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DEHP Migration from Solid PVC Discs Soaked in Groundnut Oil: Experimental Study and Mathematical Simulation

Badria Bouchelaghem and Djelloul Messadi
Laboratoire de Sécurité Environnementale et Alimentaire (LASEA),
Badji Mokhtar University-Annaba, BP 12, 23 000 Annaba, Algeria

Abstract: The use of labelled DEHP and radioactivity measurements in conjunction with weight loss give quantitative information on the mass exchanged when plasticized PVC discs are soaked in groundnut oil and lead to DEHP concentration profiles that are developed through the bulk of polymer during the process. Low penetration advantage of the edible oil within the PVC samples in order to test a simplified mathematical model is considered. Mathematical simulation led to correct figures of migration and it is all interesting since it requires measurements at short times. Rapid determination of the quantity transported after infinite time is the principal difficulty in this kind of study. This last constraint can be get round, while using thinner discs plasticized at high rates.

Key words: Plasticizer transfer, phenomenological study, simplified mathematical model, DEHP, PVC

INTRODUCTION

Polyvinylchloride (PVC) is an important linear halogen-containing polymer, which is used for many different purposes, including food contact materials. The polymer can be moulded in almost any form and at ambient temperature it is hard in its pure form. By adding plasticizers in increasing amounts, the hard material gradually becomes more rubbery and flexible. Soft plasticized PVC occasionally contains as much as 50% plasticizer.

The most frequently used plasticizers for PVC are the phthalates such as di-(2-ethylhexyl)phthalate (DEHP).

In all applications, the plasticized PVC is in contact with the surrounding medium and the plasticizer may migrate with the following results (Messadi and Gheid, 1994, 1996; Messadi and Vergnaud, 1997; Papaspyrides and Tingas, 1998; Tawfik and Huyghebaert, 1999; Djilani *et al*., 2000; Scholler *et al*., 2003; Scotter and Castle, 2004):

- Because the loss of plasticizer, the polymer deteriorates its mechanical properties.
- The surrounding medium is contaminated by the plasticizer. This problem is complicated by several factors:
- In a variety of contexts, there is a simultaneous transport of the liquid into and the plasticizer out of the PVC. However, the amount of liquid transported into PVC often follows a more complex phenomenon. This amount increases rapidly to a maximum value. then the liquid comes out partially (Counterdiffusion) (Messadi, 1981).
- For both these transfers, the diffusivity is concentration-dependent.
- Many factors may affect the migration process, including the nature of the polymer and plasticization process, the surrounding medium, the nature and amount of plasticizer and the conditions of migration process, i.e., stirring, time and temperature.

The migration is a slow process which can take several months at storage temperatures, thus shorter time tests at higher temperatures were proposed. On the other hand, the problem of identifying migrating species in the presence of chemically complex structures led very quickly to the simulation of real foodstuffs by pure products. However such simulations are not conclusive.

Some authors (Vergnaud, 1991) consider it better to derive mathematical models rather than change the conditions of the experiments. Sophisticated theoretical models, concerned with transfer of plasticizer into pure solvents have been referred to in the literature and they must be adjusted to real foodstuffs.

In this study, the results of long time tests are first given for migration of the plasticizer (DEHP) from solid PVC discs into well-stirred groundnut oil (T = 50°C; % DEHP = 30) using a method based on labelled plasticizer

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Corresponding Author: Djelloul Messadi, Laboratoire de Sécurité Environnementale et Alimentaire (LASEA), Badji Mokhtar University-Annaba, BP 12, 23 000 Annaba, Algeria

and measurements of the radioactivity of the two in-contact phases. Low penetration advantage of the edible oil within the PVC samples in order to test a simplified mathematical model is considered. Calculated and measured DEHP concentrations in the liquid phase, as well as calculated and measured DEHP concentration profiles that are developed through PVC matrix are compared by using the one-way analysis of variance.

Theory: The following assumptions were made:

- PVC discs are used and the case of one dimensional diffusion in a medium bounded by two parallel planes is considered, e.g., the planes x = ± L.
- Concentration of liquid in bulk polymer is neglected.
- The transfer of DEHP through PVC mass is obtained by diffusion in unsteady state, as the diffusivity is dependent on the plasticizer concentration.
- The concentration of the plasticizer on the PVC surface reaches the equilibrium value as the PVC sample is soaked in the liquid.

It has been generally assumed that diffusion under transient conditions is described by Fick's. equation (Crank, 1975):

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

Where t, x and D are the time, abscissa measured through the thickness (= 2L) of the disc and diffusivity, respectively, the latter depends on the concentration of the diffusing plasticizer according to the relationship:

$$D\,(x,\,t) = D_0 \exp\,(-A/C) \quad (2)$$

The values of the coefficients A and Do depend on the nature of the liquid and the temperature.

Mathematical analysis of short tests: Equation 1 is analytically intractable with the above conditions. However, for very short times, the small amount of matter transferred at time t is very low, so that, the concentration of the plasticizer is almost constant. In this case, the value of Mt, as a fraction of the quantity transported after infinite time M_∞, can be expressed in terms of the square root of the time (Vergnaud, 1991; Crank, 1975).

$$\frac{M_t}{M_\infty} = \frac{2}{L}\left(\frac{Dt}{\pi}\right)^{0.5} \quad (3)$$

This equation is very useful for determining the diffusivity which corresponds to the concentration of plasticizer in the PVC at the beginning of this short test.

Numerical analysis for long tests: In this study, the problem is solved using a numerical explicit method with finite differences. The numerical analysis (Smith, 1975) applied to Eq. 1 leads to:

$$C(x,t+\Delta t)=\frac{1}{M}[C(x-\Delta x,t)+C(x,t)(M-2)+C(x+\Delta x,t)] \quad (4)$$

with the dimensionless modulus M:

$$M = \frac{(\Delta x)^2}{\Delta t}\cdot\frac{1}{D(x,\ t)} \quad (5)$$

The concentration inside the disc is then computed at the abscissa x and time (t + Δt), knowing the concentrations at time t, at the abscissa (x- Δx), x and (x + Δx). The total amount of plasticizer transferred at time t can be obtained by integrating the profile of concentrations with respect to time.

MATERIALS AND METHODS

Synthesis of labelled DEHP: Labelled phthalic anhydride (74 mg, 7-^{14}C; 0.5 mCi; CEA (Paris)] was transferred to a four necked flask and mixed with 5 g of unlabelled phthalic anhydride dissolved in 50 mL of acetone. The flask is equipped with a thermometer, an inlet tube, a dropping funnel, a magnetic stirrer and a side condenser. The mixture is heated with continuous stirring until all the acetone is evaporated. Forty five gram phthalic anhydride is added with 2-ethylhexanol (200 mL), toluene (60 mL) to promote the removal of water and 0.6 mL conc. H_2SO_4. The mixture is heated in an oil bath for 200 min while the temperature is gradually raised to 170°C. All the phthalic anhydride is dissolved after 80 min. After 110 min the temperature of the vapor is stabilized at ca. 82°C for 50 min then increases again to indicate the end of the reaction. During this period, a slow N_2 stream is passed and an equimolecular mixture of 2-ethylhexanol and toluene is periodically added.

At the end of the experiment, the mixture is cooled and diluted with 2×500 mL (10%) aqueous sodium carbonate solution and dried for 12 h over anhydrous ($CaCl_2$). The solution is then filtered and finally evaporated to remove diethylether, toluene and unreacted

2-ethylhexanol. The diester is purified using vacuum distillation and yields 92%. Products with lower radioactivities are obtained by dilution with pure unlabelled DEHP.

Sample preparation: Commercial PVC [Sicron 540 HV (Sonatrach.-Algeria); K 70] is blended at 80°C with the calculated amounts of labelled DEHP (from 20 to 50 wt %) and a fixed amount of barium-cadminum-zinc stabilizer [Irgastab B C 447 (ENPC-Algeria)]. The resulting dry blend is plasticized in a plastograph (Haake) working at 135°C, 35 rev min^{-1} for 10 min. The plasticized mass is pressed using a steel mould operated by a power press at 150°C for 10 min under 50 bars, to form a sheet of ca. 3 mm thick. Several discs are cut, having nearly the same characteristics (18 mm in diameter and 3 mm thick); those with a weight difference not exceeding 5% are selected for use and distributed into groups of 20 samples.

Mass transfer study: All experiments were carried out with 20 PVC solid discs immersed in 200 mL of groundnut oil contained in a 250 mL flask, kept at a temperature fixed to 0.1°C, using a controlled rate of stirring. At intervals, PVC samples and liquid were taken for analysis, so that the PVC-liquid ratio remains constant. Each PVC disc is weighted and the concentration of the plasticizer in the liquid is measured, so that the amounts of DEHP and liquid transferred can be determined. Then, each disc is peeled off into 15 slices of 0.200 mm thick using a lathe with a knife at the end of it. These slices are parallel to each other and to the flat faces of the discs (Fig. 1). This operation works properly when the PVC disc is hardened with liquid N_2.

Measurements: The variations of the DEHP contents of the 2 phases in contact are monitored using the radioactive tracer technique, with automatic quenching correction and the external standard technique. The method is proved simple and reproducible and it is, therefore, used to find the amounts of the DEHP in complex mixtures prepared in the laboratory. The accuracy was 3% for the least successful test and the reproducibility was 0.25%.

The radioactivity of the liquid medium removed at a given time after immersion, is measured by transferring 0.5 mL of liquid to a plastic measuring vial containing 10 mL of the scintillation solution (Ready-solv. N A-Beckman). The mixture was shaken to ensure complete solubization; the radioactivity was measured by means of a Beckman β-L S 2800 spectrophotometer over a period of 10 min. The analyses were carried out in duplicate; thus each quoted result represents the average of 6 measurements.

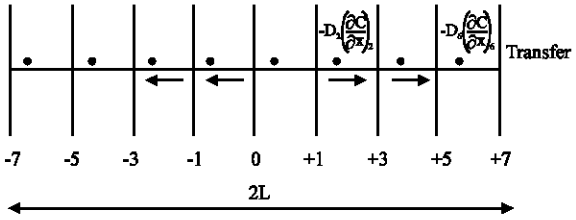

Fig. 1: Diffusion of the DEHP through the plane disc

The following operations were carried out successively in order to measure the concentration of plasticizer mixture inside every PVC disc, for different x values of abscissa along the thickness of disc: Weighting of peeled slices; dissolution of slices in 3 mL of THF and analysis on 0.5 mL of the obtained solution as described previously.

RESULTS AND DISCUSSION

Control of the homogeneity of the samples: An analysis of variance (Dagnelie, 1998) for the control of the homogeneity of the sheet was performed. The statistical results show that there is a good overall homogeneity of the sheet and that there is a significant difference in the homogeneity of the concentration of the external and internal layers of a particular disc (with a p-value = 0.05). However, the experimentally shown gradients are fairly flat; they were neglected in the treatment of the results.

Matter transfers: Table 1 shows that there is a weak penetration of the groundnut oil into the PVC samples coupled with DEHP diffusion out of the plastic discs; the rates of these 2 transfers are quite different.

Chemically the groundnut oil used is a complex mixture of triacylglycerols which comprise ca. 98% of the oil and other minor components, such as sterols, ketones, aldehydes, hydrocarbons and pigments. The triacyclglycerols with acyl groups containing 12 or more carbon atoms can not diffuse into the plastic (Figge, 1980). Thus the role of the minor components may be important.

The effect of stirring was found to be important throughout the test and this result was quite different from previous results with other liquids (Messadi and Vergnaud, 1981, 1982) for which the degree of agitation was shown to be particularly important at times (<50 h). DEHP transport in groundnut oil was controlled by the diffusion at the solid/liquid interface and by a thin layer of triacylglycerols which adheres to the surface of the polymer.

Table 1: Simultaneous diffusion of groundnut oil and DEHP T = 50°C; % DEHP = 30

Time (h)		12	24	48	72	120	240	360
°/° DEHP	*	4.45	5.50	9.00	12.00	16.02	20.10	21.72
	**	3.17	4.53	7.83	10.86	14.80	19.70	20.61
°/° oil	*	0.49	0.82	1.11	1.50	1.83	2.30	2.85

* Stirred liquid characterized by the value of the Reynold's number Re = 2000, ** Stationary liquid

Profiles of DEHP concentration through PVC discs: According to the process described above, PVC discs were removed from groundnut oil at various times and every disc was converted to 15 slices 0.200 mm thick. The DEHP Concentration (C) was measured in every slice, C_0 being the plasticizer concentration at zero time. The relative concentration C/C_0 was plotted against the position of the centre plane of every slice in the PVC disc before cutting; this position was expressed by the relative abscissa X, where $-7 \leq X \leq 7$. Point 0 on the abscissa is taken for the centre plane of the PVC disc, parallel to the faces and ±7 the abscissa at the centre plane of the 2 layers close to each disc face. The problem is symmetric with respect to X = 0, so the data are given only for $0 \leq X \leq 7$ (Fig. 2).

DEHP concentration near both surfaces of the disc is very high at the beginning of plasticizer transfer, so explaining the fast migration in the early stages of the process. After several hours, a large decrease in DEHP concentration appeared, slowing down the migration.

Modelling and simulation: The parameters D_0 and A (Eq. 2) are determined under isothermal condition at 50°C in the liquid in motion using PVC discs with plasticization levels ranging from 20 to 50 wt %. Diffusivities of DEHP are calculated from the slopes of the straight lines obtained by plotting the DEHP values transferred at short times (≤5 h) against the square root of time. As the logarithm of diffusivities of the DEHP are found to be related to the reciprocal of the initial plasticizer level (Fig. 3), it is easy to obtain the following equation

$$D = 1.12 \times 10^{-7} \exp(^{-}171/C) \qquad (6)$$

The amount of plasticizer transferred at equilibrium M_8 is obtained from long test experiments (over 500 h) which were made under the same conditions such as for determining of the diffusivities.

Parameters of calculations: $\Delta x = 0.01$ cm; thickness $2L = 0.30$ cm; $\Delta t = 3600$ s (algorithm I) allow the best possible compromise between a good precision and the stability of calculations.

The regression line:

$$C_{th} = a + b\,C_m \qquad (7)$$

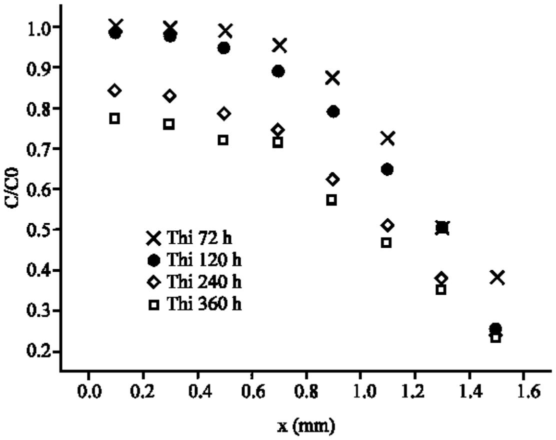

Fig. 2: Variation in measured relative plasticizer concentration C/C_0 along the PVC disc thickness for different times (h): T = 50°C; initial plasticizer concentration C_0 = 30%

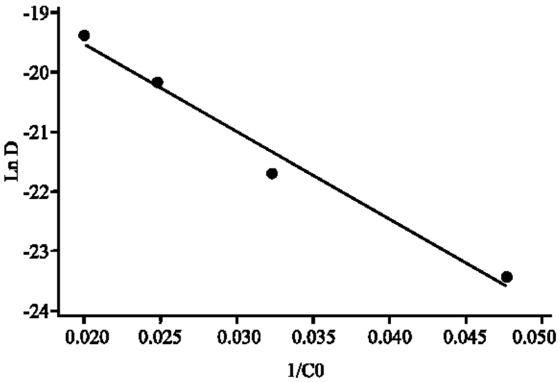

Fig. 3: Variation of Ln D Vs. $1/C_0$

fitting the pairs of values C_m (measured) and C_{th} (calculated) was found by the method of least squares. The calculation of parameters a and b and the subsequent variance analysis (Dagnelie, 1998; Minitab, 2000) were worked out for the combined results, using the MINITAB software of processing data. The level of significance, α, was fixed at 0.05 for the introduction as for the expulsion of the variables. The regression equation is:

$$C_{thI} = -0.27\ (\pm 0.07) + 0.10\ (\pm 0.02)\ C_m$$
$$N = 32;\ S = 0.053;\ R^2 = 0.9850;\ F_{obs} = 1964.55 \qquad (8)$$

Where N is the number of paired value of C_m and C_{th}; $F_{obs} = s_1^2/s_2^2$, s_1^2 is the variance due to the regression line (variation of C_{th} with C_m) and s_2^2 is the residual variance about the regression line (measures the scatter of the C_{th} values about the regression line); s is the standard error.

The observed F value is very higher than the value which was given by the table for 99.9% confidence level. The test is therefore, highly meaningful and, thus, at a time, there is a correlation between C_{thI} and C_m.

We also calculated after each iteration the statistical parameters and we took the results which carry out at the same time, the best line of least squares (weakest intercept; slope closest to unity), weakest sum of the squares about the regression and best value of the F-statistic (algorithm II). The regression equation is then:

$$C_{thII} = -0.007\ (\pm 0.016) + 1.02\ (\pm 0.023)\ C_m$$
$$N = 32;\ S = 0.022;\ R^2 = 0.9939;\ F_{obs} = 4865.12 \qquad (9)$$

We don't note traces of inadequacy of the adjustment.
Way in which it was obtained, the regression line (9) is the best possible one and it is interesting to compare it to that provided by algorithm I (Eq. 8).

We first compared the ordinate values of the average points (C_{thI} and C_{thII}) the difference of which is not significant since t observed (= 0.02) is lower than the limit of t given by the table of Student, for $N_I + N_{II} - 4 = 60$ degrees of freedom (df), on the degree of confidence 95% ($t_{0.975} = 2.00$) and on the degree of confidence 99% ($t_{0.995} = 2.06$).

Then we tested the difference between the angular coefficients of the two lines. Test is not significant, insofar as t observed (= 0.95) is lower than the limit given by the table of Student, on the degrees of confidence 90 and 99% per 60 df.

Finally we compared the variances for the risk $\alpha = 0.05$ divided in α_1 and α_2 such as $\alpha_1 + \alpha_2 = 0.025$ and $N_1 = N_2 = 32$ df, the table of Snedecor gives:

$$F_{1-\alpha 2} = F_{0.975}; \qquad F_{\alpha 1} = \frac{1}{F_{1-\alpha 2}} = 0.49$$

The experimental value F = 0.18 being smaller than $F\alpha_1 = 0.49$, the assumption of equality of the variances have to be refused ($\sigma_{II}^2 \neq \sigma_I^2$).

Thus, tests emphasize the lack of translation or rotation of the one of the straight regression lines compared to the other. On the other hand, the comparison carried out makes it possible to highlight an increase in the dispersion of the results provided by algorithm I, when the profiles of concentration are simulated over a large interval of time, with consequences substantial residuals for the local concentrations such as the masses transferred at different times.

Calculated local concentrations check closely Eq. 2. Results summarized hereafter:

N	$LnD_0 \pm \sigma$	$A \pm \sigma$	S	r	F_{obs}
32	16.0048 ± 0.0003	171.175 ± 0.0098	0.0004	1	1.775×10^8

show that the model is self-consistent, that is the diffusion is well concentration-dependent as indicated above.

CONCLUSION

When plasticized PVC discs are soaked in groundnut oil, there is a simultaneous transport of the liquid into and the DEHP out of the PVC. The transport kinetics in the liquid food were completed by the study of the migratory phenomenon in PVC itself, leading to the profiles of the DEHP concentrations developed through the polymer bulk during the process. Groundnut oil penetrates into PVC discs with difficulty resulting in weak rates of sorption and small amounts of sorbed oil.

A mathematical analysis was undertaken by neglecting the small amounts of groundnut oil transferred into the polymer matrix. The simplified model was found to be available for determining the DEHP concentration profiles, which integration provide correct values for transferred mass DEHP into groundnut oil. The straight regression lines of C_{th} (calculated profile) against C_m (measured profile) can mingle (algorithm II) or not (algorithm I) with the first bisecting line, which influence the precision of the evaluation of the transferred mass DEHP.The precision is about 6 % in the first case and it practically doubles (13%) in the second.

The model is self-consistent; that is the data obtained verify the assumption of an exponential concentration-dependent diffusivity.

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