STUDY OF HOTMELT ADHESIVES USED IN FOOD PACKAGING MULTILAYER LAMINATES. EVALUATION OF THE MAIN FACTORS AFFECTING MIGRATION TO FOOD

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Abstract

Hotmelt adhesives are widely used in the manufacture of multilayer laminates, commonly used as food packaging materials. For this reason, it is very important to determine the composition of the adhesives and to identify which compounds could migrate from the laminate to the food. Twenty four compounds were identified in 2 different hotmelt adhesives, some of them with high toxicity levels according to theoretical model of Cramer such as 9,10-dihydroanthracene and retene. Some physico-chemical properties of these compounds, such as their partition and diffusion coefficients in the different materials used in the laminates, provide useful information for evaluating their potential migration to the food. The determination of the partition and diffusion coefficients was performed with two different laminates made of cardboard or polypropylene cardboard substrates and the adhesive. Partition and diffusion coefficients of the migrants in the adhesives and substrates were calculated from the experimental results. It was found that diffusion was always lower in the adhesive than in the cardboard. All diffusion coefficients determined increased with temperature while the partition coefficients showed the opposite effect. Migration results confirmed that the migration value of a compound was closely related to the calculated partition and diffusion coefficients. None of the migrants exceeded the recommended Cramer exposure values.

Keywords: food packaging, hotmelt, adhesives, cardboard, partition, diffusion, migration.

1. Introduction

Adhesives are composed by a complex formulation of components that perform a specific function. The major component is a polymer called base or binder which provides the name of the adhesive and the main characteristics, such as wettability, curing properties, strength and environmental resistance. The adhesives also contain other substances such as fillers, hardener, solvents, plasticizers, tackifiers and antioxidants, which are added to the base in order to improve its properties.

The hotmelt adhesives are thermoplastic adhesives whose principal polymer can be ethylene-vinyl acetate copolymer, polyvinyl acetate, polyethylene, amorphous polypropylene, block copolymer (styrene butadiene rubber), polyamide or polyester. They are originally solid polymers (powders, tapes, films, granules, pellets…) at temperatures below 80ºC. When they are heated at 150ºC - 200ºC they soften and melt. Once the adhesive is melted, it is applied over the substrates, the substrates are joined and the adhesive hardens by cooling. The hotmelt system must achieve a relatively low viscosity in order to cover the roughness of the substrate and it must not cool rapidly. The substrates more commonly used with hotmelt adhesives are paper, cardboard, wood, leather, selected thermoplastics, selected plastic films, selected metals and selected glasses [1].

Adhesives are commonly used in the packaging industry. They can be used to manufacture multilayer packaging materials (laminates) where different substrates are combined (metal plate, sheet tinplate, metallized films, commonly polymers, paper, cardboard or glass), forming the geometric shape of the package (for example in paper and cardboard industries) or applied on labels [2]. Various criteria and requirements must be considered for its use in food packaging such as consumer appeal, temperature resistance, barrier properties and an optimal combination of cost and performance. One of the main parameters that must be considered is the potential migration of the compounds present in the adhesive to the food in contact with the packaging [3].

General trends in the adhesive industry are the reduction in the use of solvents and the minimization of low molecular weight components that might migrate to food, but no specific legislation exists in the EU for adhesives. They must fulfill the Framework Regulation (EC) Nº 1935/2004 [4] which is the basic community legislation that covers all food contact materials and articles. Adhesives used in plastic materials must also fulfill the plastics Directive 2002/72/EC [5]. The general principles set down in the Framework Regulation are inertness and safety. The

inertness is translated into a maximum overall migration limit (OML), it means, the maximum total amount of the all substances that can be transferred to the food. The safety is translated into specific migration limits (SML), it means, the maximum amount of a single substance that can be transferred to the food. SML is based on the toxicological evaluation of the substance and it can be also expressed as a tolerable daily intake (TDI). The migration analysis from food contact materials to food can be performed in the foodstuff itself or in food simulants (Directive 82/711/EEC and Directive 85/572/EEC).

Previous works have been published about migration from adhesives into food, focusing on acrylic adhesives [6, 7] and polyurethane adhesives [8-10]. In this work, migration from hotmelt adhesives will be studied after having identified first its main volatile compounds.

Migration is a mass transfer phenomenon, resulting from a tendency to balance all chemical potentials in the system, and is controlled by diffusion and partition mechanisms [11-13]. In a laminate with an adhesive, migration is controlled by partition of the migrating molecule/s between the adhesive and the substrate/s and their diffusion in the adhesives and the substrates [14].

In a two phase system, the migrant is transferred from one phase to the other one in order to reach a thermodynamic equilibrium. The partition coefficient, $K_{1,2}$, is defined as the ratio of the migrant concentration at equilibrium between both phases, $C_{eq}(1)$ and $C_{eq}(2)$, in (mol m^{-3}),

Equation 1.

$$K_{1,2} = \frac{C_{eq}\,(1)}{C_{eq}\,(2)} \qquad \text{(Equation 1)}$$

The diffusion coefficient, D, of a molecule in a matrix is a kinetic parameter, which is related to the mobility of the molecules in that material. Perpendicularly to the unit area of the matrix the product between D and the concentration gradient, dC/dx, determines the magnitude of the flux, J, through that unit area. In a one dimensional diffusional process this can we written as:

$$J = -D(C)\frac{dC}{dx} \qquad \text{(Equation 2)}$$

Equation 2 is known as Fick's first law where C is the migrant concentration (mol m^{-3}), J the migrant flux (mol m^{-2} s^{-1}), D(C) is the diffusion coefficient (m^2s^{-1}) and x is the space coordinate in the material (m) [3, 14, 15].

The main aims of this study were: i) to identify the main compounds present in 2 hotmelt adhesives, ii) to determine their partition coefficient between the adhesive and the substrates that conformed the laminate, iii) to determine their diffusion coefficients in the adhesives and the substrates, iv) to evaluate the influence of temperature on these parameters and v) finally, to correlate these values with the values obtained from migration experiments.

The technique selected for the identification of the main compounds of hotmelt adhesives was the solid phase microextraction in headspace mode coupled to gas chromatography and mass spectrometry detection (HS-SPME-GC-MS). SPME is a relatively new technique introduced in 1990 by Arthur and Pawliszyn [16]. It is a fast technique that with only 4 types of adsorbent materials covers most of the more volatile analytes and it provides a very important preconcentration factor of the analytes. This technique coupled to GC-MS allows to obtain a high sensitivity and selectivity in the determination of the compounds present in the adhesives. [ref CN]

2. Materials and methods

2.1. Reagents

The standards 2,6-di-tert-butyl-1,4-benzoquinone, butylated hydroxyl toluene, hexadecane, eicosane, 9,10-dihydroanthracene, retene (phenanthrene, 1-methyl-7-(1-methylethyl)), octadecane, docosane, tetracosane and 4-tert-butylphenol were purchased from Sigma-Aldrich Química S.A (Madrid, Spain). All of them had analytical quality. Dicloromethane, acetone, methanol and hexane were supplied by Scharlau Chemie S.A (Sentmenat, Spain). All of them were HPLC grade. A solution of 4-tert-butylphenol at 1000 μg/g in dichloromethane was used as internal standard solution. Solution A contained seven standards (2,6-di-tert-butyl-1,4 benzoquinone, butylated hydroxyl toluene, hexadecane, 9,10-dihydroanthracene, octadecane, eicosane, docosane, retene and tetracosane) at 75 μg/g in dichloromethane. Tenax TA 80/100 mesh was supplied by Supelco (Bellefonde, PA, USA).

2.2. Adhesive samples and laminates.

Two hotmelt adhesives, both supplied by the same adhesive company, were studied. Hotmelt1 (HM1) was based on EVA (ethylene vinyl acetate) and hotmelt 2 (HM2) was based on a polyolefin enriched in propene. Both adhesives contained tackifiers and an antioxidant but no more precise information about formulation can be supplied due to confidentiality reasons.

The adhesives were studied individually and as part of the multilayer laminates.

The structure of the laminates studied was: [Substrate- hotmelt adhesive- Substrate].

Laminates were manufactured in the laboratory. First, the hotmelt adhesive was heated at 160-180ºC and then it was applied and extended on a 10 x 10 cm substrate forming a uniform layer using an extender machin.

Two types of substrates were used, cardboard (CB), 380 μm of thickness, and polypropylene laminated cardboard (ppCB), 410 μm of thickness. The quantity of adhesive applied was 27.2±2.5 g/m^2 per laminate, which was weight controlled. Afterwards, a second 10 x 10 cm substrate was placed on the top of it and the laminate was pressed. Finally, the laminate was stored in the laboratory at 23ºC.

Using these procedures the following laminates were manufactured:

- Laminate 1: [CB-HM1 -CB]
- Laminate 2: [ppCB-HM1-ppCB]
- Laminate 3: [CB-HM2-CB]
- Laminate 4: [ppCB-HM2-ppCB]

2.3. GC-MS

A CTC Analytics system from Agilent Technologies (Madrid, Spain) was used as autosampler. The gas chromatograph system was a HP 6890 Series connected to a HP 5973 series mass selective detector. Chromatographic separations were carried out on a DB-5 (30 m x 0.25 mm x 0.25 μm) from Agilent Technologies (Madrid, Spain). The oven temperature program was as follows; initial temperature at 40°C (2 min), temperature was programmed from 40 to 130ºC at 15 °C/min and

from 130 to 300ºC at 10ºC/min, final temperature was maintained for 2 minutes. Helium was used as carrier gas at 1 mL/min flow.

Acquisition was carried out in SCAN mode (50-350 m/z). For liquid injection, 1 µL of the sample was injected in split mode (1:20). For HS-SPME injection 1 gram of sample was placed in a 20 mL vial and analyzed in splitless mode. HS-SPME extraction conditions were as follows, 80ºC extraction temperature, 25 min extraction time and 1 min desorption time at 250 ºC.

2.4. Optimization of HS-SPME conditions

The first step was the selection of the most appropriate SPME fiber for each adhesive. Four fibers with different polarities and thickness were tested to cover all of possible analytes:

- Polydimethylsiloxane (PDMS) fiber of 100 µm
- Polyacrylate (PA) fiber of 85 µm
- Carboxen/polydimethylsiloxane (CAR/PDMS) fiber of 85 µm
- Polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber of 65 µm.

Fibers were supplied by Supelco (Bellefonte, PA, USA).

An experimental design was used for the optimization of HS-SPME parameters. It was carried out with the software MODDE v6.0 (Umetrics AB). The parameters optimized were:

- Absorption temperature: 40-80ºC.
- Absorption time: 5-25 minutes.
- Desorption time: 1-15 minutes.

2.5. Identification and classification of the compounds present in hotmelt adhesives

The identification of the compounds detected was carried out by comparing the retention time and the mass spectrum of the compounds with those of the pure standards. Toxicity was evaluated according to Cramer rules [17] with the software Toxtree v1.51 (Ideaconsult Ltd.).

2.6. Determination of initial concentration profile of hotmelt adhesives (CP_0)

To determine the initial concentration of the compounds identified in the adhesives, a liquid extraction of the laminates was carried out. First, the extraction step was optimized. For this purpose, three solvents with different polarities were tested: dichloromethane, methanol and hexane and consecutive extractions of the laminates were carried out. The laminates were cut into small pieces and 0.5grams of such snippets were three consecutive times extracted with 2.5 mL of solvent. Each extraction was carried out at 40ºC during 24 hours. Then, the extracts were mixed together and 10 µL of internal standard solution was added and it was concentrated under a stream of pure N_2 to 200 µL. Finally, the extracts were analyzed by GC-MS. Three replicates of each sample were analyzed.

Cardboards used as substrates in the laminates, were also extracted and analyzed following the same procedure.

The final liquid extraction methodology was as follows: 0.5 grams of laminate snippets were extracted three consecutive times with 2.5 mL of dichloromethane (24 hours, 40ºC), the three extraction solutions were mixed and 10 µL of internal standard solution were added. The solution was concentrated under a stream of pure N_2 to 200 µL and analyzed by GC-MS. Recoveries above 98 % were obtained for all the volatiles.

For building the calibration curves, solutions of the compounds at different concentration levels were prepared in dichloromethane and analyzed by GC-MS. Three replicates of each concentration level were analyzed.

2.7. Determination of the partition and diffusion coefficients

Partition and diffusion experiments were only carried out in laminates manufactured with the HM1 adhesive since no volatiles were detected in the HM2 extracts.

The partition coefficient of a compound between the adhesive and the substrate, $K_{A,S}$, can be calculated according to Equation 1 where phases 1 and 2 are the adhesive and the substrate respectively:

As it was impossible to separate the substrates from the adhesive once they had been glued, the methodology proposed by Canellas et al for calculating $K_{A,S}$ was used [7]. By sandwiching the laminate between two substrates, identical to those used to manufacture the laminate, the following structures were obtained:

- CB - [CB-HM1-CB] - CB.
- ppCB - [ppCB-HM1-ppCB] - ppCB.

These sandwiches were placed in a migration cell similar to that proposed by Dole et al. [15] and Moisan et al. [18]. The migration cell consists of two aluminum plates of 1 x 1 dm of surface which can be tightened together with a controlled torque of 0.8 Nm.

In order to allow the compounds to reach an equilibrium concentration in each layer of these sandwiches, the cells were kept closed in a constant temperature oven, at 40 and 60 °C respectively, for 30 days. All the experiments were carried out by duplicate. After this period, cutouts from the central part of the two sandwiched substrates and of the laminate, about 0.5 grams each, were liquid extracted and analyzed following the methodology described in the previous section. Afterward, the concentration at equilibrium of the compound in the sandwiched substrate and C_{eq}*(substrate)* was determined. One can assume that in these experiments there is no partitioning of the compound at the interface between the added substrates and the identical substrate from the laminate. Thus, at equilibrium C_{eq}*(substrate)* = C_{eq}*(substrate)* and from here one can calculate with a mass balance equation the equilibrium concentration of the compound in the adhesive, C_{eq}*(adhesive)* [7]. The calculation of the $K_{A,S}$ coefficients with Equation 1 is then straightforward[13].

To determine diffusion coefficients of the compounds in the adhesives and substrates a slightly modified design of experiment was used. A series of migration cells were prepared with laminates sandwiched between 10 sheets of virgin substrates put at each side of the laminate. These cells were then tightened with a torque of 0.8 Nm and placed in constant temperature ovens at 40 and 60°C. After 24 hours two cells were removed from the oven and opened. Cut-outs, about 0.5 grams, from the central parts of the added 2x10 substrates and from the laminate itself were produced. They were liquid extracted and analyzed following the same methodology as above. The results obtained were mean concentrations of migrants in each of the 2 x10 added substrates at time t, *C'(substrate)(t)* and the laminate *C'(adhesive)(t)* itself. The same procedure was followed with other migration cells after 48 and 72 hours respectively. In this design of experiment one can

assume that there is no partitioning of the migrating compounds at the interfaces between the identical substrate materials. Then the sandwiches investigated can be regarded in fact as an adhesive layer in contact with thick substrate material (made of 11 identical layers). In such a structure one can calculate at a given time point, t, the concentration profile of a compound diffusing from the adhesive into the thick material by solving the time dependent Fick equation, Equation 3 [15,16]:

$$\frac{dC}{dt} = -D(C)\frac{d^2C}{dx^2} \qquad \text{(Equation 3)}$$

In our case the assumptions made to solve this equation are: i) the adhesive and the substrates system are homogenous and of constant thickness, ii) at a given temperature, T, the diffusion coefficients of the compound in the adhesive, D_A, and substrates, D_S, as well as the partition coefficient at the adhesive-substrate boundary, $K_{A,S}$ are constant, and iii) there is no loss of migrant/compound in the system/sandwich due to degradation or another process. For the experiment described above is complicated to find an analytical solution for Equation 3 by the fact that the solution depends on three parameters, namely D_A, D_S and $K_{A,S}$. Because of that, in this work Equation 3 was solved by using a one-dimensional finite difference (FD) numerical method [19, 20]. The concentration profiles computed with the FD algorithm were then fitted to the experimental results. For this, in each added substrate, the x-coordinate of the experimental *C'(substrate)(t),* was chosen to be in the middle of that substrate/layer. The $K_{A,S}$ parameter was taken as known from the equilibrium experiments with one added substrate on each side of the laminate. Then, by adjusting the D_A and D_S parameters in the calculations, eventually a best fit between the calculated concentration profiles and the experimental *C'(substrate)(t)* was obtained. The iteration method used for this fitting procedure was described by Canellas et al.[13].

2.8. Migration tests

Migration tests from these laminates were carried out using Tenax as food simulant. The tests were performed only in laminates 1 and 2, corresponding to HM1 adhesive, since no compounds were detected during the liquid extraction of laminates 3 and 4, corresponding to HM2 adhesive.

First, the extraction methodology from Tenax was optimized. For this purpose, a recovery experiment was carried out. Two samples of Tenax were spiked with 200 µL of solution A and afterwards they were 3 consecutive times extracted with two different solvents of different polarities, acetone and methanol. Each extract was analyzed separately by GC-MS.

The final extraction method was as follows: 0.34 grams of Tenax was 2 consecutive times extracted with 3.4 mL each time of acetone, solutions were put together, added with 10 µL of internal standard solution, concentrated under a stream of N_2 to 200 µL and finally analyzed by GC-MS. Recoveries above 90% were obtained for all the volatiles.

The migration tests were performed as follows. Cutouts of each laminate, size 1x8.5 cm, were covered with 0.34 grams of Tenax forming a uniform layer (UNE-EN 14338) [21]. The Tenax used was previously purified by soxhlet extraction with acetone during 6 hours.

This system was placed inside a Petri dish and kept in the oven at 40ºC during 10 days. Then Tenax was extracted and analyzed following the methodology previously described. Three replicates of the migration test were carried out in each sample.

The partition coefficient between Tenax and substrates was also determined. For this purpose, 1 x 8.5 cm cut-outs of both virgin substrates (CB and CBpp) were spiked with 200 µL of solution A and stored during 24 hours. After this time, migration experiments, in which the substrates were covered with Tenax and kept at constant a temperature of 40°C for 10 days, were carried out. Then Tenax was extracted and the amount of compounds migrated into it were quantified. The substrates were also extracted three consecutive times with 1.3 mL of dichloromethane, following the optimized methodology presented in section 2.6.

The partition coefficient between Tenax and both substrates ($K_{Tenax,CB}$) and ($K_{Tenax,ppCB}$) was calculated again with Equation 1 by assigning phase 1 as Tenax and phase 2 as the substrate in contact with Tenax. Thus, C_{eq}(Tenax) and C_{eq}(substrate) in Equation 1 are now the concentrations at equilibrium of the compound in Tenax and in the substrate in contact with this food simulant respectively. Three replicates of each sample for each test were prepared and analyzed.

After having calculated the mg of compound that migrated to Tenax (food simulant) per dm^2 of laminate in contact with it, these values were expressed as mg of compound per Kg of food simulant. For this conversion it was used the proportion 6 dm^2 of laminate per 1 Kg of food

simulant established by the plastics Directive 2007/19/EC [5]. From these data, the estimated daily intake (EDI) of each compound, expressed as estimated mg of compound ingested per person per day, was calculated using the equations established by the FDA (Food and Drug Administration of United States) [22]:

$$EDI\ (\frac{mg}{person\ x\ day}) = migration\ value\ \left(\frac{mg}{Kg}\right) \times 3Kg\ (total\ food\ intake\ per\ person\ per\ day) \times CF$$

(Equation 4)

Where CF is the consumption factor, what means the fraction of the daily diet expected to be in contact with a specific packaging material (for adhesives CF = 0.14).

3. Results

Hotmelt adhesives are commonly used in the manufacture of food packaging multilayer laminates and for this reason it is important to determine its composition and to evaluate possible migration to food. Since in multilayer laminates, adhesives are not in direct contact with food several coefficients need to be calculated in order to estimate migration, partition coefficients between the adhesive and the substrates that form the laminates and also the diffusion coefficients of the compounds in the adhesives and in the substrates

3.1. Optimization of HS-SPME conditions

The first aim of this work was to identify the main volatile and semi volatile compounds present in two hotmelt adhesives. For this purpose, the HS-SPME-GC-MS technique was chosen due to its high sensitivity [6]. The first step was the selection of the most appropriate SPME fiber for each adhesive, for this purpose the four fibers specified in *2.4 section* were tested.

Table 1 shows all the compounds detected in the two adhesives. A total of 22 compounds were detected in HM1. With the PDMS fiber (non polar phase) all the compounds were detected, probably because most of the compounds present in these kind of adhesives have low polarities. The PA fiber (polar phase) extracted from HM1 mainly the most polar compounds (7^a, 8^a, 12^a and 20^a), while the CAR/PDMS fiber, which has a micropores structure, only extracted the low molecular weight compound. Finally, the PDMS/DVB fiber, which has bigger pores, allowed

higher sensitivity for the high molecular weight molecules. Based on these results the PDMS fiber was selected for achieving the most representative profile (Figure 1).

For HM2 adhesive, only 2 compounds were detected, the maximum sensitivity for both was achieved with the CAR/PDMS fiber (Figure 2).

The second step was the optimization of the HS-SPME extraction conditions. The results from the experimental design showed that, for all compounds, sensitivity increased when the absorption temperature increased from 40 to 80ºC. Some of the heaviest compounds (17^a, 19^a, 20^a, 21^a, 22^a) were even not extracted at low extraction temperatures. The absorption time had also a positive effect in sensitivity. However, the desorption time did not have any influence. Finally, the optimal extraction conditions were as follows: 80ºC absorption temperature, 25 minutes absorption time and 1 minute desorption time at 250ºC.

3.2. Identification and toxicity classification of compounds present in the adhesives.

Table1 shows the compounds detected in each adhesive and their toxicity class (TC) according to Cramer Rules [17]. The Cramer rules are based on a theoretical model that classify the compounds in three toxicity levels depending on their molecular structure. According to the TC a maximum daily intake (mg/ person/ day) is proposed:

- Level I (low toxicity): 1.8 mg/ person/ day
- Level II (moderate toxicity): 0.54 mg/ person/ day
- Level III (high toxicity): 0.09 mg / person / day

Most of the 22 compounds found in HM1 had low or moderate toxicity and only two of them were classified as highly toxic according to the Cramer´s rules; 9,10-dihydroanthracene (12^a) and retene (19^a), both derivatives of abietic acid. Abietic acid is the main compound of the acid resins used for the manufacture of this kind of adhesives. It is added as a tackifier in order to reduce the adhesive viscosity, improving the wetting properties and therefore the adhesion [1]. This compound undergoes a thermal degradation when the adhesive is heated to be cured. Several authors consider that the thermal degradation starts with the dehydrogenation of abietic acid to dehydroabietic acid methyl ester (21^a), this is followed by a decarboxylation to give dehydroabietin (16^a) and finally by a full aromatization to retene (19^a). The compounds 15^a, 17^a 20^a were then intermediate

compounds of thermal degradation of abietic acid [23-25]. The compounds 4ª, 6ª are essential oils coming from the resin [26].

HM1 was also analyzed after a curing process at 160-180ºC. The compounds found in the cured HM1 were the same as those found in the fresh adhesive. Nevertheless, their concentrations changed during the curing process. Whereas some of the compounds increased their signal when the adhesive was cured, such as dehydroabietal, dehydroabietic acid methyl ester and eicosane, others decreased their signal, such as 2,5-di-tert-butyl-1,4-benzoquinone and hexadecane.

Only two compounds were found in HM2, *cis* and *trans* naphthalene-decahydro, none of them gave a considerable toxicity level according to the Cramer's rules. The same results were found when the adhesive was cured. Hotmelt adhesives based on polyolefins, such as HM2, are relative pure compounds with very high molecular weight and this can be the reason why only two compounds were detected [1]. This result makes these adhesives very suitable for food packaging applications.

3.3 Initial concentration profile of adhesive samples (CP_0)

The initial concentration of the compounds, CP_0, in the adhesive samples was determined by a liquid extraction of the laminates and a GC-MS analysis of the extracts. Table 2 shows the analytical parameters of the GC-MS method for quantifying the compounds found in HM1. An adjusted calibration curve was developed for some of the compounds since it was observed that the standard deviation increased at higher concentration levels. Low limits of detection (LODs), in the range of the low ppb's, were obtained, with values between 0,028 μg/g (butylated hydroxyl toluene) and 0,465 μg/g (eicosane). RSD values were always below 10%.

Table 3 shows the CP_0 of the compounds detected in HM1. Due to the difficulty of finding the standards of the compounds 4b-8-dimethyl-2-isopropylphenantrhene, dehydroabietin, 1-methyl 10,18-bisnorabieta 8,11,13-triene, dehydroabietal and dehydroabietic acid methyl ester, they were quantified using retene as standard. This compound was chosen since it has a similar structure to these compounds.

The major compounds found in HM1 were alkanes, with concentrations ranging from 400 μg/g to 4000 μg/g, and also compounds derivated of the abietic acid, with concentrations ranging from

120 µg/g to 700 µg/g. The most toxic compounds, according to Cramer´s rules, 9,10-dihydroanthracene and retene showed low concentrations in the adhesive, 15±4 and 34±5 µg/g corresponding to 3.3±0.9 and 11±1.6 µg of compound per dm^2 of laminate respectively. Results also showed that the concentration of the compounds in the substrates was always below a 3% of the CP_0.

3.4. Partition coefficients

Partition coefficients between HM1 and both substrates, CB and ppCB ($K_{HM1,CB}$ and $K_{HM1,ppCB}$), are shown in table 3. Coefficients were calculated at 40 and 60ºC.

There was a wide range of partition coefficient values among the compounds which can be attributed to the differences in the solubility of the compounds in the adhesives and substrates. The solubility parameter, called the Hildebrand solubility parameter (∂), is a numerical value that indicates the relative solvency behavior of a specific compound. The solubility of two materials is only possible when their intermolecular attractive forces are similar, and therefore similar ∂ values are required for a good solubility [14, 27-29]. Designating with ∂_A the Hildebrand parameter of the adhesive and with ∂_m that of the migrant then a small $\Delta\partial_{Am} = |\partial_A - \partial_m|$ indicates a good solubility of the migrant in the adhesive. Following the same rationale, it can be defined a $\Delta\partial_{Sm} = |\partial_S - \partial_m|$ where ∂_S would be the Hildebrand parameter of the substrate. According to the literature, the Hildebrand solubility value for a polymer based on EVA is $\partial_A \sim 17.5$ $MPa^{1/2}$ at 25ºC [30]. The ∂_m value for hexadecane is 16.3 $MPa^{1/2}$, for 9,10-dihydroanthracene 20.3 $MPa^{1/2}$, for octadecane 16.4 $MPa^{1/2}$, for eicosane 16.5 $MPa^{1/2}$, for retene 20.2 $MPa^{1/2}$ [31] and for BHT 24.1 $MPa^{1/2}$ [28]. No data about ∂ values of the rest of the compounds or of the two substrates were found.

For $K_{HM1,CB}$ values, it was observed that the compounds with low $\Delta\partial_{Am}$ values such as hexadecane ($\Delta\partial_{Am}$ =1.2), octadecane ($\Delta\partial_{Am}$ =1.1) and eicosane ($\Delta\partial_{Am}$ =1.0) are characterized by higher $K_{HM1,CB}$ values than those compounds with higher $\Delta\partial_{Am}$ values such as 9,10-dihydroanthracene ($\Delta\partial_{Am}$ =4.3), retene ($\Delta\partial_{Am}$ =2.7) and BHT ($\Delta\partial_{Am}$ =6.6). This seems to indicate that the solubility of the compounds in the adhesive plays the central role in determining the magnitude of $K_{A,S}$. All $K_{A,S} >> 1$ shows that the equilibrium solubility of the compounds is much higher in the adhesives than

in the substrates used to manufacture the two laminates. This means in fact that $\Delta\partial_{Am} < \Delta\partial_{Sm}$. In such cases a high tendency of the compound to remain in the adhesive is registered (high $K_{A,S}$ values). For the laminates manufactured with ppCB two different trends can be observed in Table 3. The first one is that the $K_{A,S}$ values are higher in this laminate than in the laminate made only with CB for all the compounds except for three. This may be attributed to the fact that the solubility of these compounds in the PP layer of the ppCB substrate is smaller than in CB. Thus the mean equilibrium concentration of these compounds in the ppCB substrate is lower than in a CB one.

For the remaining three compounds (namely hexadecane, octadecane and eicosane) to explain the lower $K_{A,S}$ obtained in the laminate with ppCB as in that with CB the ∂_S value of the PP has been taken into account. The ∂_S value of PP is 16 $MPa^{1/2}$ [30]. Consequently for hexadecane, octadecane, and eicosane, the $\Delta\partial_{Sm} = |\partial_S - \partial_m|$ value related to the PP is smaller than the $\Delta\partial_{Am} = |\partial_A - \partial_m|$ (0.3, 0.4 and 0.5 vs. 1.2, 1.1 and 1.0 respectively). This implies a better solubility of these compounds in PP than in the adhesive. The result of this is that at equilibrium the mean concentration of these three compounds in ppCB is higher than in CB, which implies, as was experimentally found, smaller $K_{A,S}$ values for the laminate made with ppCB. However the magnitude of this trend seems to depend on the nature of the compound. While for hexadecane and octadecane the trend is quite clear, it is smaller for eicosane where at 40°C $K_{A,S}$ become, in the limits of the experimental errors, almost identical. Further for docosane, a compound from the same family, the $K_{A,S}$ are about the same for both laminates and temperatures.

For the rest of the compounds, no specific bibliographic data were found about their Hildebrand solubility values. But their solubility can also be explained by Hansen´s equation, an updated version of Hildebrand equation, where the Hildebrand´s solubility (∂_T) depends on three types of interactions, dispersion forces (∂_D), polar forces (∂_P), and hydrogen bonding forces (∂_H) [14, 28, 29]

$$\partial_T = \sqrt{\partial_D^2 + \partial_P^2 + \partial_H^2} \qquad \text{(Equation 5)}$$

For the aromatic compounds the main parameter is the dispersion force, which is higher in the aromatic hydrocarbons than in the aliphatic hydrocarbons. The higher the number of aromatic rings in a compound the higher the dispersion forces. Therefore, it will be more difficult for a compound to be dissolved in the adhesive (an aliphatic hydrocarbon) if it has a high number of aromatic rings.

This could explain why retene (3 aromatic rings) and 9,10-dihydroanthracene (2 aromatic rings) had low partition coefficients [31].

In addition to this, the partition coefficients can be also influenced by the different affinity of the compounds to be absorbed by the cardboard. This affinity depends on the polarity and structure of the migrant compounds and their interaction with the pulp of the cardboard [32, 33].

In Table 3 it can be observe, except for BHT, a decrease of the $K_{A,S}$ values when the partition experiment temperature increased from 40ºC to 60ºC. The higher partition coefficient for BHT found at 60°C in laminate CB-HM1-CB than at 40°C may be the result of fluctuations in the experimental conditions.

In a thermally activated process the temperature dependence of the solubility of a compound in an adhesive or polymer can be usually quantified with an Arrhenius-type equation:

$$K_{A,S} = K^{o}_{A,S}\ exp\left(-\frac{\Delta H}{RT}\right) \qquad \text{(Equation 6)}$$

Where $K^{o}_{A,S}$ is the partition coefficient at very high temperatures T→∞, $\Delta H = H_A - H_S$ difference of enthalpies of solution (J mol) in the adhesive and substrate and R the universal gas constant (8.314 J mol^{-1} K^{-1}).

Table 3 shows the parameters for the Arrhenius equation for the partition coefficients $K_{HM1,CB.}$

These results can be explained by the changes produced in the solubility of the compounds in the adhesive and substrate as T increases. For an endothermic solution of a compound in a material, the enthalpy of solution is $H > 0$, the solubility of the compound in that material increases with T. This phenomenon is to be expected both in the adhesive and in the polymer or cardboard substrates. The fact that $K_{A,S}$ generally decrease with T [14, 27, 30]indicates that the equilibrium concentration of the compound in the substrates increases faster with T than in the adhesive, which implies in Equation 6 a $H_S > H_A$.

The ΔH enthalpies summarized in Table 3 show that the influence of the temperature is not the same for all the compounds migrating in laminate CB-HM1-CB. While for some compounds the temperature has a big impact in their partition coefficients, ΔH >100 kJ/mol, such as 9,10-

dihydroanthracene and 2,5-di-tert-butyl-1,4 benzoquinone, for other compounds, such as the series of alkanes it had a much smaller impact $\Delta H < 50$ kJ/mol.

3.5. Diffusion coefficients

Figure 3 shows the experimental results of migration of 2,5-di-tert-butyl-1,4 benzoquinone at 60ºC in a stack of 10 cardboard substrates and the fitted curved obtained by solving the corresponding Equation 3 with the FD algorithm. Similar results have been obtained for most of the compounds found in the laminates made of adhesive HM1 and substrates cardboard (CB) at 40 and 60°C. However, for some of the compounds the scatter of the experimental points in the concentration profiles was too large for a reasonably good fitting with the diffusion equation 3. For the laminates made with polypropylene-cardboard (ppCB) the experimental results are much more difficult to interpret with Equation 3 and therefore it is not possible to obtain a good fitting. First, since these laminates contain pp–layers the penetration/diffusion of the compounds in the stack of added ppCB substrates is strongly diminished. This led, even after 72 hours, to no detect measurable compound concentrations in the added ppCB substrates. Thus no curve fitting, with adjustable D_A and D_S coefficients, was possible. An extension of the duration of these experiments beyond 72 hours, with the aim to obtain measurable mean concentrations of compounds in the added ppCB substrates, would have not necessarily solved all problems. This is caused by the fact that the added substrates are made of a pp film laminated on a CB. This means that in the added stack successively a pp layer is in contact with a CB. But as already mentioned, at a given temperature, the solubility of the compounds in these two materials is not the same. Thus in fact there is a partitioning, $K_{pp,CB}$, of a compound at each pp-CB interface. But this $K_{pp,CB}$ is not known and therefore a fitting of the non-continuous concentration profile of the compound in the added ppCB stack with Equation 3 is very difficult. Because of that no diffusion coefficients in the ppCB substrates are reported in this work.

The D_A and D_S coefficients determined for the HM1 adhesive and the CB substrates are summarized in Table 4. It can be observed from this table that the magnitude of these coefficients depends both on the nature of the migrating compound, on the matrix (adhesive or substrate) and on the temperature.

The molecular weight of the molecule, the degree of crystallinity of a polymer are known to be the main parameters affecting, at a given temperature, the diffusion coefficients [34]. Other parameters such as the geometry and the polarity the compound or the interaction between the compound and the polymer seem to have less importance [15]. It is known that diffusion coefficients are higher for small molecules and for polymers with a low crystallinity degree and low thickness [35, 36].

Table 4 shows that diffusion coefficients values in adhesive HM1 at 40ºC for the compounds with the highest molecular weight such as docosane, dehydroabietin, 4b-8-dimethyl-2-isopropylphenanthrene and octadecane were lower than those of the smaller molecules. The values obtained for the compounds with the lowest molecular weights (hexadecane, 2,5-di-tert-butyl-1,4-benzoquinone and 9,10-dihydroanthracene) in HM1 adhesive were close to those reported in a previous work for EVA based polymers [15]. The same trend is found for the diffusion coefficients of the compounds in the CB substrate.

Temperature has also a high impact in the diffusion of the molecules in adhesives and substrates. It was shown that) diffusion in rubbery polymers is a thermally activated process that follows an Arrhenius-type equation [34].

$$D(T) = D_o exp\left(-\frac{E_D}{RT}\right) \qquad \text{(Equation 7)}$$

Where D_0 is the diffusion coefficient for very high temperatures, $T \rightarrow \infty$, and had an entropic character while E_D is the activation energy of the diffusion process. Both parameters may depend on the morphology of the polymer, the size of the penetrant and also the temperature [34].Table 4 confirms that for the volatile compounds studied the diffusion coefficients are increasing function of the temperature T, which means E_D is positive for both the adhesive and the substrate. A paired student t-test statistical analysis was carried out and results showed that diffusion coefficients were significantly higher at 60 ºC than at 40ºC ($p<0.01$). The free volume in a polymer is directly related to the expansion of the polymer due to the increased of motions and therefore the diffusion of the molecules is facilitated at high tempertures[12, 37].

Since little is reported in the literature related to the diffusion processes in cardboard, discussion on the D_S data given in Table 4 is based on paper and cardboard transport properties. Paper is a network of natural cellulose fibers make up of porous microfibrils, which are composed of hygroscopic long chain cellulose molecules in a crystalline state, with amorphous regions.

Transport properties in porous media will depend on its porosity, tortuosity and permeability [38-40]. Thus, in fact, the D_S data listed in Table 4 for CB should be regarded as macroscopic "apparent" diffusion coefficients. For most of the compounds diffusion in the cardboard was higher than in the adhesive.

In a certain application one can reduce the effect of the porosity and hydroscopicity of paper and cardboard by coating them with a non porous material (for example a polymeric film). Such a coating can severely decrease the global mass transport through the paper or cardboard substrate. This is probably the reason why no results were obtained in the diffusion experiments carried out with stacks of ppCB.

Table 4 also shows the parameters D_0 and E_D for the Arrhenius equation 7 for the diffusion coefficients in the hotmelt adhesive (D_{HM1}) and in the cardboard (D_{CB}). They were derived from linear regressions of the Arrhenius plots, as shows for example Figure 4 for octadecane in Laminate 1. The influence of the nature of the migrating compound on the temperature dependence of the diffusion coefficients seems to have a bigger role in CB than in the adhesive. This might be the result of the fact that the polarity of the compounds has a bigger effect of diffusion in CB than in an adhesive of polymeric nature.

3.6. Migration results

Migration experiments were carried out with Tenax as food simulant since these kinds of laminates are commonly used for dry food packaging and Tenax is recommended for the migration test. In addition, liquid simulants can not be used with cardboard packaging.

Table 5 shows the migration results from laminate 1 and 2 to Tenax, expressed as μg of migrant in Tenax per dm^2 of laminate and also as the percentage of compound migrated from the laminate. Alkanes showed in general high values of migration in both laminates, migration values for docosane, eicosane and octadecane for example, ranged between 97.5 and 322 $\mu g/dm^2$.

As it was expected, those compounds with a low partition coefficient ($K_{MH1,CB}$) presented a high percentage of migration. For example, butylated hydroxyl toluene (81.8%) and 9,10-dihydroanthracene (71.0%), these compounds were classified medium and highly toxic

respectively according to Cramer´s rules. Nevertheless, since the CP_0 of 9,10-dihydroanthracene was very low, the final migration value was the lowest (2.34 μg/dm^2). On the other hand, the compounds with a high partition coefficient had a low percentage of migration, for example dehydroabietic acid methyl ester (3.33%) or 1-methyl 10,18-bisnorabieta 8,11,13-triene (16.3%). Tenax is commonly used as food simulant of dry food, its selectivity to certain kind of compounds, due to its chemical nature, will also affect migration value. For example, 2,5-di-tert-butyl-1,4 benzoquinone, has a high $K_{Tenax,CB}$ value, this indicates that this compound will have a higher tendency to migrate to Tenax than others with lower values. This fact could explain why this compound that has a high $K_{HM1,CB}$ value showed a high percentage of migration. The opposite happened to retene. For most of the compounds migration values were higher in laminate 1 than in laminate 2. The presence of a PP coating in the cardboard seems to reduce migration processes. Only hexadecane and octane showed higher migration values in laminate 2, and this result agrees with the partition coefficient results that showed that, for these compounds, $K_{HM1,ppCB}$ was lower than $K_{HM1,CB}$.

In order to study the possible risks of the migrant compounds, migration values were compared with the specific migration limits (SML). Only butylated hydroxyl toluene compound has a SML, it corresponded to 3 mg/Kg [5]. For laminate 1 the migration result was 24.1μg/dm^2, corresponding to 0.15 mg/Kg of food (assuming a cube with a surface area of 6dm^2 in contact with 1 Kg of food [4]), and for laminate 2, the migration value was 3.04μg/dm^2 (0.02 mg/Kg). These values were below its SML value. Secondly, for the rest of the compounds the estimated daily intake (EDI) was calculated according to equation 4 and none of the migration values exceeded the recommended Cramer exposure values.

4. Conclusions.

Two hotmelt adhesives commonly used in food packaging multilayer materials have been studied. Adhesive formulation was very different depending on the base polymer used. While in the adhesive based on polyolefin only 2 compounds were detected, in the adhesive based on EVA a total of 22 compounds were detected. Most of the compounds detected in the EVA adhesive were derivates of the abietic acid, a compound which is used as takckifier in the manufacturing process of the adhesive. Only two of the compounds identified showed a high toxicity according to the

theoretical model of Cramer, 9,10-dihydroanthracene and retene, nevertheless, their migration values were bellow the recommended Cramer exposure values. Results showed that the substrates used in the manufacture of the multilayer materials had an important role in the final migration. The use of cardboards coated with polypropylene reduced migration values for most of the compounds. Migration results confirmed that the migration value of a compound was closely related to its partition and diffusion coefficients. Partition coefficient depended mainly on the solubility of the compounds in the adhesives and substrates and the facility of the compounds to be absorbed by the cardboard, and diffusion coefficient depended mainly on the nature of the migrating compound and the matrix of the adhesive and substrate. Another important factor affecting migration was temperature, since it modified the partition and diffusion coefficients of the compounds, but it showed opposite effects, while all diffusion coefficients determined increased with temperature, the partition coefficients decreased.

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Table 1: Compounds detected in hotmelt adhesives analyzed by HS-SPME-GC-MS with different fibers (A: PDMS fiber, B: PDMS/DVB fiber, C: CAR/PDMS fiber, D: PA fiber) and their toxicity class (TC) according to Cramer Rules.

	Compounds (CAS No)	**Hotmelt**	**TC**	**Fiber**
1[a]	Dodecane * (112-40-3)	1	I	A, B, C
2[a]	Tridecane, 5-methyl * (25117-31-1)	1	I	A, B, C
3[a]	Tridecane, 3-methyl * (6418-41-3)	1	I	A, B, C
4[a]	Longicyclene * (1137-12-8)	1	I	A, B, C
5[a]	Tetradecane * (629-59-4)	1	I	A, B, C
6[a]	Longifolene * (475-20-7)	1	I	A, B, C
7[a]	2,5-Di-tert-butyl-1,4 benzoquinone ** (2460-77-7)	1	II	A, B, C, D
1[b]	Naphthalene, decahydro, *trans* ** (493-02-7)	2	I	A, B, C
8[a]	Butylated hydroxyl toluene ** (128-37-0)	1	II	A, B, C, D
9[a]	Pentadecane, 5-methyl * (25117-33-3)	1	I	A, B
10[a]	Pentadecane, 3-methyl * (2882-96-4)	1	I	A, B
11[a]	Hexadecane ** (544-76-3)	1	I	A, B
2[b]	Naphthalene, decahydro, *cis* ** (493-01-6)	2	I	A, B, C
12[a]	9,10-dihydroanthracene ** (613-31-0)	1	III	A, B, C, D
13[a]	Octadecane ** (593-45-3)	1	I	A, B
14[a]	Eicosane ** (112-95-8)	1	I	A, B
15[a]	4b,8-dimethyl-2-isopropylphenantrhene * (1000197-14-1)	1	II	A, B
16[a]	Dehydroabietin * (32624-67-2)	1	II	A, B
17[a]	1-Methyl 10,18-bisnorabieta 8,11,13-triene * (1000293-16-9)	1	II	A, B
18[a]	Docosane ** (629-97-0)	1	I	A, B
19[a]	Retene ** (483-65-8)	1	III	A, B
20[a]	Dehydroabietal * (13601-88-2)	1	II	A, B, D
21[a]	Dehydroabietic acid methyl ester * (1235-74-1)	1	II	A, B
22[a]	Tetracosane ** (646-31-1)	1	I	A, B

[a] peaks in Figure 1, [b] peaks in Figure 2, *compounds identified by the NIST library **compounds identified by NIST library and similar retention time with those of pure standards.

Table 2: Analytical parameters of the GC-MS method

Compounds	**Equation**	**R^2**	**Linear range (µg/g)**	**LOD (µg/g)**	**LOQ (µg/g)**	**RSD (%)**
2,6-Di-tert-butyl-1,4 benzoquinone	y = 0.066x-0.004	1*	0.589 – 23.8	0.177	0.589	5.3
Butylated hydroxyl toluene	y = 1.82x	0.997	0.092 – 13.8	0.028	0.092	3.6
Hexadecane	y = 0.570x-0.093	0.996	0.360 – 9.61	0.108	0.360	8.4
9,10-dihydroanthracene	y = 1.42x	0.999	0.135 – 4.78	0.040	0.135	4.4
Octadecane	y = 0.580x-0.093	0.995	0.995 – 7.43	0.297	0.995	8.6
Eicosane	y = 0.557x+0.004	0.999	1.55 – 6.97	0.465	1.55	2.3
Docosane	y = 0.241x-0.004	1*	0.788 – 6.09	0.236	0.788	9.7
Retene	y = 0.641x-0.012	1*	0.226 – 48.6	0.068	0.226	6.2
Tetracosane	y = 0.311x-0.003	0.991	0.165 – 13.8	0.050	0.165	7.3

* Adjusted calibration curves

Table 3: Initial concentration profile of HM1 adhesive (CP_0) expressed as µg of compound per g of cured adhesive, partition coefficients between adhesive HM1 and substrates ($K_{HM1,CB}$ and $K_{HM1,ppCB}$) at 2 different temperatures and the Arrhenius equation for $K_{HM1,CB}$.

Compounds	**CP_o**	**$K_{HM1,CB}$**		**$K_{HM1,ppCB}$**		**Arrhenius equation parameters**	
	(µg/g)	**40ºC**	**60ºC**	**40ºC**	**60ºC**	**$K°_{HM1,CB}$ (g/cm³)/(g/cm³)**	**-ΔH (KJ/mol)**
2,5-Di-tert-butyl-1,4 benzoquinone	250±41	720	36	1130	110	1.53E-19	129.88
Butylated hydroxyl toluene	220±36	20	28	140	80	5.43E+03	-14.59
Hexadecane	430±65	150	70	60	26	4.60E-04	33.05
9,10-dihydroanthracene	15±4	15	0,5	220	190	3.72E-24	147.50
Octadecane	1000±150	110	67	53	20	2.85E-02	21.50
Eicosane	1300±200	90	64	110	50	3.07E-01	14.78
4b-8-dimethyl-2-isopropylphenantrhene	120±19	110	35	820	370	5.72E-07	49.66
Dehydroabietin	630±79	170	45	2800	620	4.12E-08	57.64
1-Methyl 10,18-bisnorabieta 8,11,13-triene	140±26	380	80	930	430	2.03E-09	65.67
Docosane	2300±63	68	33	70	40	4.00E-04	31.35
Retene	34±5	30	9	150	45	5.85E-08	52.21
Dehydroabietal	340±58	370	70	1700	750	3.33E-10	71.21
Dehydroabietic acid methyl ester	700±85	850	130	2700	540	2.22E-11	81.43
Tetracosane	4000±540	100	40	500	130	2.35E-05	39.74

T is the absolute temperature in Kelvin degrees and R is the perfect gas constant (8.3144 $J.mol^{-1}K^{-1}$)

Table 4: Diffusion coefficients for HM1 migrating substances in the adhesive (D_{HM1}) and in cardboard (D_{CB}) at 2 different temperatures, the Arrhenius equation for D_{HM1} and D_{CB} and substances molecular weight (MW).

Compounds	**MW**	**D_{HM1} (cm^2/s)**		**Arrhenius equation parameters**		**D_{CB} (cm^2/s)**		**Arrhenius equation parameters**	
	(g/mol)	**40ºC**	**60ºC**	**D_O(HM1) (cm^2/s)**	**E_D(HM1) (kJ/mol)**	**40ºC**	**60ºC**	**D_O(CB) (cm^2/s)**	**E_D(CB) (kJ/mol)**
2,5-Di-tert-butyl-1,4 benzoquinone	220.3	1.0E-08	8.7E-08	8.4E+05	82.99	2.4E-08	1.6E-07	7.5E+04	74.64
Butylated hydroxyl toluene	220.3	8.0E-09	4.8E-08	5.5E+04	83.16	1.2E-08	7.2E-08	3.7E+03	68.50
Hexadecane	226.5	1.1E-08	7.4E-08	6.6E+06	88.86	1.6E-07	5.6E-07	9.6E+06	83.79
9,10-dihydroanthracene	180.3	1.0E-08	5.5E-08	7.4E+04	77.24	1.9E-08	6.0E-08	12	52.84
Octadecane	254.6	8.2E-09	4.4E-08	6.4E+03	71.23	4.4E-08	2.0E-07	3.8E+03	65.34
Eicosane	282.6	5.3E-09	2.9E-08	8.9E+03	73.26	1.2E-09	7.0E-08	1.2E+04	71.79
4b-8-dimethyl-2-isopropylphenantrhene	256.5	7.5E-09	4.3E-08	2.1E+05	80.82	4.6E-09	3.0E-08	2.1E+03	69.84
Dehydroabietin	242.4	7.1E-09	4.3E-08	1.8E+05	80.44	1.2E-08	4.6E-08	26	55.90
Docosane	310.7	5.8E-09	3.4E-08	2.4E+06	88.12	8.8E-09	4.0E-08	64	58.83

T is the absolute temperature in Kelvin degrees and R is the perfect gas constant (8,3144 $J.mol^{-1}K^{-1}$)

Table 5: Migration values from laminate 1 and laminate 2 expressed as μg of compound per dm^2 of laminate and as the percentage of compound migrated related to the initial concentration in the laminate. The partition coefficient between Tenax and both substrates, CB ($K_{Tenax,CB}$) and ppCB ($K_{Tenax,ppCB}$), and the limit of detection expressed as μg of compounds per dm^2 of laminate.

Compounds	**LOD (μg/dm²)**	**Migration Laminate 1 μg/dm² (%)**	**$K_{Tenax,CB}$**	**Migration Laminate 2 μg/dm² (%)**	**$K_{Tenax,ppCB}$**
2,5-Di-tert-butyl-1,4 benzoquinone	1.49	32.0 (40.7%)	130	20.0 (25.4%)	59
Butylated hydroxyl toluene	0.075	24.1 (81.8%)	98	3.04 (10.3%)	17
Hexadecane	0.64	24.6 (12.4%)	32	159 (80.3%)	11
9,10-Dihydroanthracene	0.88	2.34 (71.0%)	49	0.34 (10.3%)	11
Octadecane	2.21	104 (23.2%)	170	322 (71.7%)	13
Eicosane	0.30	198 (33.9%)	200	174 (29.7%)	4.3
4b-8-Dimethyl-2-isopropylphenantrhene	nc	12.2 (31.2%)	nc	3.83 (9.84%)	nc
Dehydroabietin	nc	56.2 (28.5%)	nc	6.90 (3.25%)	nc
1-Methyl 10,18-bisnorabieta 8,11,13-triene	nc	7.30 (16.3%)	nc	3.90 (8.71%)	nc
Docosane	0.15	205 (41.0%)	25	97.5 (19.5%)	1.1
Retene	0.24	0.88 (8.21%)	13	< LOD	0.6
Dehydroabietal	nc	13.2 (12.3%)	nc	6.68 (6.24%)	nc
Dehydroabietic acid methyl ester	nc	28.8 (3.33%)	nc	14.5 (1.67%)	nc
Tetracosane	0.24	63.8 (29.3%)	18	37.5 (17.2%)	0.3

nc: not calculated since the standard was not found

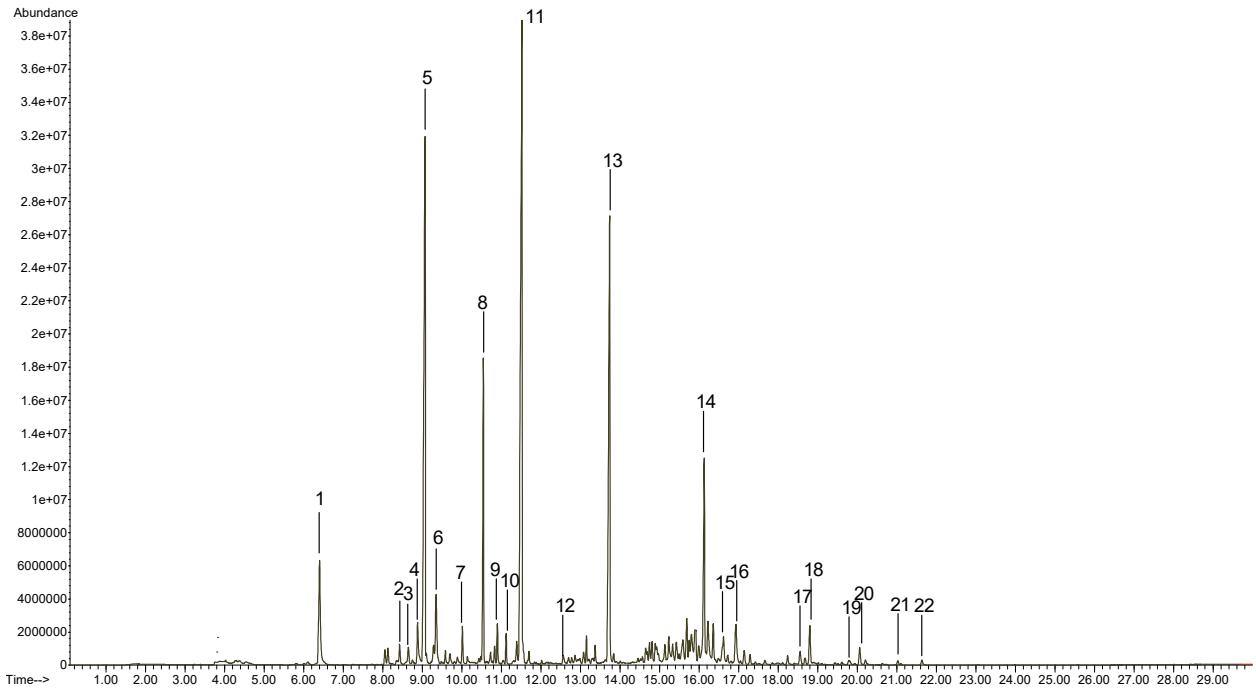

Figure 1: Chromatogram of the pure HM1 adhesive analyzed with a PDMS fiber by HS-SPME-GC-MS (identification numbers in table 1).

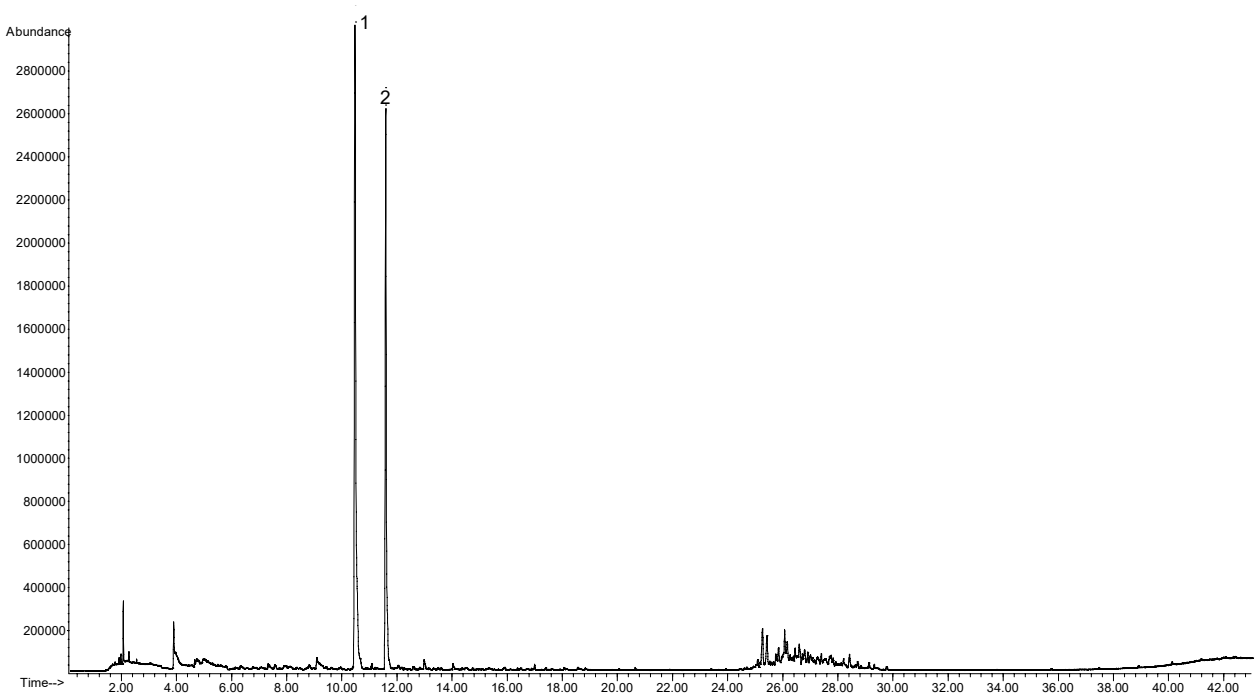

Figure 2: Chromatogram of the pure HM2 adhesive analyzed with a CAR/PDMS fiber by HS-SPME-GC-MS (identification numbers in table 1).

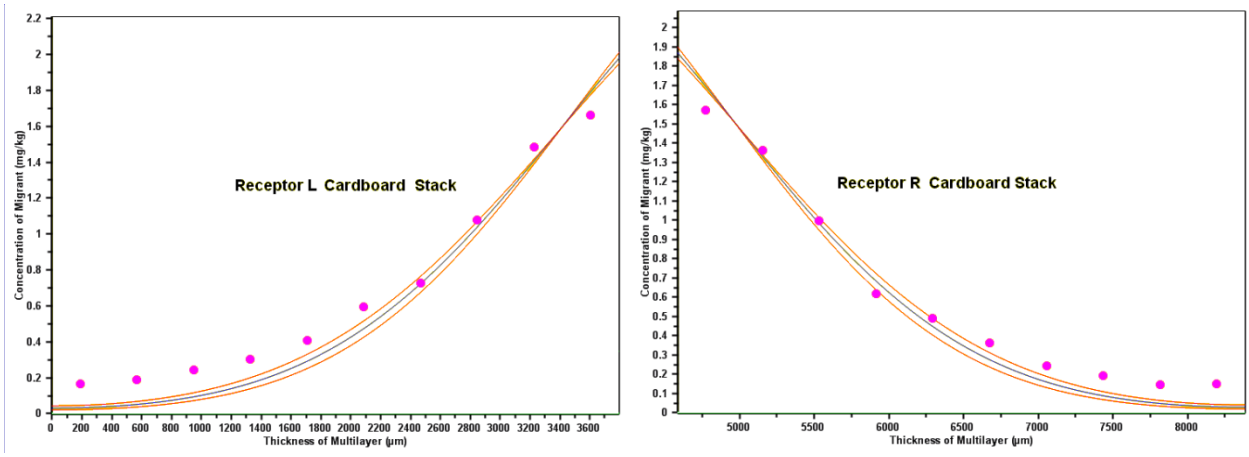

Figure 3: Experimental results (dots) and calculated results (lines) of the concentration profile of 2,5-di-tert-butyl-1,4 benzoquinone in a stack of 10 CB films (380µm) in contact with the left (L) and right(R) side of laminate 1 for 24 hours at 60ºC.

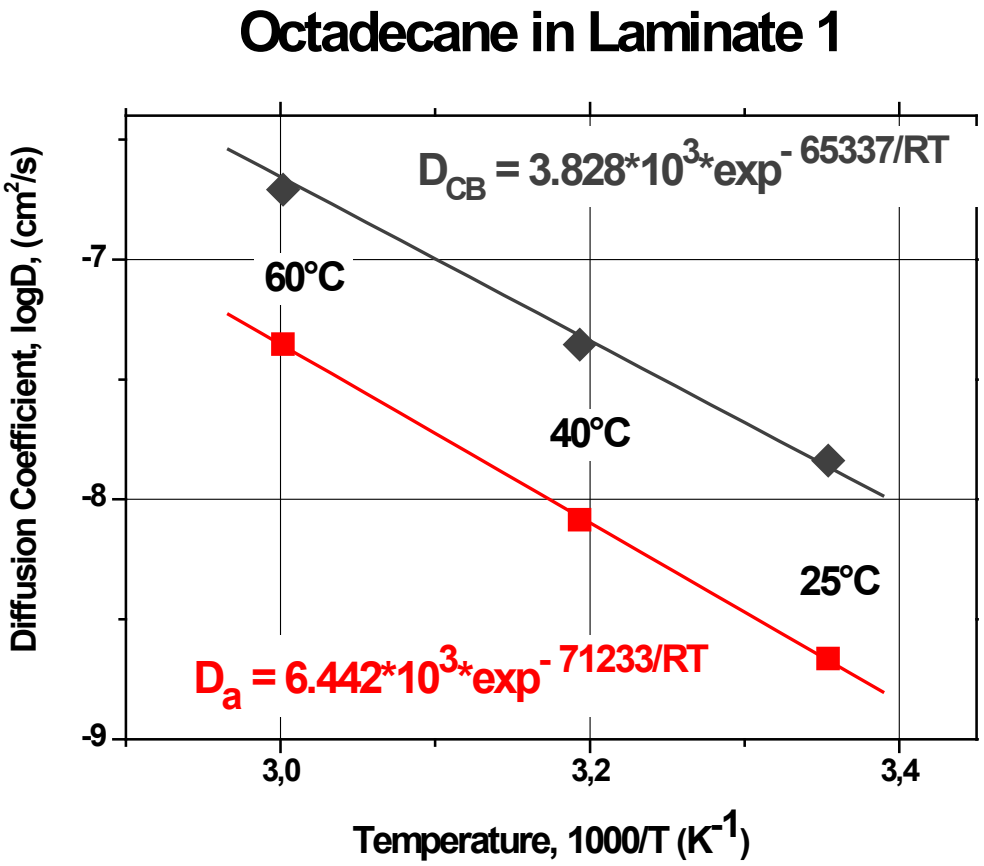

Figure 4: Dependence of diffusion coefficients on temperature, experimental results (dots) and calculated linear regressions (lines).