# Partition and diffusion of volatile compounds from acrylic adhesives used for food packaging multilayers manufacturing

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Partition and diffusion coefficients of volatile compounds in polymers have been broadly studied in the literature in order to provide the tools necessary to predict migration from the packaging materials to the food using the appropriate mathematical models. But often, food packaging materials are mutlilayer materials where several substrates are joint by adhesive layers. Little is known about the partition coefficients between adhesives and substrates used in these materials and about the diffusion coefficients in some of the materials commonly used such as paper or cardboard. All of these parameters will have a direct effect on the final migration of the compound. The objective of this work was to study the behaviour of the compounds found on the acrylic adhesives in 4 different real laminates. Partition coefficients between several types of acrylic adhesives and substrate materials (polyethylene, polypropylene, couche paper and kraft paper) were experimentally calculated. Moreover, diffusion coefficients of the compounds in these four materials were derived from experimental data. Finally, a migration test with Tenax was carried out.

A wide variation of results for partition coefficients was found due to the difference on the chemical properties of the compounds studied. In fact, it was found a relation between the coefficients and their Hildebrandt solubility parameters. Moreover, the most relevant result found in the diffusion coefficients values was that the coefficients in paper were lower than in PE but higher than in PP.

Migration results showed that only 4 out of 11 compounds were found in Tenax. Only 2,4,7,9-tetramethyldec-5-yne-4,7-diol belong to a high toxic class according to Cramer rules.

## Introduction

Acrylic adhesives are commonly used in the manufacturing of laminates consisting of two or more substrates such as plastics, paper, cardboard or aluminum, glued with the adhesive. Laminates are used as food packaging materials or as sticky labels attached either directly or indirectly to a foodstuff [1].

In contrast to plastics, no specific legislation exists in the EU for adhesives used in food packaging. Nevertheless, all food contact materials must comply with the Framework Regulation (EC) 1935/2004 [2]. This is the basic European legislation that covers all food contact materials and articles. Article 3 states that materials and articles should not transfer their constituents to food at levels which could: (i) endanger human health; (ii) bring about an unacceptable change in the composition of the food; or (iii) bring about a deterioration in the organoleptic characteristics thereof.

The migration of a compound from a food contact material into food depends on the chemical and physical properties of the compound, the food and the polymer [3, 4]. Migrant concentration, molecular weight, solubility, diffusivity, partition coefficient between polymer and food, time, temperature, polymer and food composition, and structural properties (density, crystallinity, chain branching) are the main factors influencing the migration processes [5, 6]. In most of the situations from practice the mass transfer from a plastic material into foodstuffs is predictable [7]. In many of these cases the diffusion process in the plastic material and migration from it into the foodstuff can be quantified by Fick's laws [8, 9]. In fact, the estimation of migration values is also accepted in the EU legislation [10], and valid models based on scientific evidences can be applied to test compliance with existing legislation [7, 11]. For a reasonable prediction of migration using Fick's laws two fundamental constants are needed: the partition coefficient, of the migrating compound between the packaging material and the foodstuff or food simulant ($K_{P,F}$), and the diffusion coefficient of the compound in the packaging material ($D_P$). Several studies have reported partition coefficients between

polymers and foods or food simulants [10, 12-16]. On the other hand in the last decades substance diffusion has been intensively studied, by using a broad range of experimental methods, in many of the polymers used in food packaging. One of these experimental methods relies on the study of the diffusion concentration profile in a polymer. A thick polymer film is replaced by a stack of several identical thin polymer films maintained in strict contact. This stack is brought into contact with an additive/substance source. After a certain time the films of the stack are separated and the concentration of the additive/substance in each of them can be monitored by some conventional analytical technique, such as FTIR, UV spectrophotometry, gas or liquid chromatography. A concentration profile in the thin film stack can be plotted, then fitted with the appropriate solution of Fick's equation and the diffusion coefficient, Dp, of the additive/substance in the polymer derived hereof. Similarly to migration from mono-layer plastics into foods migration from adhesives included in multilayer structures (laminates) into food is predictable, too. However, for migration calculations from such laminates, it is necessary to know the diffusion coefficients in each layer of the laminate as well as the partition coefficient at each interface of the laminate-food system. Among these coefficients the partition between the adhesive and its substrate, $K_{AS,}$ plays an important role in determining the level of migration from the laminate into the food. Unfortunately little is known yet about the $K_{AS}$ coefficients. Because of that one of the main aims of this work was to determine them for several types of adhesives and substrate materials.

In practice laminates with adhesives are manufactured not only from plastic films but often adhesives are used to stick plastic with paper or cardboard as well as to stick paper/cardboard to paper/cardboard. Little is known about the diffusion of substances which are contained in the adhesives in cardboard or paper. Therefore in this work results are reported on the diffusion of compounds coming from acrylic adhesives through different substrates including two different kinds of papers.

## Material and methods

### Reagents

Polyacrylate fibers, 85 µm thick, were purchased from Supelco (Bellefonte, PA, USA).

Butyl isobutyrate, benzaldehyde, butyl butyrate, benzene 1,3,5-triethyl, octanol, 1-hexanol-2-ethyl, 2-ethylhexylacetate, 2-ethylhexylacrylate, ethanol, 2-2(butoxyethoxy), dimethyl adipate, ethanol, 2-2(butoxyethoxy) acetate and 2,4,7,9-tetramethyl-5-decyne-4,7-diol standards were supplied by Sigma-Aldrich (St. Lois, MO, USA).

Tenax TA 80/100 mesh was supplied by Supelco (Bellefonte, PA, USA).

Supergradient HPLC-grade methanol was purchased from Scharlau Chemie (Sentmenat, Spain). Purified water obtained with a Milli-Q 185 Plus system (Millipore, Bedford, MA, USA) was used.

Internal standard solution A was an octanol solution at 100µg/g in methanol.

**Samples**

Four water-based acrylic adhesives (ADH1, ADH2, ADH3 and ADH4) were supplied by several adhesive companies. ADH1 was supplied as a shelf adhesive aluminum label. These adhesives are commonly used for manufacturing laminates used in food packaging. The laminates manufactured consisted of two substrates glued with an adhesive to form a three-layer system. Different grammages of adhesive were used in each laminate as will be described later.

Several substrates were used in this work: 40 µm thick polyethylene (PE), 25 µm thick sheen polypropylene (sPP), 17.5 µm thick matt polypropylene (mPP), 70µm thick couché paper (cpaper), 32 µm thick kraft paper (Kpaper), and respectively 25 µm thick polyethylene terephthalate (PET). Real laminates that are used in food contact materials to manufacture packages were made as follows:

- Laminate 1: [Al-ADH1-PE], ADH 1 applied at 45 g/m²
- Laminates 2a and 2b: [sPP-ADH2-cpaper] and [sPP-ADH2-sPP], ADH 2 applied at 18 g/m²
- Laminates 3a, 3b and 3c: [PET-ADH3-Kpaper], [PET-ADH3-PET] and [Kpaper-ADH3-Kpaper], ADH 3 applied at 20 g/m²
- Laminates 4a, 4b and 4c: [mPP-ADH4-cpaper], [mPP-ADH4-mPP] and [cpaper-ADH4-cpaper], ADH 4 applied at 20 g/m².

**HS-SPME-GC-MS**

A CTC Analytics CombiPal autosampler was coupled to a 5975B Agilent gas chromatograph and connected to a 6890N mass spectrometer.

The selection of the most sensitive solid phase micro-extraction (SPME) fiber and the optimization of the HS-SPME conditions were carried out in a previous work [17]. A 85 µm polyacrylate fiber was chosen and the SPME conditions were as follows: 80ºC extraction temperature, 25 minutes extraction time and 1 minute desorption time at 250ºC.

Chromatographic separation was carried out on a BPX5 (30 m × 0.25 mm I.D., 0.25 µm film thickness) from SGE Europe Ltd. The oven temperature was set at 40 °C for 5 min, temperature increased from 40 to 100ºC at 10 °C $min^{-1}$, and from 100 to 210ºC at 5ºC $min^{-1}$, remaining at the maximum temperature for 2 min. Helium was used as carrier gas at 1.5 mL $min^{-1}$.

Mass spectra were recorded in electron impact (EI) mode at 70 eV, SIM mode was used for the acquisition (quantification ions are shown in table 1). Quadrupole and source temperature were set at 150 and 230 °C respectively.

**Determination of the initial migrants concentration profile, $C_{P0}$, in the acrylic adhesives**

For the $CP_0$ determination, adhesives were previously water diluted to avoid matrix effects. In order to calculate the minimum water dilution needed, a recovery study was performed. Adhesive samples were water diluted at different proportions and spiked with the studied volatiles, the signal obtained by SPME-GC-MS was compared with the signal obtained when 100% water samples were spiked at the same concentration level.

Determination of $C_{P0}$ was then carried out by HS-SPME-GC-MS. Dilution factor was selected on the basis of obtaining minimum matrix effects and maximum sensitivity in each sample. Matrix effects were found to be stronger in adhesives 3 and 4 and thus a higher water dilution was needed. To achieve recoveries over 80% for all the volatiles adhesive 1 and 2 were water diluted 1/100 (w/w) and adhesive 3 and 4 were diluted 1/500 (w/w). Aliquots of 5 ml of each solution were placed in headspace vials and

100µl of solution A were added as internal standard. Three replicates of each sample were prepared and analyzed by HS-SPME-GC-MS.

For building the calibration curves, solutions of the compounds were prepared in purified water. Aliquots of 5 ml of each solution were placed in headspace vials and 100µl of solution A were added. Three replicates of each concentration were prepared and analyzed by HS-SPME-GC-MS.

**Determination of the partition and diffusion coefficients**

**Experimental work.**

The partition coefficient of a substance between the adhesive and a substrate ($K_{AS}$) is defined as the ratio between the concentration in the adhesive and the concentration in the substrate at equilibrium. As it was impossible to separate substrate and adhesive once they had been glued, experimental methods were designed (further called "partition experiments") to measure indirectly this parameter.

The partition experiments were carried out in a migration cell as suggested by Moisan et al. [18]. The cell consists of two 10 x 10 cm aluminum plates of 1 cm thickness. For the partition experiments a 10x10 cm large sample of each of the laminates listed in § 2.2 was sandwiched between two sheets of substrate material (10x10 cm of a polymer film or paper sheet identical to the one used in the corresponding laminate). The following sandwiches resulted for the partitioning experiments (two replicates for each one were prepared):

1. [Al-ADH1-PE]-PE
2. sPP-[sPP-ADH2-sPP]-sPP
3. sPP-[sPP-ADH2-cpaper]-cpaper
4. PET-[PET-ADH3-PET]-PET
5. Kpaper-[Kpaper-ADH3-Kpaper]-Kpaper
6. mPP-[mPP-ADH4-mPP]-mPP
7. cpaper-[cpaper-ADH4-cpaper]-cpaper

Each of these sandwiches was then placed in a migration cell which was closed using four screws and a dynamometric tool in order to apply a constant twisting force of 0.8 Nm. In the partition experiments, the cells were then kept at 40ºC for 1 month.

The diffusion experiments were conducted with identical cells and in a similar manner with the difference that not a single but 10 sheets of polymer or paper were sandwiched to the corresponding laminates. The migration cells were afterwards kept closed, at 40°C, for 2h, 24h, 48 h and 72 h respectively.

At the end of each partition or diffusion experiment the cells were opened and a 2.5 x 2.5 $cm^2$ piece from the central part of the added polymer or paper sheet/s was cut and placed in headspace vials. Then, these substrate cut-outs were spiked with 10 µl of solution A as internal standard and were kept at room temperature for 24 h before the analysis so as to the compounds reached the equilibrium. The vials were analyzed by HS-SPME-GC-MS.

For building the calibration curves, solutions of the compounds were prepared at different concentrations in methanol. In order to build the calibration curve, 2.5x2,5 $cm^2$ pieces of virgin substrates were placed in headspace vials and spiked with 10 µl of the standards solutions at different concentration levels and 10 µl of solution A. To assure that the compounds could reach the equilibrium before the analysis the vials were kept at room temperature for 24 hours. Three replicates of each concentration were prepared and analyzed.

**Deriving the diffusion and partition coefficients from the experimental results.**

The partitioning coefficient can be easily calculated with mass balance equations from the results obtained in experiments performed with all sandwiches listed in § 2.5.1. However, when performing such calculations there are two conditions that are assumed to be fulfilled, namely.

First the migration time of 30 days at 40°C is considered to be long enough to allow the migrant to reach equilibrium across all the layers of the sandwich (laminate plus added substrates). To check this assumption let's consider two identical substrates of thickness, dp, the one containing uniformly distributed a migrant, concentration Cpo,

the other film containing no migrant at all. Bringing these substrates in strict contact the time, t*, needed by the system to reach equilibrium (the same concentration of migrant in both substrates) is:

$$t^* \sim 7.5 \frac{dp^2}{Dp} \qquad \text{(Eq.1)}$$

The thickest and thinnest substrates used in the partitioning experiments had 70 and 17.5 µm respectively, (cpaper and mPP respectively, see § 2.2). That means that in 30 days one can expect that equilibrium is reached in the above systems if the diffusion coefficient in the substrates ranges from about $5x10^{-10}$ $cm^2/s$ to respectively about $2x10^{-11}$ $cm^2/s$. Data from literature show that at 40°C all migrants identified in this work, see Table 1, exhibit higher diffusion coefficients in the substrates used than the range given above [19, 20]. Thus, one can consider that in 30 days at 40°C in all partitioning runs equilibrium in the sandwiches was reached.

The second assumption is that, due to the strict contact between the laminate and the added substrates, there is no partitioning of the migrant at the interface of the laminate with the substrate sandwiched to it. This assumption cannot be directly checked because at the end of the partitioning experiment it is not possible to determine the local migrant concentration in the substrates of the laminates. By performing identical partitioning experiments in which the thickness of the adhesive layer is varied one obtains different equilibrium concentrations in the substrates sandwiched to the laminates. Applying the same mass balance equations for these experiments one can see if the assumption of no-partitioning at the substrate-laminate interface is valid or not. Experiments performed in this respect showed that, in the limits of the experimental errors, a constant twisting force of 0.8 Nm applied to a surface of $10x10cm^2$, is enough to compress the sandwich so that no interface resistance results for the migrant at the laminate-substrate interfaces.

The mass-balance equation used for a unit surface of the laminate-substrate sandwich at equilibrium in the partitioning experiments was:

$$C^A_{po}\, d_A\, \rho_A = 2\, C^{s1}\, d_{s1}\, \rho_{s1} + K_{AS1}\, C^{s1}\, d_A\, \rho_A + 2\, C^{s2}\, d_{s2}\, \rho_{s2} \qquad \text{(Eq.2)}$$

where:

$C^{A}_{po}$ – initial concentration of migrant in the adhesive

$C^{s1}$ and $C^{s2}$ - equilibrium concentration of migrant in the added substrates 1 and 2

$K_{AS1}$ and $K_{AS2}$ - partition coefficients between adhesive and substrates 1 and 2 of the laminate respectively

$d_A$ and $d_{s1}$ and $d_{s2}$ - thickness of adhesive and substrates 1 and 2 respectively

$\rho_A$ and $\rho_{s1}$ and $\rho_{s2}$- density of adhesive and substrates 1 and 2 respectively.

For sample 1 in which an impenetrable Al substrate was used, the right-hand of Eq. (2) reduces to the first two terms. For the so-called "homogeneous samples" (2b, 3b, 3c, 4b and 4c, in which only one type of substrate was used, the right-hand of the Eq. (2) reduces to two terms.

Typical results obtained in the diffusion experiments are shown in figure 1 for 10 PE films sandwiched to sample 1. Because at the end of the diffusion experiment the migrant was extracted from each film, the experimental concentrations shown in this figure represent mean concentrations in each individual layer. Because of that they were plotted in the middle of each added film. The key parameters which determine the magnitude of the concentration in each of the 10 films are, besides the initial concentration of the migrant in the adhesive, $C^{A}po$, the diffusion coefficients in the adhesive, $D_A$, and respectively substrate $D_{S1}$, as well as the partition coefficient $K_{AS1}$ defined above. It is assumed that due to the strict contact between the 10 PE films there is no partitioning of migrant between them.

The concentration profile of a substance migrating from a laminate into a stack of substrate films can be calculated by solving the appropriate time dependent Fick equation [9, 21]. In our case the assumptions made to solve this equation are: all layers of the laminate-substrate/s system are homogenous and of constant thickness, at a given temperature all migration parameters (diffusion and partition coefficients) in the system are constant, and there is no loss of migrant/substance in the system due to degradation or another process. With these assumptions and the initial and boundary conditions which are appropriate for the diffusion experiments, Fick's equation can be solved with numerical methods [21, 22]. In this work a one-dimensional finite differences, FD, method

was used for this purpose [22]. The concentration profile computed by this FD algorithm can be then fitted to the experimental data by adjusting the diffusion and partition coefficients which correspond to the laminate-substrate system. How this was done in this work will be presented below for the case of sample 1 in contact with a stack of 10 PE films.

A first set of input data in the FD algorithm are the "composition parameter" $C^{A}_{po}$ and the "geometrical-physical parameters" $d_A$ , $d_{s1}$ and respectively $\rho_A$ and $\rho_{s1}$. This data was ascertained at the beginning of the diffusion/partition experiments. A starting value for the $K_{AS1}$ coefficient can be taken from the results of the partitioning experiments (see Table 2). A starting value for the diffusion coefficient in PE, $D_{S1}$, can be estimated by using the "upper-bound" estimation formula given in [23] for low density polyethylene. For the diffusion coefficient in the adhesive, $D_A$, only a rough first approximate, based on similitude with data obtained for other adhesive [20] can be made. With this starting set of values a "first-run" concentration profile is calculated with the FD algorithm. Most likely the fit between experiment and this first concentration profile is (very) modest. This can be improved by appropriately adjusting the $D_A$, $D_{S1}$ and $K_{AS1}$ parameters. However to develop a consistent mathematical algorithm to fit, with three parameters, Fick's equation is not a trivial task and was beyond the scope of this work. Therefore to obtain good fits between experiment and theory we used alternatively the following method.

First the total mean square deviation, $\Sigma_1$, between the experimental results and the "first-run" concentration profile was calculated.

Then, a visual examination of the matching between the calculated profile and the experimental results was made. If the calculated concentration profile is found to be considerably above (or below) the experimental points the $K_{AS1}$ coefficient must be adjusted accordingly (decreased or increased). If the calculated concentration profile is much (or less) steeper than the experimental points the $D_{S1}$ coefficient must be adjusted (decreased or increased). After making this first adjustments one calculates with the FD algorithm a new concentration profile for which again a total mean square deviation, $\Sigma_2$, van be calculated. If it is found that $\Sigma_2 < \Sigma_1$ the first adjustments improved the quality of the fit. Then the procedure with visual examination and $\Sigma$ calculation can be continued in the same manner until a minimum for $\Sigma$ is obtained for a certain set of $K_{AS1}$ and $D_{S1}$

coefficients. The above method was used to estimate all diffusion coefficients listed in Table 5. In this table cpaper and Kpaper are in fact not homogeneous materials, as required for solving appropriately Fick's equation with the FD algorithm used.

## Migration tests

Migration tests with Tenax as food simulant were carried out on laminates 1, 2a and 4a. In the case of laminate 3a the migration test was not carried out since it was found previously that PET, the side in contact with food, was a barrier material for the compounds studied.

Pieces of the laminates with an area of 0.16 $dm^2$ were placed in Petri dishes and covered with 0.2 g of Tenax. Tenax was applied on the side of the laminate that will be in contact with food. The sides in contact with food for the other laminates were: PE for laminate 1, sheen PP for laminate 2a and mate PP for laminate 4a. Laminates in contact with Tenax were kept in the oven at 40ºC for 10 days. After this time, Tenax was extracted with 2,5 ml of acetone shaking for 1 h. Then acetone was removed and concentrated to 200 µl under a nitrogen flow. Two replicates of each laminate were prepared and analyzed by GC-MS. A recovery experiment, carried out spiking Tenax with the compounds studied, showed recovery values above 95%.

## Results and discussion

### The initial migrants concentration profile, $CP_0$, in acrylic adhesives

The 11 compounds quantified in this study are shown in Table 1. They had been previously identified in a screening study of acrylic adhesives carried out in the laboratory[17, 24].

Analytical parameters of the HS-SPME-GC-MS method and the ions used for their quantification are shown in table 1. Good results were obtained in terms of linearity, limits of detection (LOD) and reproducibility. LODs were below 10 ng/g for all the compounds except for dimethyladipate (33 ng/g), reaching values below 1ng/g for

benzaldehyde and benzene-1,3,5-triethyl. Relative standard deviation (RSD) had an average value of 11.1% .

The concentration of the compounds in the adhesives and their toxicity according to Cramer rules [25] are shown in table 2. These rules classify the compounds taking into account their molecular structure. There are three toxicity classes: I, II and III, toxicity is considered low in class I compounds, moderate in class II and high in class III. Results of this study showed that 10 of the 11 compounds had low toxicity (class I). Only 2,4,7,9-tetramethyldec-5-yne-4,7-diol belonged to the class III. Nevertheless, some of these compounds had a restriction or specification in the Commission Directive 2002/72/EC[10] relating to plastic materials and articles intended to come into contact with foodstuffs. 1-hexanol-2-ethyl had a specific migration limit (SML) of 30 mg/Kg, 2-ethylhexyl acrylate has a SML of 0,05 mg/Kg and benzaldehyde had a risk of deteriorate the organoleptic characteristics of the food [10].

Three of the compounds, 1-hexanol-2-ethyl, 2-ethylhexylacetate and 2-ethylhexylacrylate were present at least in 3 of the 4 adhesives. This has sense since 2-ethylhexylacrylate is a residual monomer in acrylic based adhesives, and 1-hexanol-2-ethyl and 2-ethylhxylacetate are impurities of commercial 2-ethylhexylacrylate. Results showed that adhesive 3 and 4 had a very similar composition. The amount of ethanol,2-(2-butoxyethoxy) and ethanol,2(2-butoxyethoxy) acetate was found to be up to 1% (weight) of the adhesive, and the reason of such a high concentration is that they are used as solvents in some acrylic adhesives. Also, dimethyladipate (a plasticizer) got a concentration close to a 1% (weight) of adhesive. The concentration of the most toxic compound, 2,4,7,9-tetramethyldec-5-yne-4,7-diol, used as non-ionic surfactant, was up to 2000 μg/g in both adhesive 3 and 4. Its high toxicity and concentration make this compound a target for the migration studies.

When an adhesive is part of a laminate, not only the initial concentration of a substance in the adhesive is determinant for a possible migration to the food. Other important factors are the partition coefficient of the compound between the adhesive and the laminate substrates and the diffusion coefficient of the compound in these substrates.

**Partition coefficients**

The analytical parameters of the HS-SPME-GC-MS method used for the analysis of the different substrates in the partition experiments are shown in table 3. Four different substrates were analyzed: couche paper, kraft paper, PP and PE. Good results were obtained in terms of linearity, limits of detection (LOD) and reproducibility except for 2-butoxyethoxy ethanol where equation was considered no linear because $R^2$ was below 0.95. LODs were below 15 ng/g for all the compounds in all the substrates except for 2-ethylhexyl acetate (33.4 ng/g) in kraft paper and 2-ethylhexylacrylate (38,4 ng/g) in PP. Average values were 3.4 ng/g for couche paper, 6.9 ng/g for kraft paper, 3.0 ng/g for PE and 7.6 ng/g for PP. Relative standard deviation (RSD) had an average value of 11% for couche paper, 9.2% for kraft paper, 8.5% for PE and 11% for PP.

Matrix effect for the volatile compounds under study was also studied in two different scenarios, the substrates spiked with the pure compounds and the substrates resulting from the diffusion or partition experiments. For this purpose, a multiple HS-SPME extraction was carried out in both scenarios. This technique involves sampling repeatedly the same vial by HS-SPME, with several subsequent consecutive extractions of volatile compounds at equilibrium[26]. The slope of the linear plot ln Ai versus (i−1), being A the area and i the number of extraction (usually three or four) is defined as β value, directly correlated to the compound matrix effects.

β values were calculated in both cases and are plotted in figure 2. As it can be seen, a significant correlation was found, with a Pearson correlation coefficient of 0.92 ($p<0.05$). Therefore, it was considered that it was possible to determine the concentration of the compounds in the samples using the spiked substrates to build the calibration curves. This study demonstrates that the tests were carried at equilibrium conditions.

Table 4 shows the partition coefficients between each adhesive and the substrates in the corresponding laminates ($K_{AS}$). They were calculated using the method explained above. The partition coefficient between ADH 1 and aluminum and between ADH 3 and PET were not included in the study because aluminum was considered a barrier material and no compound was found in PET after the partition experiment. This might be the result of a very low diffusivity of the migrants in this polymer (see § 3.3).

The logP value for a compound is defined as the logarithm of the ratio of its concentration in an octanol/water solution. Log P values were calculated with XlogP

software [27]. Low logP values indicates that the molecules are more hydrophilic and have a higher tendency to stay in a polar medium rather than in a non polar one . Acrylic adhesives used in this work were based on polar acrylic polymers, in contrast PE and PP used as substrates were non polar polymers based on polyolefin monomers. In addition to this, previous works reported that sorption in cellulose fibers decrease with increasing polarity [26, 28] so polar compounds were supposed to have a lower tendency to be sorpted by the paper used as substrate. Taking into account these polarities it is reasonable to find that compounds with low logP values had a higher tendency to stay in the adhesive. In fact, it was observed that the two compounds with logP values below 1, ethanol,2-(2-butoxyethoxy) and dimethyladipate, got the highest partition coefficients (17736 and 7758).

In addition to this, partition coefficients depend also on the solubility coefficient, which indicates the polymer-solvent compatibility. Solubility can be measured using the Hildebrand solubility parameter (δ) [29]. The smaller the difference between the δ values of two substances, the greater the solubility [30]. Polyethylene, polypropylene and PET had the following δ values respectively: 15.8, 16.6 and 20.5. A high value in Δδ (compound – polymer) would indicate a low solubility of the compound in the polymer and therefore a high $K_{AS}$ would be expected. The results obtained in the partition experiment agreed with this theory. For PE, 2-ethylhexyl acrylate obtained the highest Δδ (1.9) and also the highest $K_{A/PE}$ (1318), and the same pattern was obtained for PP, ethanol, 2-(2-butoxyetoxy) which obtained the highest Δδ (3.5) and also the highest $K_{A/PP}$ (17736). Differences in solubility would also explain why compounds with very similar logP values such as 2-ethylhexyl acetate and 2-ethylhexyl acrylate and with very similar chemical structure, had so high differences in their $K_{AS}$ values both in PE and PP. It must be taken into account that partitioning depends also on other factors and that the partition coefficient of a compound when solid substrates are involved may be different when it is alone than when it is in a mixture [31].

The results obtained relative to paper as a substrate in a laminate are also of great interest. There is short information about diffusion in paper or about its solubility properties according to Hildebrand. In this work, 2 different kind of papers were studied, couche and kraft paper. Couche paper (in contact with adhesive 2 and adhesive 4) is a type of paper that has been coated to impart certain qualities to the paper,

including weight and surface gloss, smoothness or ink absorbency. Kaolinite and calcium carbonate are the most often treatments used for coating papers used in commercial printing. Nevertheless, no coating processes were applied in the kraft paper used in this study (in contact with adhesive 3).

It has been reported that compounds with hydrogen donors interact with cellulose by H-bonding interactions [32]; this would explain the low $K_{A/paper}$ values obtained for 2,4,7,9-tetramethyldec-5-yne-4,7-diol in both papers. This compound is the only one with 2 hydrogen donors. Compounds with 1 or none hydrogen donor seemed to be influenced by other factors.

**Diffusion coefficients**

Table 5 shows molecular weight and diffusion coefficients of the compounds studied in this work. Literature has shown that the diffusion coefficients are related to the characteristics of the polymer (the container): molecular weight, degree of crystallinity, glass transition temperature, the temperature of the environment as well as those related to the size, the shape, chemical nature and the polarity of diffusing molecules [33-36]. It is known that the diffusion coefficient decreases when the degree of crystallinity increases and when the size of the sorbed molecule increases [36].

Crystallinity of the polymer can be measured through the glass transition temperature (Tg). This is the temperature in which a polymer leaves its rigid state to become soft. Tg for PE ranges from -120 to -35ºC, for PP it ranges from -25 to -15ºC and for PET it is around 80ºC. This implies that PET is the only one that is rigid at room temperature. This could explain that none of the compounds appeared in PET after one month at 40ºC. An ANOVA study was carried out with the diffusion coefficient data shown in table 5. Significant differences in diffusion values ($p<0.01$) were obtained between PE-paper, PP-paper and PP-PE respectively. Diffusion was faster in PE, followed by paper and finally PP.

The influence of the molecular weight in the diffusion coefficient was studied in the compounds from PP matt experiments, since it was the polymer with the highest number of detected compounds in the diffusion experiments. Between the lightest compound (MW = 130.23 g/mol) and the heaviest compound (MW = 226.35 g/mol), it

was found a difference of almost an order of magnitude in the diffusion coefficient. (1.6 x $10^{-11}$ and 3.1 x $10^{-12}$ respectively). For compounds with a similar molecular weight other factors seemed to have also influence in their diffusion coefficients.

On the other hand, results for both kraft and couche paper were analyzed. Diffusion in porous media are usually referred to geometric properties of the pore space [37, 38]. Tortuosity is a common term for defining pore geometry, calculated as the ratio of the along-pore to end-to-end distance. [39].

In this work it was found that in general, compounds had higher diffusion coefficients in couche paper than in kraft paper. This could mean that kraft paper had a more tortuous pore space where molecules have to cross a bigger length in the same period of time.

In addition to this, couche paper is a coated material. The coating fills up the voids and crevices between the fibers in the paper surface and gives the paper a more even surface with smaller pores and a narrower pore size distribution (10–100 nm) than those of the uncoated paper (0.1–10 μm). The small pores in couche paper could explain the high influence of the molecule size in this type of paper. In couche paper the diffusion coefficients between the smallest molecule and the bigger ranged between 1.1 x $10^{-8}$ and 5.3 x $10^{-9}$ respectively. Nevertheless, these differences were not found in kraft paper, where diffusion coefficient ranged between 1.6 x $10^{-9}$ and 3.0 x $10^{-9}$ between the smallest and the biggest molecule.

**Migration to Tenax**

Table 6 shows the migration results obtained using Tenax as food simulant. Results are expressed as micrograms of migrant compound per $dm^2$ of laminate in contact with the simulant and as micrograms of migrants per Kg of food simulant. Migrating compounds were only detected in Tenax coming from laminate 1 and laminate 4a. Only 1 compound migrated from laminate 1, 1-ethyl-2-hexanol but the concentration detected (188.4 μg/Kg) was below its SML value (30 mg/Kg). Three compounds migrated from laminate 4a, ethanol,2-(2-butoxyethoxy) (1.2mg/kg), ethanol,2,2-butoxyethoxy acetate (27.9 mg/Kg) and 2,4,7,9-tetramethyldec-5-yne-4,7-diol (621 μg/Kg), all of them with very high $CP_0$ values. No legislation was found for these compounds, therefore their migration values should be below10 μg/Kg according to the Directive 2007/19/EC [12].

Nevertheless only 2,4,7,9-tetramethyldec-5-yne-4,7-diol was found to have a high toxicity level according to Cramer rules. In order to check the possible risks, the estimated daily intake (EDI) of the compounds was compared to the maximum intake values recommended by Cramer for each toxicity group.

EDI of each compound was calculated following FDA equations. EDI was calculated as the product of: the migration value (M), the total food intake (3 Kg per person per day) and the consumption factor (CF). The CF describes the fraction of the daily diet expected to contact specific packaging materials[40]. For adhesives, CF is established as 0.14

Values of EDI for ethanol,2-(2-butoxyethoxy), ethanol,2,2-butoxyethoxy acetate and 2,4,7,9-tetramethyldec-5-yne-4,7-diol were 0.51, 11.7 and 0.26 mg/person/day respectively.

These values were compared with the maximum recommended human exposure (mg/person/day) that was established by Cramer for each toxicity class [41].. The values for class I, II and III are 1.8, 0.54 and 0.09 mg/person/day respectively [42].

Ethanol,2,2-butoxyethoxy acetate as well as 2,4,7,9-tetramethyldec-5-yne-4,7-diol were above the recommended Cramer exposure value, therefore more toxixity test would be recommended.

**Conclusions**

A HS-SPME-GC-MS method has been developed as a fast and reliable tool to study concentrations in different substrates. Partition coefficients between different acrylic adhesives and substrates have been calculated and diffusion coefficients have been studied for different polymers and papers. A wide variation in the $K_{AS}$ and $D_s$ values was observed depending on the substrates used in the laminates as well as the physica-chemical properties of the studied compound. Moreover migration experiments with Tenax as solid food simulant were carried out. Only 4 compounds migrated to Tenax, and 2,4,7,9-tetramethyldec-5-yne-4,7-diol was the only one with a high toxicity level according to Cramer rules. From the migration values, the EDI was calculated, taking into account a CF of 0.14 (adhesives). Higher EDI values than those recommended by

Cramer classification were found for ethanol,2,2-butoxyethoxy acetate and 2,4,7,9-tetramethyldec-5-yne-4,7-diol.


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