

Food and Packaging Interactions: Penetration of Fatty Food Simulants into Rigid Poly(vinyl chloride)

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Two complementary methods for the determination of the extent of polymeric packaging penetration by food simulants which are in contact with rigid poly(vinyl chloride) (PVC) are presented: (i) the depth of penetration of the simulant is measured by optical microscopy of sectioned slices of the material; (ii) methyl red, dissolved in methyl palmitate, was incorporated in the PVC. Subsequent spectrophotometric analysis of the samples from method ii reveals that the penetration of the dye is governed by the penetration of the simulant. Absorbance measurements can thus be used for an indirect evaluation of the penetration of the simulant. Mixtures of olive oil and methyl palmitate have been studied, and general considerations on the use of binary mixtures used as food simulants are discussed.

INTRODUCTION

The overall interaction of plastic packaging materials with foodstuffs is best described by global migration, which is the sum of all of the specific—or individual—migrations of the plastic constituents into foodstuffs or model food. Global migration is usually measured as the difference of weight of the package before and after contact. Existing regulations have defined possible food simulants (sunflower oil, olive oil, and HB 307 for fat foods) and the highest tolerable global migration level (60 mg/kg of food simulant) (Food and Drug Administration, 1976; Council of European Communities, 1982, 1985; Risch, 1988). Especially with fatty food simulants, the lengths of both contact times and analytical procedures are not suitable for on-line control, since the weight of the package after contact has to be corrected by the amount of fat adsorbed by the plastic, a determination that requires a tedious procedure. Furthermore, there is a need for a worldwide standardization of control methods. These considerations are currently stimulating the search for improved quick methods. Three main strategies can be envisaged for this purpose.

Strategy 1. Improvement of the Present Global Migration Analytical Procedure. Improvements should concern the procedure for quantitative extraction and determination of the oil adsorbed by the plastic material, e.g., by the use of radiolabeled simulants (Figge, 1980).

Strategy 2. Modification of the Present Global Migration Analytical Procedure. The present trend is to replace the triglyceride mixtures by volatile compounds, such as 2,2,4-trimethylpentane (isooctane) (Gramiccioni et al., 1986; De Kruijff and Rijk, 1988), aqueous tetrahydrofuran (Adcock et al., 1984), and aqueous ethanol (Piringer, 1990; Figge and Hilpert, 1991).

Strategy 3. Replacement of the Global Migration Method by New Methods. These include optical density measurements of the simulant at 200 nm, which increase with the migration (Lox et al., 1988), or determination of the main potential migrants by the extraction of the packages, followed by a chromatographic (Van Battum and Van Lierop, 1988) or spectrometric (Bouquant et al., 1991) analysis.

Most of the recent work has focused on strategy 2, since

the results can also help to simplify specific migration measurements. The main feature under discussion concerns the threefold relationship between the penetration of the simulant into the plastic, its interaction with the polymer, and the migration of plastic package components (such as residual monomers and additives) into the foodstuff or food simulant. If penetration is the predominant process governing migration phenomena, then, in some instances, global migration tests could be replaced by penetration tests.

The influence of penetration on the migration of additives has been frequently noted (Pfab, 1973; Piringer, 1990; Papaspyrides and Duvis, 1990; Riquet et al., 1991). However, the recent observation that 2,6-di-*tert*-butyl-4-methylphenol (BHT) can migrate with similar efficiency both into olive oil and into porous solids, such as dry foods and charcoal (Schwope and Reid, 1988), led to a reexamination of the exact role played by penetration. On the basis of the literature data on polyolefins, the penetration of food simulants into the plastic has been shown to have no influence on migration for the following extreme situations (Piringer, 1990): (a) with high molecular weight simulants and mobile low molecular weight additives [this is precisely the case for the olive oil/BHT system (average MW = 908 and 220, respectively)]; (b) with low molecular weight simulants which exhibit little interaction with plastics (this is observed with ethanol in contact with apolar polyolefins, provided the temperature does not exceed room temperature).

To define adequate new simulants, several other factors have to be taken into account: (i) Migration into foodstuffs or food simulants implies not only the highly mobile constituents of plastics but also other additives, with higher molecular masses and hence lower mobilities (Castle, 1991). (ii) Plastics that are more polar than polyolefins (e.g., PVC) interact more strongly with ethanol, even at room temperature. (iii) Temperatures exceeding room temperature are often used for the tests to speed up the experiments; under such conditions, simulants like ethanol may also interact with the least polar plastics.

For a better understanding of food and packaging interactions, simple and sensitive methods are needed to evaluate the depth of penetration of foodstuffs or their

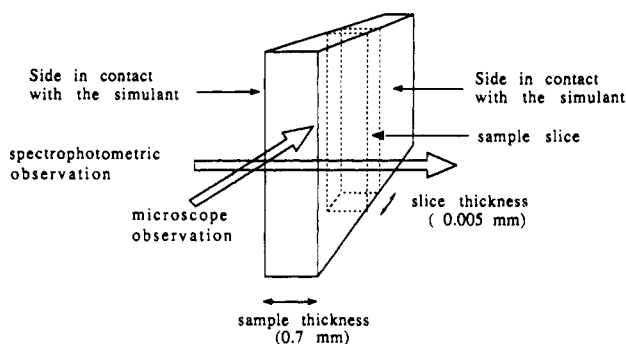


Figure 1. Sampling and observation of rigid PVC.

simulants into plastics. Radiotracer methods are often used for this purpose (Figue, 1980), but they require special laboratory equipment and practice. Weight uptake measurements are much simpler to carry out (Adcock et al., 1984), but they can be altered by weight losses due to migration of additives (Papaspyrides and Duvis, 1990). Other techniques have recently been proposed in the literature, such as longitudinal (i.e., parallel to the contact surface) microtomy of polymer samples, followed by appropriate analysis of the slices (Adcock et al., 1984; Lum Wan et al., 1991), electron spin resonance imaging (Berliner et al., 1986), or nuclear magnetic resonance imaging (Webb and Hall, 1990). It should be noted, however, that the resolution of these methods is never better than 10 μm , too high a value for appropriate measurements of the penetration of many fatty foodstuffs. In the present paper, we report on the evaluation of the penetration depth using optical microscopy, which affords a much better resolution (1 μm). These measurements are further complemented by a spectrophotometric method.

MATERIALS AND METHODS

The PVC sheets studied were prepared by Dorlyl, Le Havre; they were transparent and had the same composition as rigid PVC bottles for mineral water. Methyl palmitate, methylene blue, β -carotene, and methyl red were obtained from Aldrich. Olive oil (nonrefined) was purchased in a retail store.

Conditions of Contact. Each PVC sample ($0.08 \times 0.4 \times 1$ cm) was cut out from a sheet and immersed in the simulant (2 mL) in a screw-stopped flask. Whenever dyes were added to the simulant, their concentration is indicated in the text. The flasks were then held at 50 $^{\circ}\text{C}$ in an oven for the appropriate time. Three samples were analyzed for each contact time.

Spectrophotometric Measurements. After immersion, the samples were wiped, washed briefly with ethanol, and dried; the optical density of the colored samples was measured at 498 nm (λ_{max} of methyl red) with a Perkin-Elmer Lambda spectrophotometer, the plastic sheets being held between two quartz plates, mounted on a spring cell holder (Hellma). To account for the slight yellowing of PVC, appearing with time of contact, a sample which had been in contact under the same conditions, but without dye, was used as reference (Figure 1). Each absorbance value was measured four times independently.

Sectioning. The samples, recovered after spectrophotometric analysis, were microtomed to slices of 5- μm thickness, as shown in Figure 1 (Gabel and Wittmann, 1991). The depth of the diffusion layer was measured by image analysis with a Biocom 200 instrument. Each depth value was measured 40 times independently.

RESULTS AND DISCUSSION

Penetration of Methyl Palmitate in PVC. According to strategy 2, volatile organic compounds (heptane, isooctane, tetrahydrofuran, and ethanol) are good candidates for simulating the contact of fatty foods with plastics. They are, however, very different from fats with respect to their

polarity, their affinity for polymers, and their molecular mass. We therefore based the present study on a fatty ester, methyl palmitate, which is structurally closer to fats while bearing some similarity to the volatile simulants regarding its molecular mass and its mobility. Similar fatty esters have been used for the modelization of food and packaging interactions in two recent studies (Riquet et al., 1991, methyl oleate; Lum Wan et al., 1991, methyl stearate).

Diffusion Constant of the Simulant. When the PVC samples were immersed in methyl palmitate at 50 $^{\circ}\text{C}$, a well-defined diffusion layer was observed in transmitted light or phase contrast microscopy (Figure 2), similar to those observed for diffusion of solvents in PVC (Lapcik and Panak, 1976). In the absence of defects, the inner boundary of the diffusion layer was parallel to the contact surface (Figure 2B), and for a given time of contact, its thickness, e , remained remarkably constant. Defects in the sheet (cracks, inhomogeneities) dramatically altered the otherwise straight profile of the diffusion front (Figure 2C). In contrast to what has been reported for solvents (Lapcik, 1976), no marked swelling was observed with methyl palmitate. After 9 days at 50 $^{\circ}\text{C}$, the penetration depth was about 100 μm . Individual measurements ranged from 70 to 120 μm .

The diffusion depth of organic compounds (chloroform, toluene, cyclohexanone) in PVC has been shown to follow a linear relationship with the square root of time (Lapcik and Panak, 1976). As shown in Figure 3, a similar correlation was observed for methyl palmitate over a 58-day period, with a slope of $8.7 \times 10^{-6} \text{ m h}^{-0.5}$. The diffusion constant of the simulant could thus be calculated from this value and from eq 1 (Lapcik and Panak, 1976):

$$e = 2(Dt)^{0.5} \quad D = 18.9 \times 10^{-12} \text{ m}^2 \text{ h}^{-1} \quad (1)$$

Use of optical microscopy allows determination of the penetration with good accuracy. However, at the microscopic level, local inhomogeneities of PVC are responsible for the large dispersion of e values apparent in Figure 3. A macroscopic method, which could average these local variations, was therefore investigated.

Use of Dyes as Probes for the Penetration of the Simulant. Fat-soluble dyes, namely β -carotene and methyl red, were dissolved separately in simulant. With both dyes, the recovered samples were red in color and it was possible to measure their optical density as shown in Figure 3, but since much deeper colorations were obtained with methyl red, only this dye was used for further experiments. Two types of experiments were run to follow the incorporation of the dye into the PVC.

1. **Contact with Saturated Solutions of Dyes.** When the simulant was saturated with methyl red, the coloration of the diffusion layer in the microtomed slices was apparent by optical microscopy. Observation of these slices then revealed the following main features [Figure 2B; for a color picture, see Gabel and Wittmann (1991)]: (a) The dye was **exclusively** located in the diffusion layer of the simulant. (b) This diffusion layer, up to 100 μm in thickness, was apparently uniformly colored. For higher e values, the coloration faded near the inner border of the diffusion layer. Defects in the plastic had similar effects. Figure 2C shows the case of a sample with defects which has been deeply penetrated.

These observations suggested that the dye can be used as a probe reflecting the penetration of the simulants.

However, after a contact of 10 days at 50 $^{\circ}\text{C}$ with saturated solutions of dye in the simulant, the optical

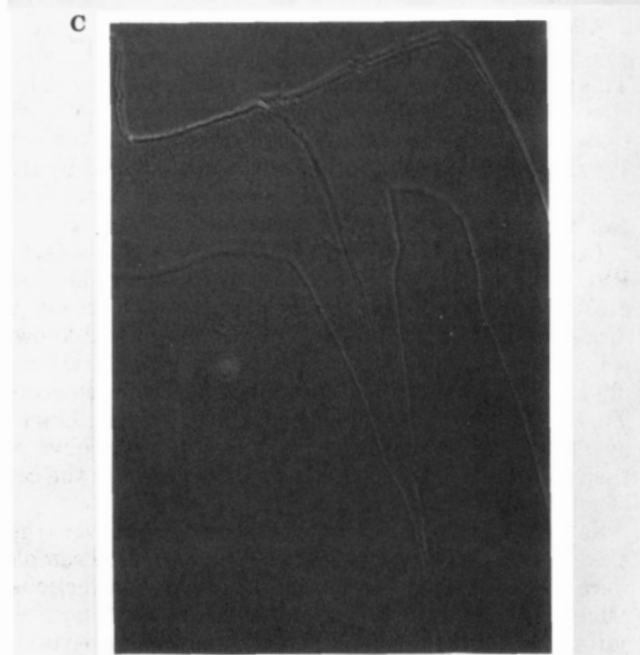
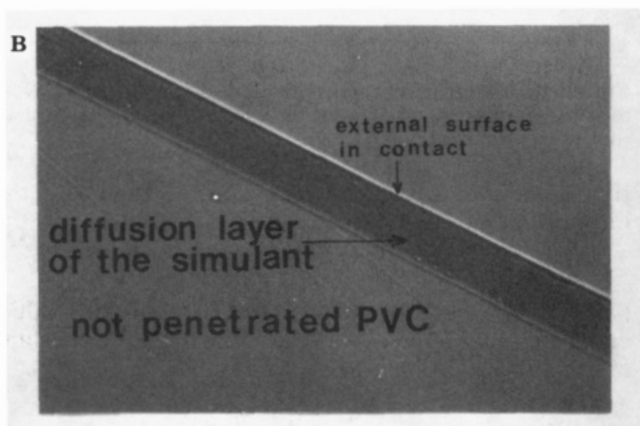
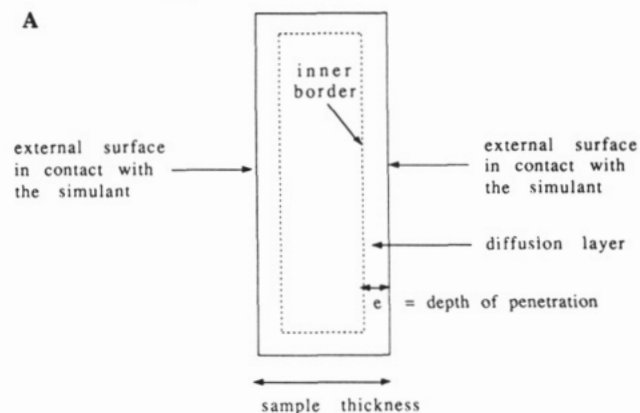


Figure 2. (A) PVC slice after contact of the sample with methyl palmitate. (B) Diffusion layer of methyl palmitate in rigid PVC after a contact of 9 days at 50 °C (the depth of the diffusion layer is here 100 μm). (C) Influence of defects on the diffusion layer of methyl palmitate in rigid PVC.

density of the recovered samples was higher than 3 absorbance units, rendering these conditions unsuitable for kinetic measurements. The experiments were therefore repeated, using more dilute solutions of the dye in the simulant.

2. *Contact with Dilute Solutions of the Dye in the Simulant. The Spectrophotometric Approach.* With dilute solutions of the dye in the simulant (0.01–0.04 g L^{-1}), the optical density (OD) of the sample could be determined as shown in Figure 1. OD was measured as

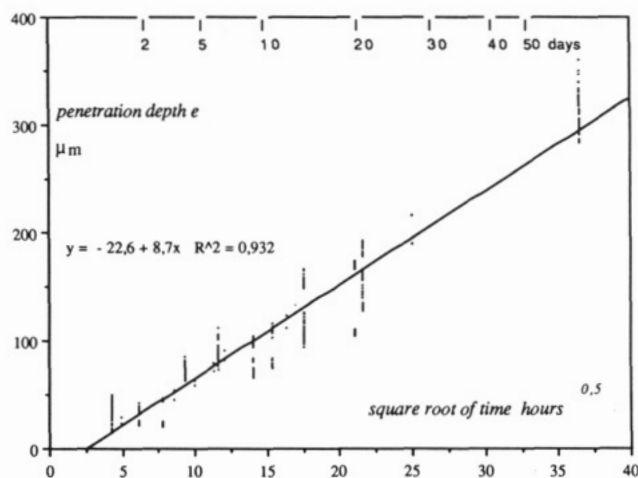


Figure 3. Variation of the depth of penetration of methyl palmitate in rigid PVC with square root of time at 50 °C.

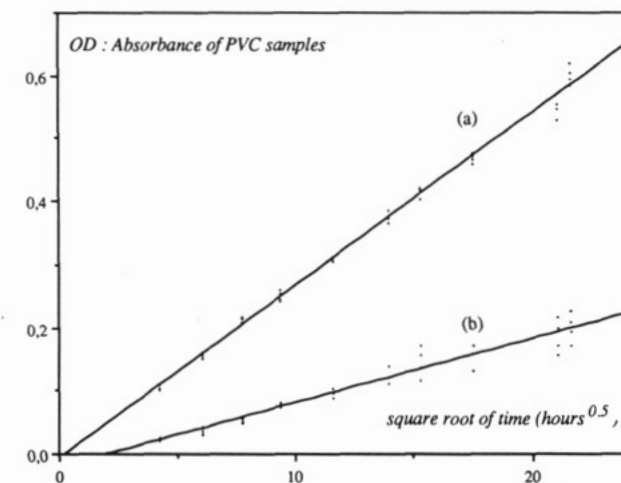


Figure 4. Penetration of methyl red [(a) 0.04 g L^{-1} ; (b) 0.01 g L^{-1}]/methyl palmitate into rigid PVC: optical density vs square root of time.

a function of the time of contact, and the results are shown in Figure 4.

The observation shown in Figure 2B and mentioned in the preceding section suggests that the OD of the sample can be correlated to the depth of penetration of the simulant.

Assuming that the Beer–Lambert law can be applied to the PVC samples, eq 2 can be derived

$$\text{OD} = 2e\epsilon c \quad (2)$$

where ϵ and c are, respectively, the extinction coefficient and the concentration of the dye in the diffusion layer; $2e$ is the optical path (e on each side, as the sample is immersed).

Combining eqs 1 and 2 gives

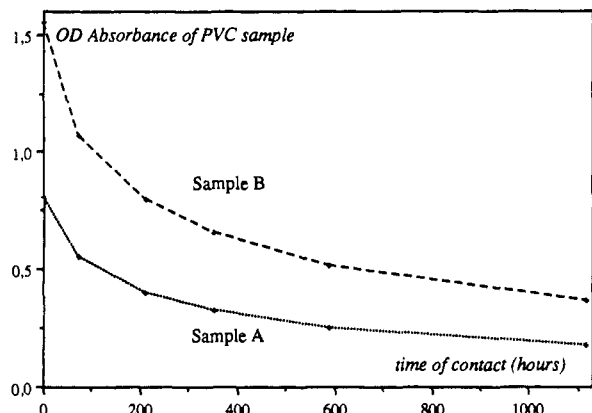
$$\text{OD} = 4(Dt)^{0.5}\epsilon c \quad (3)$$

Figure 4 shows that linear plots of OD vs square root of time are indeed obtained, in agreement with eq 3. Using eq 2, the extent of penetration of the simulant can thus be evaluated with the help of optical density measurements. An advantage of this approach is the lower dispersion of measured OD values: as expected, this method is not affected by the heterogeneities of PVC.

Diffusion Constant of the Dye in the Penetrated Layer. As observed with concentrated solutions of dye in the simulant, the penetration of the dye in the polymeric network is very similar to that of the simulant. Additional

Table I. Preparation of PVC Samples A and B

sample	duration of first contact with methyl palmitate, days	concn of methyl red in the simulant, g L ⁻¹	OD of PVC samples at 498 nm (OD ⁰)
A	9	0.08	0.810
B	9	0.16	1.552

**Figure 5.** Migration of methyl red out of the diffusion layer: absorbance of PVC samples A and B vs time of contact.

support for this statement could be provided by the measurement of the diffusion constant of methyl red in the diffusion layer.

In a first step, two PVC samples, A and B, were immersed in methyl palmitate containing methyl red at two concentrations c_A and c_B (Table I). In a second step, these samples were placed in contact with dye-free methyl palmitate, and their loss of color was then followed by measuring their optical densities as a function of time of contact (Figure 5).

Definitions of parameters used and elements for eqs 4–7: t , duration of the second incubation, with dye-free methyl palmitate (hours); c_t , concentration of the dye in the diffusion layer at time t ; OD_t , optical density of PVC sample after contact for time t (second incubation); OD^0 , optical density of PVC sample at $t = 0$ (just before the second incubation); e_0 , e , depth of the diffusion layer at times 0 and t , respectively; ϵ , extinction coefficient of methyl red in the diffusion layer at 498 nm; S , surface of sample in contact with the simulant; m_0 , mass of dye initially incorporated in the sample; m_t , mass of dye present in the sample at time t ; $(m_0 - m_t)$, mass of dye migrated from sample to simulant after contact time t ; $M_t = (m_0 - m_t)/S$, mass of dye migrated per unit area at time t ; D' , diffusion constant of the dye in the diffusion layer.

According to eq 2

$$OD_t = 2\epsilon c_t$$

and since $c_t = m_t/eS$

$$OD_t = 2\epsilon m_t/S \quad (4)$$

and similarly $OD^0 = 2\epsilon m_0/S$.

Therefore

$$M_t = (OD^0 - OD_t)/2\epsilon \quad (5)$$

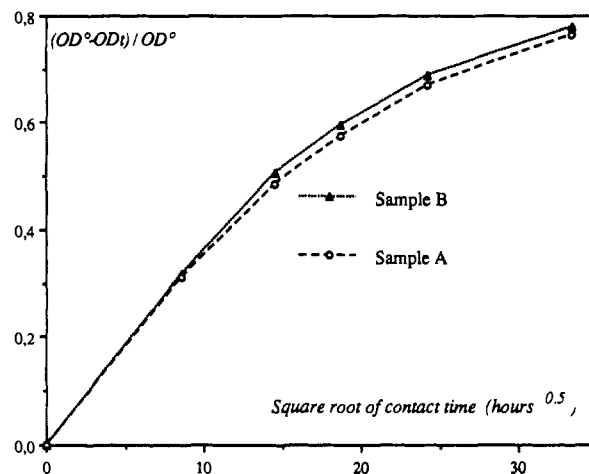
For the initial stages of migration, M_t can be expressed by eq 6 (Kondily et al., 1990):

$$M_t = 2c_0(D't/\pi)^{0.5} \quad (6)$$

Combining eqs 2 and 4–6, we obtain

$$(OD^0 - OD_t)/OD^0 = 2(D't/\pi)^{0.5}/e_0 \quad (7)$$

The plots of $(OD^0 - OD_t)/OD^0$ vs the square root of

**Figure 6.** Migration of methyl red out of the diffusion layers of PVC samples A and B: plot of $(OD^0 - OD_t)/OD^0$ vs square root of contact time.

time are shown in Figure 6. As expected from eq 7, the initial slope of these curves

$$2(D'/\pi)^{0.5}/e_0 = 0.035 \text{ h}^{0.5}$$

is identical for both samples A and B. From this value, and from a measured $e_0 = 100 \text{ m}^{-6}$, the diffusion constant of the dye in PVC can be calculated:

$$D' = 9.6 \times 10^{-12} \text{ m}^2 \text{ h}^{-1}$$

Although not identical, the values of D and D' can be considered to be in agreement, within experimental error. This is justified by considering the variation of the e values shown in Figure 3. This therefore confirms the observations made with concentrated solutions of dye (Figure 2B), showing that the penetration of the dye is ruled by that of the simulant. This also confirms the equivalence of the two approaches: e and OD measurements.

Interaction of PVC with Olive Oil. After contact of PVC samples with olive oil, for up to 25 days at 50 °C, no diffusion layer could be observed by optical microscopy. Since the sorption of olive oil by plastics is well-known, this can be interpreted as the depth of penetration of olive oil being below the resolution of optical microscopy. This explanation seems likely, as due to the much higher average molecular mass of the constituents of olive oil, their penetration could be much slower than in the case of methyl palmitate.

Saturated solutions of methyl red in olive oil were then used as simulants. After 25 days, the recovered samples were pink in color. These samples were then sectioned aslant, to take as much as possible the layer near the surface. A thin colored layer could thus be observed under the microscope. Indeed, the sorption of dyes and, more generally, that of food constituents by plastics can be ruled by several types of effect: (i) by their partition coefficients between the simulant and the polymer [such phenomena have been reported for aqueous foods such as fruit juices (Landois-Garza and Hotchkiss, 1987; Moshonas and Shaw, 1989) or dairy products (Akermann et al., 1991) in contact with apolar plastics]; (ii) by penetration of the food or food simulant in the polymer (this is what has been demonstrated above for the methyl red/methyl palmitate system).

The latter mechanism seems more likely for the methyl red/olive oil system because of the functional and structural similarities between methyl palmitate and the olive oil triglycerides. However, since other interpretations of these observations are still possible, further work is needed,

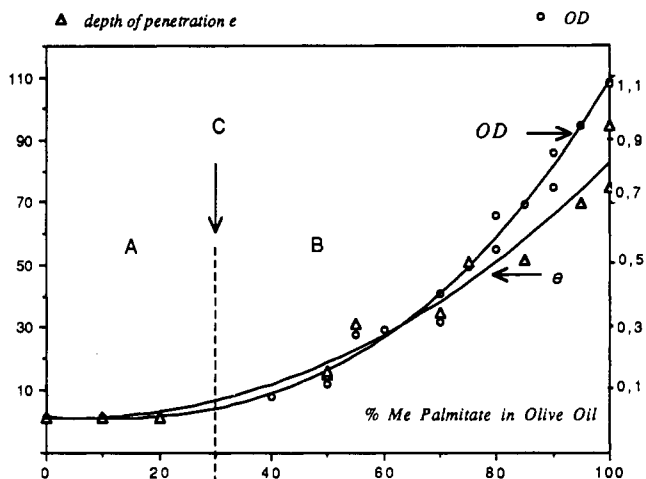


Figure 7. Penetration of olive oil/methyl palmitate mixtures in rigid PVC: (Δ) depth of penetration (in μm); (\circ) methyl red absorbance; (A) area for realistic simulants giving slow migration tests; (B) area for simulant giving fast migration tests but unrealistic food simulation; (C) the compromise, the composition of the breaking point.

in conjunction with other techniques, to confirm whether the colored layer observed here is a diffusion layer of olive oil in PVC.

Binary Mixtures of Simulants: Olive Oil and Methyl Palmitate. Since olive oil is a natural mixture, variations in the composition can cause different penetration and migration results, and the synthetic standardized mixture of triglycerides HB 307 had therefore been proposed for migration tests (Figge, 1980). We investigated the influence of the percentage of added methyl palmitate on the penetration of olive oil in rigid PVC, using both slice analysis under the microscope and the spectrophotometric method.

As expected, both parameters, e and OD, exhibit the same behavior, as shown in Figure 7. It appears that addition of methyl palmitate up to 30% in olive oil has little effect on the penetration depth: such mixtures behave essentially like olive oil. Deviations in the composition of olive oil do not appear to induce changes in behavior with the techniques used here. At around 30%, there is a break in the curve, and the penetration increases rapidly with the percentage of methyl palmitate.

It is remarkable that similar results were reported by weight uptake measurements for simulants prepared from binary mixtures of a nonpenetrating, or weakly penetrating, compound (e.g., water or methanol) with a more strongly penetrating substance (e.g., chloroform, toluene, or tetrahydrofuran) (Adcock et al., 1984): for different polyolefins, the plots of weight uptake as a function of the composition of the simulant exhibit such breaking points, which can thus be considered as typical of the interactions. There is also some evidence in the literature that such breaking points occur for migration as a function of the composition of ethanol-water mixtures used as simulants (Messadi and Vergnaud, 1982).

This breaking point represents the transition between weak and strong interaction of the simulant with the polymer. It represents also a compromise between the conflicting requirements of rapid migration tests vs realistic fatty food simulation: On one hand, the higher the percentage of the most penetrating compound, the higher the solubility of additives in the simulant and the faster the migration. Such simulants, however, interact much more strongly with the polymer than do most real foods. On the other hand, the lower the interaction, the

more realistic the food model. But simulants which interact weakly with the polymer tend to give slow migration tests.

To develop adequate new migration simulants, the good compromise could be to adjust the composition of a binary mixture to that of the breaking point. The spectrophotometric method presented here can be very useful for the determination of this critical composition of the mixture.

CONCLUSION

The two methods presented here are very complementary: by optical microscopy, it is possible to measure depths of penetration of simulants in transparent PVC; the spectrophotometric method does not require any special laboratory equipment and is very easy to carry out. It should be pointed out, however, that this spectrophotometric approach needs to be validated by microscope observations. The different incorporations of methyl red into PVC from methyl palmitate and from olive oil confirm that the sorption of this dye by the packaging material is controlled by the penetration of the fatty food simulant. This is probably true for many low molecular mass food constituents. Correlation of the penetration data with migration of plastic additives into the simulants is now in progress.

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