long t , small D), eqn (4) reduces to eqn (3). At very small values of Y (e.g. over short periods of time) eqn (4) simplifies to

$$Mt = kK(C_{po}t) \quad (6)$$

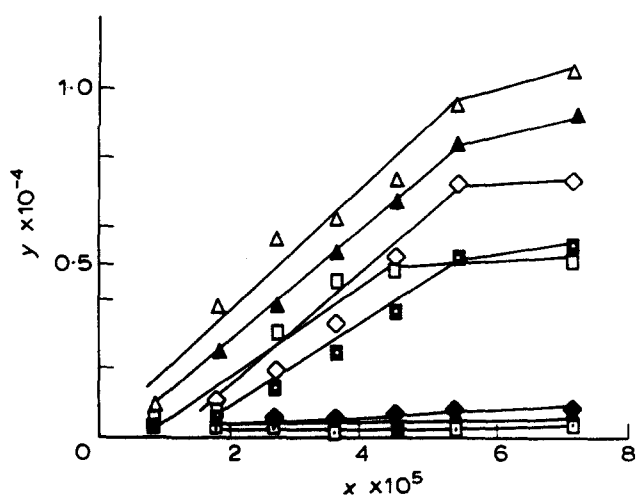


Fig. 4. Plot of $x = t$ versus $y = Mt/C_{po}$ for DOP into ground-meat samples of 3% (\square), 12% (\diamond), 30% (\blacksquare) and 55% (\diamond) fat contents and for DOA into ground-meat samples of 3% (\blacksquare), 12% (\square), 30% (\blacktriangle) and 55% (\triangle) fat contents at 4°C.

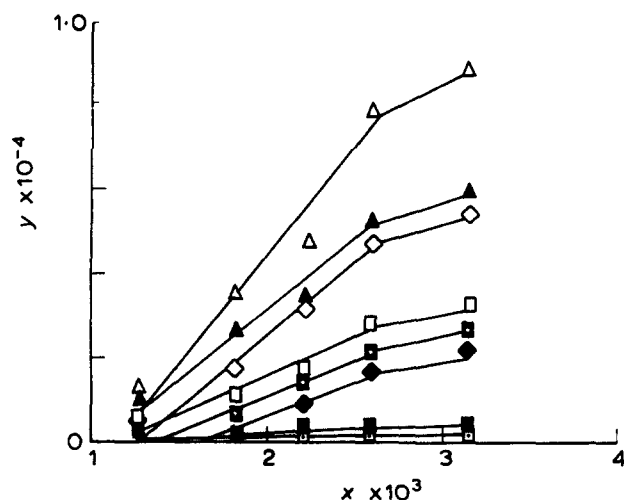


Fig. 5. Plot of $x = 2(t/\pi)^{1/2}$ versus $y = Mt/C_{po}$ for DOP into ground-meat samples of 3% (\square), 12% (\diamond), 30% (\blacksquare) and 55% (\diamond) fat contents and for DOA into ground-meat samples of 3% (\blacksquare), 12% (\square), 30% (\blacktriangle) and 55% (\triangle) fat contents at -20°C .

Table 1. Values of D and kK for migration of DOP and DOA from PVC films into ground-meat samples of different fat contents at 4°C

Fat content of meat sample (%)	DOP		DOA	
	D ($\text{cm}^2 \text{ s}^{-1}$)	kK (cm s^{-1})	D ($\text{cm}^2 \text{ s}^{-1}$)	kK (cm s^{-1})
3	1.26×10^{-17}	3.94×10^{-12}	1.64×10^{-17}	4.46×10^{-12}
12	1.80×10^{-17}	4.56×10^{-12}	2.85×10^{-15}	7.81×10^{-11}
30	1.95×10^{-15}	4.94×10^{-11}	6.18×10^{-15}	8.52×10^{-11}
55	4.20×10^{-15}	7.29×10^{-11}	6.63×10^{-15}	8.71×10^{-11}

Table 2. Values of D and kK for migration of DOP and DOA from PVC films into ground-meat samples of different fat contents at -20°C

Fat content of meat sample (%)	DOP		DOA	
	D ($\text{cm}^2 \text{s}^{-1}$)	kK (cm s^{-1})	D ($\text{cm}^2 \text{s}^{-1}$)	kK (cm s^{-1})
3	4.32×10^{-19}	1.97×10^{-13}	5.61×10^{-19}	2.53×10^{-13}
12	3.30×10^{-17}	1.65×10^{-12}	6.08×10^{-17}	2.85×10^{-12}
30	4.73×10^{-17}	2.42×10^{-12}	2.49×10^{-16}	5.32×10^{-12}
55	2.19×10^{-16}	5.73×10^{-12}	5.80×10^{-16}	8.16×10^{-12}

Under these conditions migration is proportional to time, and the external mass transfer process is the rate-determining step.

The important point here is to note that the simple diffusion model (eqn (3)) when modified for an external mass transfer resistance coefficient can predict the observed linear time period of migration at short times, and it is an experimental fact that such a period exists.

These two different time dependencies have been noted previously by Small (1947) and Quackenbos (1954) for plasticizer loss from PVC into air and flowing water.

Plots of Mt/C_{po} versus $2(t/\pi)^{1/2}$ and of Mt/C_{po} versus t are initially linear, with slopes equal to $D^{1/2}$ and kK , respectively (Figs 3 and 4 at 4°C , Figs 5 and 6 at -20°C).

Values of D and the product kK calculated using the above figures are given in Tables 1 and 2. It is observed that, for both temperatures, values of D for DOA are higher than those for DOP, especially in the case of meat samples of high fat content (12, 30 and 55% fat).

These results are in agreement with respective results of Figs 1 and 2 and their interpretation is analogous to that previously presented.

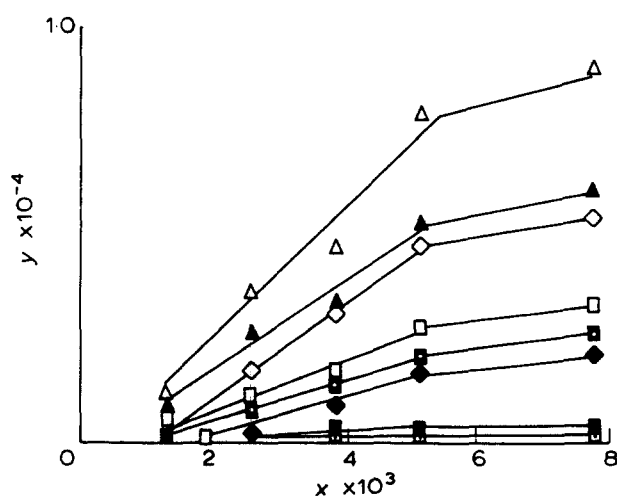


Fig. 6. Plot of $x = t$ versus $y = Mt/C_{po}$ for DOP into ground-meat samples of 3% (■), 12% (◻), 30% (▲) and 55% (◊) fat contents and for DOA into ground-meat samples of 3% (■), 12% (◻), 30% (▲) and 55% (Δ) fat contents at -20°C .

It can also be seen in Tables 1 and 2 that values of the product kK were found to be significantly higher than respective values of D for all the food systems studied. Assuming a K value in the order of magnitude of unity, then $kK = k$ and, consequently, $D \ll k$. This suggests that the diffusion process in the bulk of the polymer controls the rate of migration, since the resistance to mass transfer in the food phase is a lot lower than that in the polymer phase.

Thus, under present experimental conditions, a solid contacting phase such as ground meat may be treated as well mixed. This has shown to be the usual case when a solid food is wrapped in a polymer film (Little, 1983).

In conclusion, modelling can be useful in identifying the critical parameters in order to minimize migration, even though it is unlikely that any model will be ever sufficiently refined to permit migration measurements in real foods, such as ground meat, to be totally avoided.

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