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**Application of FTIR and Raman microspectroscopy to the study of
food/packaging interactions**

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Abstract

This study assesses the suitability of FTIR and Raman spectroscopy for potential use as analytical tools for determining the diffusivity of a migrant in a plastic packaging material, one of the key points in safety assessment of food contact materials (FCM). Despite its relative low sensitivity, FTIR based analysis supplied data for the material on desorption of an additive (Uvitex OB) and sorption of a food constituent (olive oil) in a non-destructive and “in situ” mode. These data allowed the determination of the diffusivity of Uvitex OB ($8.0 \pm 2.5 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$) and olive oil ($6.9 \pm 3.4 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$) in LLDPE. Raman cartography innovatively supplied the profile of additive concentration in the z-direction (thickness) of the FCM and confirmed that mass transfer in the system roughly followed a Fickian behaviour.

Introduction

Testing for migration of food contact material additives into foods or food simulating liquid is a crucial point of safety assessment of packaging materials. However these tests, based on destructive extraction and quantification (e.g. chromatographic or spectrophotometric) procedures, are expensive and time-consuming. The directive 2002/72/CE considers the use of “generally recognised diffusion models based on experimental data [...] under certain conditions” to determine overestimated migration levels. Most of these models, used to describe migration, are based on Fick diffusion equation that involve (Crank 1980) at least two key parameters : (i) the diffusion coefficient (D), a kinetic parameter, which measures the average ability of molecules to diffuse across the permeable phase of polymer film, and (ii) the partition coefficient (KPL) which is the ratio of additive content in the packaging material and in the foodstuff at equilibrium. Empirical and semi-empirical relationships (Begley et al. 2005; Brandsch et al. 2002; Franz 2005; Piringier 1994; Reynier et al. 1999; Reynier et al. 2001b; Vitrac et al. 2006) enable a rough evaluation of these parameters that would require otherwise a high number of experimental mass transfer tests, to be determined experimentally. An outstanding example of such relationship is the so called “Piringier equation” used to determine the diffusivity of a migrant and needs as inputs the temperature during the process, the molecular weight of the migrant and five constants, two of which depend on the type of polymer. All these parameters have been derived from a thorough analysis of reported diffusion coefficients in order that the diffusion coefficient determined should always overestimate the real value. Alternatives to the estimation of the diffusion coefficient have used the volume of the migrant (Reynier et al. 2001b) ; the Van der Waals volume, the

gyration radius and a shape parameter (Vitrac et al. 2006) in order to refine the predictions. Less attention has been paid though to the prediction of the partition coefficient and a commonly accepted approach has been to take it as $K_{PL}=1$ if the migrant is soluble in the food/food simulant or $K_{PL}=1000$ otherwise (European Commission 2003) . A “worst case” relationship has been proposed aiming at the prediction of the partition coefficient in foodstuff depending on the partition coefficient in the n-octanol/water system ($\log P$) of the migrant and two empiric parameters (Pocas et al. 2008) .

These “predictive approaches” have been the object of some criticism whenever they are used with polymers other than polyolefins, or at high temperature or for high molecular weight migrants, at least, until more experimental data are available. Helmroth et al (2002a) found for instance that, if the Piringer model was applied to the case studied by Reynier et al (2001a) in PP at 70 °C, 50% of the predicted values underestimated the experimental ones. Other authors, such as Helmroth et al (2002b; 2003) and Reynier et al (2002) , have put in turn efforts to formulate coherent methodologies to take into account the potential swelling of the polymer caused by the sorption of a solvent, as well as to determine the influence of this swelling in the release of substances into food. Of course, the success of these approaches lies also in an efficient way to obtain the kinetic data. With this scope, spectroscopic methods have been successfully used for investigation of sorption-desorption process of small molecules in polymer films (Cava et al. 2005; Cotugno et al. 2001) .

This study aimed to explore the use of vibrational spectroscopy to study food/packaging interactions and provide data that could be used to determine the mass transfer parameters of the system. Despite its high detection limit, FT-IR based analysis supplied a very useful experimental tool to monitor transfer properties of polymer films in a non-destructive mode. Other methods, such as micro-UV(Reynier et al. 2002) , provide information about the migration process taking place inside the polymers with a micrometer-scale spatial resolution. Likewise, Raman micro-spectroscopy has been used to study to determine concentration profile of low molecular weight compounds in the polymers at a micrometric scale (Sammon et al. 1999) . This method could be considered as a promising complementary method of micro UV (active molecules in UV are not necessarily active in Raman and *vice versa*), to investigate in a versatile, quick and non-destructive way, the distribution profile of additives in plastic material. With confocal collection optics, the method should allow to follow the migration process as a function of both time and space and, consequently, to plot additive

concentration profile in the depth of polymer sample in order to easily gather mass transfer parameters. To the best of our knowledge, this has never been done up to now, partly because both methods are not considered as sensitive enough to study migration, but, as it will be seen subsequently, they can be successfully used to characterize mass transfer in model systems.

Two different approaches were used to determine the diffusivity of a migrant in a plastic packaging material by two vibrational spectroscopy methods i.e. FT-IR and Raman spectroscopy. Uvitex OB, an optical brightener and UV stabiliser approved for Food Contact Materials, was selected as model migrant to spike LLDPE films. The samples were submitted to migration test according to EC directives and analysed by FT-IR and Raman microspectroscopy during immersion in the worst case food simulating liquid *i.e.* the olive oil, with the objective to determine the diffusion coefficient on the basis of a resolution of Fick's law.

Theory

The internal diffusion of migrant in the packaging is:

$$t > 0, -L < x < L, \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (1)$$

where x is the distance (m), C the packaging concentration in migrant (kg additive/kg of polymer) and D the migrant diffusivity in the packaging (m^2s^{-1}). If D is independent of the concentration of the diffusing substances (at least at the concentration range found in the experiment), the system is said to follow Fickian kinetics.

Equation (1) was solved with the initial and boundary conditions that apply for this case study *i.e.*:

$$t = 0, -L < x < L, C = C_{in} \quad (2)$$

$$t > 0, x = +L, C = C_{L,\infty} \quad (3)$$

$$t > 0, x = 0, \frac{\partial C}{\partial x} = 0 \quad (4)$$

where C_{in} is the concentration initially present in the polymer, $C_{L,\infty}$ is the concentration of the diffusing substance on the surface of the polymer required to maintain equilibrium with the concentration of this substance in the liquid at time t .

In some cases, the diffusivity D is dependent on the concentration of the diffusing substance as it is the case of substances that alter the structure of the polymer. According to the free volume theory, D is proportional to the exponential of the free volume within the polymer (Duda and Zielinsky 1996). Based on this assumption, several authors (Helmroth et al. 2003; Reynier et al. 2002) have successfully modelled the dependence of D as:

$$D(x,t) = D_0 \exp\left(\gamma \frac{c(x,t)}{c_{MAX}}\right) \quad (5)$$

where D_0 is the zero concentration diffusivity and γ is a proportional factor. Of course, if γ is equal to zero, diffusivity is a constant and kinetics follows the Fickian model. Taking into account the potential dependency of diffusivity and concentration, several scenarios are possible; case i) diffusivity is independent of Uvitex OB and olive oil (Fickian kinetics); case ii) diffusivity depends only on Uvitex OB concentration; case iii) diffusivity depends only on olive oil concentration; and case iv) diffusivity depends on both Uvitex OB and olive oil.

Solving procedure

If the sorption/desorption phenomena follow Fickian kinetics, the system of equations (1-4), can be solved analytically and the evolution of concentration with time is given by Crank(1980):

$$\frac{C(x,t) - C_{in}}{C_{L,\infty} - C_{in}} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left[-\frac{(2n+1)^2 \pi^2}{4L^2} D.t\right] \cos\left[\frac{(2n+1)\pi x}{2L}\right] \quad (6)$$

$$\frac{\bar{C}_t - C_{in}}{C_{L,\infty} - C_{in}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{(2n+1)^2 \pi^2}{4L^2} D.t\right] \quad (7)$$

where C is the concentration in diffusing substance in x at time t and $\bar{C}_t$ is the average concentration in diffusing substance in the packaging at time t .

Nevertheless, if Fickian kinetics cannot be assumed e.g. D varies with the concentration of migrant and/or with olive oil entering the packaging, there is no analytical solution to Equation (1). Considering an exponential relationship between concentration and diffusivity (Equation (5)), Equation 1 was solved using a Crank-Nicholson-like scheme i.e. a central difference in space and a trapezoidal rule in time.

Materials & Methods

Chemicals

Uvitex OB and solvents were of reagent grade or highest purity available. 2,5-Bis-(5-tert.-butyl-benzoxazol-2-yl)-thiophen (Uvitex OB, 430.6 g mol⁻¹) was purchased from Fluka.. Methanol (99.9%), tetrahydrofuran (THF, 98%) and toluene (99%) were purchased from Carlo Erba. LLDPE pellets were purchase from Sigma Aldrich. Olive oil was purchased in a local supermarket.

Films fabrication.

LLDPE pellets were mixed with additives at 140°C (50 rpm) during 5 min in a twin counter rotating internal mixer (Rheomix 600 Haake, Germany) connected to a control unit (Rheocord 9000 Haake, Germany). Then, the dough material obtained after mixing was then thermoformed (hot press) at 100 bar during 10 min at 140°C. Films preparation was kindly carried out by IMCB (Naples, Italy). A nominal concentration of 0.4% w/w was used, higher than found in commercial polymers. The thickness obtained was 656 ± 64 µm (measured by a micrometer, Braive Instruments, Chécy, France).

Migration test

Following the conditions set in directives 85/572/EEC and 2002/72/EC, 3.5 cm² film samples were fully immersed in 6 ml olive oil at 40°C. Before each measurement the sample were removed from the olive oil and thoroughly wiped in a reproducible way with a precision wipe. The weight was recorded to determine the uptake of olive oil. FTIR measurements were done after 3, 6, 10, 15 and 26 days of storage. Raman measurements were done after 4h, 1 and 3 days of storage.

Additives extraction

3.5 cm² samples were dissolved in 3 ml of toluene and reprecipited in 15 ml of methanol then filtered with 2 x 5 ml of methanol. The extract was evaporated to dryness in a rotary evaporator (Heidolph VV 2000, Germany) and dissolved again in 10.0 ml of THF.

UV spectroscopy analysis

The quantity of additive in THF extract was determined using a Cary 100 UV-visible spectrometer (Varian) at λ = 374 nm at controlled temperature of 25 ± 2 °C. Two measurements were performed for each sample.

FTIR measurement

LLDPE film samples were analyzed by means in transmission FTIR. Spectra were recorded using a Nexus 5700 spectrometer (ThermoElectron Corp.) equipped with HeNe beam splitter and a cooled MCT detector. Spectral data were accumulated from 128 scans with a resolution of 4 cm⁻¹ in the range 800-4000 cm⁻¹. Three samples were employed for the measure and three spectra were recorded for each sample

All spectra pre-treatments were performed using Omnic v7.3 and TQ Analyst v7.3 softwares (ThermoElectron) Processing included: (1) a multipoint linear baseline correction, (2) a normalization according to the area of the LLDPE doublet (1369-1378 cm⁻¹) due to the CH₃ symmetric deformation vibration.

Raman spectroscopy

Uvitex concentration profiles in the LLDPE were determined as follow. Thin slices of LLDPE were prepared using a razor blade and stuck on a microscope slide (Figure 1).

Raman spectra were recorded between 95 and 3500 cm⁻¹ Raman shift using a confocal Raman microspectrometer Almega (Thermo-Electron) with the following configuration: excitation laser He-Ne λ_0 = 633 nm, grating 500 grooves/mm, pinhole 25 μ m, objective $\times$ 50. The collection time was about 50 sec. Measurements were carried out in the depth sample with a pitch of 2 μ m from the sample center to the interface. Samples were exposed to photobleaching for 15 s from the third day of test in order to avoid fluorescence caused by olive oil sorption. Since the concentration in the samples was too heterogeneous as it will be explained later, a measure of initial concentration was carried out by FTIR to all the samples studied.

All spectra pre-treatments were performed with Omnic v7.1 (Thermo-Electron). Processing included: (i) a multipoint linear baseline correction, (ii) normalization according to the area of the LLDPE specific band at 1129 cm⁻¹ representing the symmetric C-C stretching of all-*trans* PE chains. The relative content of Uvitex OB was assessed using the area of the specific doublet (1569-1614 cm⁻¹) assigned to the aromatic C=C and C=N bands.

Statistics

The test of normality of Anderson-Darling (Trujillo-Ortiz et al. 2007) was used to analyse the homogeneity of the samples.

The root mean square error (RMSE) was used to estimate the quality of model fitting and was calculated as follows:

$$RMSE = \sqrt{\frac{(y_{\text{exp}} - y)^2}{(N - p)}} \quad (8)$$

where y_{exp} and y are respectively the experimental and predicted additive content values (kg of additive/kg of polymer), N is the number of additive content measurements and p is the number of identified parameters.

For each experiment, the average of 95% confidence interval of all the replicates represented the experimental error ($\bar{E}$ in kg of additive/kg of polymer). For estimating the good fitting or not of the model, the RMSE and the $\bar{E}$ were compared. A fitting was considered as good when $RMSE \leq \bar{E}$.

Estimation of diffusivity

The additive diffusivity was identified from experimental data by minimizing the root mean square error (RMSE) between experimental and predicted data (Equations (6) and (7)) and by using an optimization method (Levenberg-Marquardt algorithm, *optimization* routine predefined from Matlab software). A Monte Carlo sampling was applied to the input parameters (concentration, thickness and time) in order to determine the 95% confidence intervals as explained elsewhere (Hessler 1997; Press et al. 1989).

Results

After determining the additive distribution in the film samples, the quantification of Uvitex OB and olive oil content was investigated by FTIR throughout the test and used to determine the migration level of Uvitex OB as well as the diffusivity of both olive oil and Uvitex OB. Likewise, Raman measurements were used to determine diffusivity of Uvitex OB in LLDPE and both results were compared

Uvitex OB distribution in LLDPE samples

The Uvitex OB concentration in LLDPE used for the tests turned out not to be homogeneously distributed as determined by the test of normality of Anderson-Darling

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(Trujillo-Ortiz et al. 2007) (the result was positive for an $\alpha = 0.05$). The distribution of the additive (Figure 2) proved to be heterogeneous and normally distributed. The test of normality was applied to 186 samples and gave as a result a mean concentration of 0.41% w/w with a standard deviation of 0.051%. So the coefficient of variation, i.e. the quotient between the standard deviation and the mean was of 12.2%. As an illustration, this means that the 95% of the samples will have concentrations comprised between 0.31% and 0.50% w/w. For a migration experiment, the additive content is usually assumed to be homogeneous in migration tests for all the samples. However, the distribution of additive among the samples hinders the use of standard destructive methods since the variations on the initial concentration of each sample could be comparable to the variations of concentrations throughout the test. This obstacle can be overcome either by increasing the number of samples for destructive methods (highly time consuming), either using a non-destructive method such as FTIR, that can thoroughly guarantee the traceability of the samples throughout the test and then, avoid the uncertainty caused by the variations in the initial content of additive. Finally, it must be borne in mind that the lack of sensitivity of the methods implied using a high concentration (0.4% w/w of Uvitex OB). If the additive is not completely soluble in LLDPE at that concentration, it would be the responsible for the heterogeneous distribution of the additive.

Quantification of Uvitex OB and olive oil in LLDPE

Simultaneous desorption of Uvitex OB and sorption of olive oil were investigated using FTIR. A detailed study of the additive fingerprint allowed to determine the most suitable bands for the analysis. Considering the blend LLDPE spectrum, Uvitex OB fingerprint exhibited some specific bands which could be employed to detect its occurrence in the films. Regarding the higher absorbance value, Uvitex OB occurrence was specifically detected at 1579 cm^{-1} assigned to the aromatic C=C stretching band (Figure 3). In turn, olive oil sorption into LLDPE was followed in the ester stretching band at 1750 cm^{-1} .

With LLDPE samples including variable contents in Uvitex OB, a Partial Least Square (PLS) model was calibrated on the basis of the intensity ratio $1579/1378\text{ cm}^{-1}$. The regression produced a linear relationship ($R^2 = 0.96$, RMSE= 0.034% w/w) between spectral data and additives concentration measured by UV spectroscopy analysis.

Subsequently, the same procedure was carried out to relate spectral data and olive oil content. The uptake of olive oil was considered to be equal to the increase of mass of the sample less the quantity of Uvitex desorbed (quantified with FTIR measurements). The data fitted satisfactorily the model ($R^2 = 0.99$, RMSE= 0.040% w/w).

Determination of the diffusivities of Uvitex OB and olive oil in LLDPE with FTIR

The migration of Uvitex OB in olive oil was followed during 26 days by FTIR. Spectra were normalized on a specific LLDPE doublet (1369-1378 cm^{-1}) and the decrease in absorbance at 1579 cm^{-1} showed the desorption of Uvitex OB from LLDPE film from an initial content of 0.4% w/w to a value below the detection limit after 26 days. Likewise, the uptake of olive oil in the sample was obtained as a function of time and a plateau was determined at $1.3 \pm 0.1\%$ w/w of olive oil. From data obtained from FTIR experiments, desorption curves of Uvitex OB from LLDPE in olive oil were obtained by plotting the relative concentration as a function of time (Figure 4).

The determination of diffusivity values for Uvitex desorption and olive oil sorption in the LLDPE film was evaluated during migration kinetics in olive oil using equation (7). For Uvitex OB, the resulting diffusivity value was of $8.0 \pm 2.5 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$ and the RMSE of 0.02% w/w, lower than the experimental error evaluated as a 0.04% w/w. This results was in agreement with experimental data previously reported since a value of diffusivity of $5 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$ was found by Dole et al (2006) (same temperature but in LDPE). For olive oil the diffusivity value was $6.9 \pm 3.4 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$ and the RMSE 0.07 % w/w, slightly larger than the experimental error estimated as 0.04% w/w but remaining still in an acceptable range. The use of non-destructive measurement by FTIR allowed to fully trace the content of Uvitex OB of the sample all throughout the experiment and thus, to determine an accurate value of diffusivity which would not be feasible with other common analytical procedures with a comparable accuracy. Furthermore, FTIR also provided data on the uptake of olive oil in the sample that led to the determination of its diffusivity in LLDPE. Advantages of FTIR to carry migration tests out include, besides the possibility to obtain non-destructive measurements, supplying additional information of the polymer evolution (e.g. oxidation) and of a number of substances that could be sorbed during the test. Its main disadvantage lies in its lack of sensitivity compared to other analytical methods. When dealing with complex migration behaviour, as for instance, when diffusivity can no longer be considered as a constant (non-

Fickian kinetics), a large number of data are required that are difficult to obtain by FTIR or other similar method that provided the average concentration of a sample. Raman microspectroscopy was explored as a promising tool to obtain a further insight of mass transfer in the polymer for it gives access to more information on migration kinetics such as concentration profiles of Uvitex OB in the depth of the LLDPE sample as a function of time.

Raman Measurements

Concentration profiles were determined after contact times of 4h, one day and three days, shorter than those required by FTIR, proving to be an efficient method for the determination of diffusivity. For each contact time, Raman intensity profile obtained was compared to the total mass of Uvitex remaining in the film determined by FTIR (Figure 5). The Raman profile allowed the determination of the total content of Uvitex OB in the film according to equation (9)

$$mass\ of\ Uvitex = \rho\ S \int_{-L}^{+L} C(z)\ dz \tag{9}$$

where ρ stands for the bulk density of the polymer (920 kg m^{-3} for LLDPE), S for the surface and C for the concentration. A linear regression was used to successfully correlate ($R^2=0.96$) the data supplied by FTIR and the band assigned to Uvitex ($1569\text{-}1614\text{ cm}^{-1}$) normalized with the area ratio of the LLDPE specific band (1129 cm^{-1}).

Determination of the diffusivity of Uvitex OB in LLDPE

The three concentration profiles obtained were treated altogether and used to determine whether diffusivity of Uvitex OB was independent of its own and/or olive oil concentration. Four scenarios were considered (table 1): i) diffusivity is independent of Uvitex OB and olive oil (Fickian kinetics), ii) diffusivity depends only on Uvitex OB concentration, iii) diffusivity depends only on olive oil concentration and iv) diffusivity depends on both Uvitex OB and olive oil. The first case was solved using equation (6) and the last three using a modification of the Crank Nicolson method as stated in the Materials and Methods section. For cases iii) and iv) olive oil was considered to modify the diffusivity of Uvitex OB in LLDPE but not its own diffusivity. Thus, the constant value of diffusivity obtained with the FTIR analysis using and equation (6) and, the concentration of olive oil in LLDPE samples was estimated as a function of space and time. These values of concentration were then used to determine the potential dependency of Uvitex OB diffusivity on olive oil content. On the basis of the RMSE

comparison (Table 1), it was verified that the increase of factors in the model did not significantly increase the accuracy of the predictions. Figure 6 shows the experimental data of concentration profiles of Uvitex OB in LLDPE as well as those predicted with the diffusivity value obtained for scenario i), i.e. Fickian kinetics and how they are well correlated if compared to previous works in which the concentration profile is fitted (Helmroth et al. 2003; Reynier et al. 2002). Therefore, scenario i) was accepted as the most likely and simplest, i.e. Fickian kinetics and a diffusivity independent of the concentration of either olive oil or Uvitex OB, at least in the concentration range found during the experiments, which confirms the results obtained by FTIR. According to Raman measurements a value of diffusivity was obtained of $(14.6 \pm 2.5 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1})$. Although significantly different for $p=0.05$, it lies in the same range as the one obtained by FTIR, and indeed both values were no longer different when considering a value of $p=0.025$. It is a quite meaningful result given the high deviations that can be found in the determination of diffusivity. For example, Dole et al. (2006) reported differences up to 350% for the diffusivity of Uvitex OB in PP measured with the same method.

Hence, the investigation of diffusivity of a model molecule by Raman spectroscopy allowed the assessment of several complex phenomena that influence migration in an integrated approach. Raman microspectroscopy was used to provide large amount of data on the inside of the polymer that can be used to assess diffusivity variations. Even though it is theoretically possible to consider a variable diffusivity with global measurements as those performed by FTIR or standard extraction/quantification methods, in reality it is often unfeasible since a high number of experimental values are needed in practice to fit several parameters correctly especially for non-linear models (Hessler 1997). In most cases, FTIR sensitivity is too low to provide such a number of values from a desorption experiment and other conventional methods turn out to be far too time-consuming.

It must be pointed out that the concentration at $15 \mu\text{m}$ of the interface was always underestimated by the predicted values (Figure 6) what could mean that there is a non-negligible mass transfer resistance in the interface. This hypothesis is attractive and it would make the Raman approach even more valuable since it would easily reveal whether mass transfer resistance at the interface can be neglected. Unfortunately, the measurements of points located so close to the interface are less reliable than those in the inside (Everall 2008).

1 Extreme care must be taken if assumptions are made based exclusively on the measurements
2 located the closest to the interface.

3
4 Regarding the effect of olive oil in desorption, it is sometimes widely accepted that, since the
5 polarity of triglycerides in olive oil is similar to that of polyolefins, olive oil is easily absorbed
6 and greatly influences the diffusivity in polyolefins. This has been tested for several low
7 molecular solvents (Helmroth et al. 2003) but very few results in the literature support this
8 hypothesis for olive oil. Several authors found that olive oil did not modify the release of
9 medium molecular weight additives from polyolefins (Goydan et al. 1990; Helmroth et al.
10 2002b; O'Brien et al. 1999) In contrast, Reynier et al.(2002) suggested an exponential
11 dependency of diffusivity with the triglyceride content, but they used glyceril tripelargonate
12 instead of olive oil, which could explain this discrepancy. Our results underpin the hypothesis
13 that olive oil does not modify the diffusivity of a medium molecular weight (431 g mol^{-1})
14 additive in polyolefins. In addition, it must be borne in mind that the olive oil uptake is only
15 of a 1-2% w/w in polyolefins (1.3% w/w in our study) whereas it is commonly stated that, as
16 a rule of thumb, 15% w/w of solvent absorption accounts for an increase of ten folds of
17 diffusivity (Helmroth et al. 2002b) . With this in mind, olive oil sorption as observed in this
18 study is too low to carry out an important modification of diffusivity.

19
20 **Conclusion**

21 With the scope of improving the analysis of food/packaging interactions, the application of
22 two types of vibrational spectroscopy (FTIR and Raman) was presented. The aim of the
23 approach was not to quantify migration levels but to characterize mass transfer parameters in
24 the system. Both, FTIR and Raman, were successfully used to determine diffusivity values of
25 Uvitex OB that could be further use to simulate its release, according to legislation. With the
26 example developed here, each of the methods (FTIR and Raman) proved to be a very efficient
27 mean to access to the parameters necessary for predicting the migration in realistic conditions.
28 FTIR was used to know the average concentration in the LLDPE sample as a function of time.
29 Raman microspectroscopy gave the possibility to gather the concentration profile in the depth
30 of the sample and use these data to perform a complex analysis of the factors that could
31 influence the diffusion coefficient, e.g. it was demonstrated that olive oil sorption did not
32 modify the diffusivity of Uvitex OB in LLDPE. Regarding the experimental set up, a non-
33 negligible time gain could be achieved.

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Figure Captions

Figure 1: Preparation of a sample for the Raman analysis. The slice is cut in order that the thickness (2L) becomes the width of the sample

Figure 2: Distribution of the Uvitex OB concentration in LLDPE samples

Figure 3. FTIR spectral fingerprint of LLDPE + Uvitex OB. Focused region shows the band selected to follow Uvitex OB desorption and its decrease throughout the test

Figure 4: Simultaneous sorption of olive oil and desorption of Uvitex OB from LLDPE at 40°C as determined by FTIR. (● represent experimental olive oil values; □ represent experimental Uvitex OB values; continuous lines represent fitted data)

Figure 5. Raman spectral fingerprint of LLDPE + Uvitex OB. Focused region shows the doublet selected to follow Uvitex OB (C=N, C=C) desorption and its variation in the depth of the film

Figure 6: Concentration profiles of Uvitex OB within the half-depth of LLDPE film submitted to a contact with olive oil at 40°C. The profiles were obtained after 4 h (■), 1 day (○) and 3 days (▲). Continuous lines represent the profiles predicted with the value obtained in case i), Fickian kinetics.

Figure 1: Preparation of a sample for the Raman analysis. The slice is cut in order that the thickness ($2L$) becomes the width of the sample

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Note: Desorption point at 26 days (represented with ◇) was determined with UV spectroscopy of the additive extract

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Table 1. Values obtained after fitting of Raman data of desorption of Uvitex OB from LLDPE in olive oil at 40°C.

	γ Uvitex OB	γ Olive oil	D_0 (10^{-14} m ² s ⁻¹)	RMSE (% w/w)
Case i (Fickian)			14.9 (2.5)	0.023
Case ii	0.12		14.2 (1.3)	0.023
Case iii		0	14.4 (1.3)	0.023
Case iv	0.19	0	13.3 (1.3)	0.022

Note: D_0 and γ values are defined in equation (5). For case i) both γ are zero and D_0 is actually the Fickian diffusivity.