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**ANALYTICAL METHODS FOR SCREENING OF POTENTIAL VOLATILE
MIGRANTS FROM ACRYLIC-BASE ADHESIVES USED IN FOOD CONTACT
MATERIALS**

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Abstract

Two different analytical techniques, were studied for screening the volatile compounds present in pure adhesives and those coming from the adhesives in different laminates. Three different adhesive formulations were used for the study, all of them acrylic-based and supplied by different producers. Laminates with polypropylene and paper, polypropylene and polyethylene and aluminium and polyethylene as substrates were prepared and studied. Adhesives themselves were acetonitrile extracted and volatiles identified by time-of-flight mass spectrometry based on accurate mass measurement of molecular and main fragments. The volatiles in the films themselves were determined by a headspace solid phase microextraction analysis followed by GC/MS. Significant differences were found within the adhesive formulations. Compounds detected in the screening were assessed in terms of migration through the laminate polypropylene and paper into polyethylene used as a matrix simulating food. The concentration of the compounds in the polyethylene ranged from 0.04 to 1.6 µg/dm² in the polypropylene side, and from 0.27 to 28 µg/dm² in the paper side. The most toxic compound detected in the screening, 2,4,7,9-tetramethyl-5-decyne-4, was not found in any of the sides. Analytical features were also calculated to provide the conditions for quantitative purposes. Sensitivity was at low ng/dm² of polyethylene and the RSD was below 10%. .

Keywords: screening, adhesives, food packaging, GC-TOF-MS, SPME, laminates, analysis, migration, acrylic

33

34 Introduction

35 Most food packages and food contact materials are multilayer materials manufactured
36 using different substrates and adhesives. Although most of the substrates have to fulfil
37 the legislation for being in contact with food (Directives 2002/72 EU, 2007/19/EC for
38 plastics and Resolution AP 2002 approved by the Council of Europe for paper and
39 boards), adhesives, are not yet regulated.

40

41 The adhesive industry uses a large variety of raw materials in food packaging, both
42 natural and synthetic (Booth, 1990). Apart from the polymer, an adhesive formulation
43 may contain the carrier, plasticizers, tackifiers, thickeners, fillers, surfactants, biocides
44 and fungicides, emulsifiers, waxes and antioxidants (Ashley et al. 1995).

45

46 The study of adhesives is a difficult task for many reasons: a) There are many different
47 formulations and standardization is not possible; b) There are a wide variety of
48 substrates, such as plastics, paper and board, aluminium foil, cork or wood; c) The
49 number of compounds involved in the adhesives formulation is very high and no
50 information is provided about them by the companies; d) Migration behaviour is
51 unknown and has never been tested. Adhesives are not as yet regulated mainly due to
52 these difficulties. Only in extremely limited cases such as the polyurethane based
53 adhesive layers, a clear legal restriction appears, specifically for aromatic amines, which
54 migration restriction is 'non-detectable' at 0.010 mg/kg (Commission Directive
55 2002/72/EC and Directive 19/2007/EC).

56

57 All these facts highlight a strong need to develop a solution for this problem, and for
58 this reason, the European Commission decided to finance the EU Project Migresives, in
59 which frame the work reported here has been carried out [www.migresives.eu].

60

61 The analysis of adhesives is the first step to find out which substances could diffuse
62 throughout the different layers and migrate to the food in contact with them (Gruner and
63 Piringer et al. 1999). Nowadays it is well accepted that molecules of molecular mass
64 lower than 1000 daltons can migrate (Figge 1996, Jickells 1997), both in direct and
65 indirect contact with the food, as the diffusion rates are high enough to cross the barrier

of the materials. Diffusion rates are higher for volatile compounds, for this reason, the volatiles are the priority migrants to be studied.

Several analytical procedures can be used for screening the potential volatile migrants coming from the adhesives. The determination of potential migrants in a food contact material usually involves an extraction step followed by the analysis using a chromatographic method. However, sample handling is often time-consuming for fast screening procedures. The methods based on the direct analysis of the headspace by gas chromatography-mass spectrometry (GC-MS) permit the fast identification of migrants with a minimum sample handling but they usually does not provide enough sensitivity (Nerín et al, 2000). Advanced analytical techniques such as GC-TOF-MS (time of flight) provide an accurate mass measurement of ions in mass spectra (Mamyrin 2000) and for this reason has been widely used to identify target and non-target compounds (Marsman et al.2008, Marsman et al. 2007, Setkova et al. 2007, Bianchi et al.2007, Hao et al. 2005, Meruva et al.2004). This technique combined with ChromaLynx software, able to deconvolve complex mass spectra, allows a reliable identification of the compounds and it was used in this work in order to identify the compounds present in the pure adhesives.

An alternative for screening purposes is the analysis of the headspace by solid phase microextraction (HS-SPME) coupled to GC-MS. HS-SPME offers several advantages versus other methods (Pawliszyn 1997, Pawliszyn 1999, Wercinski 1999), mainly a considerably improvement of the sensitivity (Nerín et al, 2008), for this reason, it has been shown as a powerful tool to analyse different solid and liquid samples (Yang et al.2008, da Silva 2008, Pena 2008 , Batlle et al, 2001; Nerín et al, 2002; Lopez et al. 2006, Domeno et al. 2005, Salafranca et al. 1999 and Batlle et al. 1999). In this work, HS-SPME-GC-MS was used in the screening of laminates, since they contained a low quantity of adhesive and a high sensitivity was necessary.

Materials and methods

Materials and reagents

Three acrylic adhesives were selected for this study (adhesive 1, 2 and 3) and they were supplied by three adhesive companies. They were representative of commonly used adhesives in commercial food packaging but their origin and main characteristics are

confidential and cannot be explained here. The laminates studied in this work were either supplied by the companies or prepared in the laboratory: Laminate 1 was prepared with adhesive 1 (grammage 45 g m⁻²) between aluminum foil and polyethylene (PE) (40 µm thickness); laminate 2 was made using the adhesive 2 (grammage 18 g m⁻²) between polypropylene (PP) (25 µm thickness) and PE (40µm thickness); and laminate 3 was made using the adhesive 3 (grammage 12 g m⁻²) with polypropylene (17.5 µm thickness) and paper (70 µm thickness).

Three different SPME fibers were used in this work, 65 µm PDMS/DVB, 85 µm Polyacrylate and 100 µm PDMS. Fibers were supplied by Supelco (Bellefonte, PA, USA). Acetonitrile was from J.T. Baker (Deventer, The Netherlands). 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).

Sample preparation

For the GC-TOF-MS analysis, 1 g of pure adhesive sample (non cured) was extracted with 10 g of acetonitrile. Then, this solution was filtered using 0.22 µm pore size filters in order to remove the acrylic polymer that had precipitated when the acetonitrile was added. After this step, samples were diluted 1/100 with acetonitrile and directly injected into the GC.

For the HS- GC-MS and HS-SPME-GC-MS analysis, 1cm x 1cm laminates prepared from the pure materials and using about 20 g.m⁻² of adhesive were cut and placed into 20 mL headspace vials.

For the migration studies a cell consisting of two plates of aluminium, among which a constant pressure could be applied was used. Two films of PE (40µm) were placed at each side of the laminate and this stack was placed between the plates and stored at 40°C for one hour. Then the cell was opened and each PE film was placed in 20 mL vials and analysed by HS-SPME-GC-MS. Virgin PE films were also analysed with the same technique.

Calibration curves were prepared placing the same amount of PE in 20 mL vials and adding over it 10 μ L of the standards solution at different concentration levels. Once the equilibrium was reached these vials were analysed by HS-SPME-GC-MS.

Instrumental

GC-TOF-MS electron ionization and chemical ionization modes

A GCT Premier from Waters Corporation (Milford, MA, USA) was used in both electron ionization (EI) and positive chemical ionization (PCI) modes, the column used was a Rtx 225 30m x 0.25mm x 0.25 μ m and the volume injected was 2 μ l. Other parameters used are shown in table 1.

HS-GC-MS and HS-SPME-GC-MS

A CTC Analytics CombiPal autosampler from Agilent was used. The autosampler was coupled to a 5975B Agilent gas chromatograph connected to a 6890N mass spectrometer , the parameters selected for the HS and the SPME analysis are shown in table 2.

Results and discussion

GC-TOF-MS electron ionization and chemical ionization modes

The first step in the screening was to study the pure adhesive formulations in their liquid state. Liquid extraction with acetonitrile was applied to the adhesive and GC-MS-TOF was used for the analysis after removing the precipitated polymeric phase by filtration. Electron ionization (EI) was used initially and chemical ionization was further applied to confirm the compound assignments and to check the reliability of the system for screening. The same procedure was applied to all the adhesive samples. Figure 1 shows the chromatogram obtained from the pure adhesive 3 extract using GC-TOF-MS in electron ionization mode. Table 3 lists the compounds identified by this method in the 3 adhesives. Deconvolution of the peaks and identification of the compounds were done using Chromalynx combined with NIST 08 library. This software establishes a list of the most feasible candidates according to the match factor obtained comparing the mass spectrum of the unknown compound with those contained in the NIST database. The match factor is a measure of the certainty of the library search result and ranges from 0 to 1000. Afterwards, for the 5 fragments the most abundant of the spectrum, it calculates the mass difference (Δ mDa) between the accurate masses of the detected

166 fragments and the accurate masses of the candidate fragments. With all these data the
167 software assigned or did not assign identification for the compound.

168
169 EI columns in table 3 show the molecular formula of the main fragment, its accurate
170 mass and the mass difference between the experimentally obtained mass fragment and
171 the theoretical mass value of the proposed compound. Even though table 3 shows the
172 data for the main fragment, mass difference was calculated for five fragments in each
173 compound. This technique enabled a reliable identification even for those compounds
174 with a low match. A total of 42 volatiles were detected by EI in the adhesives studied.
175 Most of the compounds found were esters, probably coming from the polymer involved
176 in the formulation; some alcohols, alkanes and alkoxy groups were also found. Four
177 halogenated compounds were found in adhesives 1 and 3.

178
179 To confirm the identification and complete as much as possible the screening, chemical
180 ionization (CI) GC-TOF-MS was applied to the acetonitrile extracts. Figure 2 shows the
181 chromatogram obtained from the pure adhesive 3 extract using GC-TOF-MS in CI
182 mode. In the CI mode pseudo molecular ions $[M+H]^+$ are detected, being the molecular
183 mass a good confirmation of the compound. Again the identification was based on the
184 comparison between the theoretical accurate mass of the proposed compound and the
185 experimental accurate mass, and the match factor from EI experiments. This technique
186 allowed us to identify 14 unknown compounds and in addition, it was possible to
187 confirm 17 compounds previously identified. A total of 56 compounds were detected,
188 even though the three adhesives were acrylic based, only 9 of the volatiles were found
189 in more than one sample. These results showed the variability of adhesive formulations
190 even though the three samples were acrylic-base and some similarities could be
191 expected. This gives an idea of the complexity of the adhesives and emphasizes even
192 more the importance of the study. Table 3 shows the compounds identified in the three
193 adhesives using CI mode. For some compounds CI provided a higher sensitivity than
194 EI. Some of these compounds, such as 1-hexanol-2-ethyl, n-butyric acid 2-ethylhexyl
195 ester or 3(2H)-isothiazolone-2-methyl were found in adhesives where they had not been
196 detected by EI. New compounds were also found by CI such as 4-heptanone, 3-methyl,
197 2-propanone, 1-bromo, acetic acid, 2-ethylhexyl ester, guanidine, 2-propenoic acid, 2-
198 ethylhexyl ester, hexanoic acid, 2-ethyl-2-methylpropyl ester, 2,5-pyrrolidinedione, 1-
199 (benzoyloxy)-, ethanol 2(2-butoxyethoxy), ethanol, 2(2-butoxyethoxy) acetate, 1-

dodecanol, 2,4,7,9-tetramethyl-5-decyn-4,7-diol and phenol 2,4-bis(1,1-dimethylethyl). Toxtree v 1.51 (Ideacon Ltd) was used to estimate the toxicity according to Cramer rules (Cramer 1978). Cramer rules classify the compounds in three levels of toxicity depending on its chemical structure and propose a maximum daily intake for each compound depending on its toxicity. The maximum intake is 3.0, 0.91 and 0.15 mg/bodyweight Kg/day for class I, II and III respectively. Some of the compounds found in these adhesives, such as guanidine or 2,4,7,9-tetramethyl-5-decyn-4,7-diol and phenol 2,4-bis(1,1-dimethylethyl) had a high toxicity (Class III, Cramer list). 2,4,7,9-Tetramethyl-5-decyn-4,7-diol, nevertheless, was considered as moderate toxic by EPA that means a LOAEL (lowest observed adverse effect level) of 200mg/Kg/day. From this study, it could be confirmed that GC-TOF-MS is a powerful tool for adhesives screening. The use of 2 different ionization modes allowed a more reliable identification of the compounds detected. However, once the adhesive has been applied to the substrates and cured the extraction with acetonitrile will not be so exhaustive and another screening methodology with higher sensitivity, especially for the more volatile compounds, is necessary. For these reason, HS-SPME-GC-MS analysis were carried out.

HS-GC-MS and HS-SPME-GC-MS

Once the pure adhesives were analysed, HS-GC-MS and HS-SPME-GC-MS techniques were used for screening the volatile compounds released by the laminates prepared with these adhesives.

Headspace GC-MS is the most commonly applied technique for the screening of volatile compounds when concentrations are high, as only a portion of the vapour in equilibrium is analysed, while the technique based on SPME is used at lower concentration levels since it is more sensitive due to the pre-concentration step that takes place before injection into GC-MS. Both techniques were checked in this case for screening purposes and applied under the experimental conditions described above.

The HS-SPME-GC-MS technique is based on the sorption properties of the stationary phase bonded to the microfiber, and therefore the selection of the appropriate microfiber is a key point. The first step was the selection of the SPME fibres and the optimization of the parameters for the HS-SPME analysis. This optimization was done for one of the

adhesives. As all the samples studied were acrylic adhesives and had similar chemical characteristics, the optimized method was applied to all of them.

Three SPME fibers were checked for the optimization, a polyacrylate fiber, a PDMS fiber and a PDMS/DVB fiber. Finally, the polyacrylate fiber was selected for the study since it showed the best sensitivity and the highest number of compounds detected (Figure 3).

The number of compounds detected with the polyacrylate fiber was higher than the number of compounds detected by HS-GC-MS, and the intensity of the peaks was also higher when using the SPME. This result confirmed that SPME was much more sensitive as even compounds present at very low concentration in the laminate, where the amount of adhesive was about 2 mg, were detected. Therefore this technique was selected to study the adhesives composition.

The software MODDE 6.0 (Umetrics AB) was used for the optimization of the parameters for the HS-SPME and a Plackett Burman model was selected for this purpose. Three variables were optimized: extraction time (5-30 min), extraction temperature (40-80°C) and desorption time (1-10 min). Finally, the optimum conditions were as follows: extraction temperature 80°C, extraction time 25 minutes and desorption time 1 minute.

The compounds identified using this method are shown in Table 4. Comparing these data with those obtained by GC-TOF-MS, a considerably reduced number of substances were found in SPME. This could be expected, since the samples analysed by SPME were laminates, with a low quantity of adhesive (about 2 mg), while pure adhesives were analysed by GC-TOF-MS. Some of the compounds found such as 1-hexanol-2-ethyl and 2-ethylhexylacetate were probably impurities of the monomers used to form the polymer and 2 propenoic acid, 2-ethylhexyl ester were residual monomers. Other compounds found were common additives used in adhesive formulations, 1-dodecanol is used combined with the monomer to form the polymer, and 2,4,7,9-tetramethyl-5-decyne-4,7-diol is a surfactant ..

Analytical features obtained for some compounds are shown in table 5. Good detection limits were obtained, all of them below 0.8 ng/dm² and reproducibility was always

below 9% with an average value of around 6%. These results confirm that HS-SPME-GC-MS is a valuable tool for the screening of volatile compounds coming from laminates, since it allows detecting compounds at very low concentration levels.

Migration studies and quantitative values

The presence of many compounds in the packaging material does not necessarily imply that they will migrate. In fact, it is expected that most of them remain in the adhesive or in the material layers at both sides of the adhesive. Therefore a migration test will be necessary. Since some of the laminates were manufactured using paper in one side, liquid simulants could not be used for the tests. For this reason, PE was used as receptor for a quick test of the “migration potential” of the compounds identified in the laminates, as it is well known that in general compounds diffuse very fast through it. The test was carried out at 40°C simulating the conditions used in migration tests for food contact materials at room temperature (Council Directive 82/711/EEC). PE was in contact with the laminate for 1 hour since it was observed that this time was enough for the compounds to reach the equilibrium. Nevertheless it should be taken into account that due to the low polarity of PE, the migration of very polar compounds could be underestimated with this test. The results from these migration studies are shown in table 5. None of the detected compounds were found previously in the virgin PE films. As it can be seen, the concentrations ranged from 0.04 to 1.6 µg/dm² (0.11 to 4.4 µg/g) of PE in the PP side and from 0.27 to 28 µg/dm² (0.74 to 75 µg/g) in the paper side. The concentration of the compounds was always higher in the paper side, as it was expected due to the porosity of the paper. The most toxic compound detected in the screening, 2,4,7,9-tetramethyl-5-decyne-4, was not found in none of the sides. After applying a 6 dm² to 1 kg food simulant conversion factor (Directive 82/711/EEC) the maximum value found in the PP side, that will be the side in contact with the food, was 9.8 µg/Kg of polyethylene, being 10 µg/Kg the maximum migration value which has been accepted as of no concern (Directive 2007/19/EC) This study proved that the HS-SPME-GC-MS technique could be used for screening purposes as well as for quantitative determination in migration studies from solid materials, even to quantify levels of non concern. The determination of diffusion and partition coefficients, which are important data for migration modelling, can be also determined by applying this technique.

302

303 Conclusions

304 Two analytical techniques, the GC-TOF-MS and HS-SPME-GC-MS were optimized for
305 screening the volatile compounds coming from the adhesives used in real packaging
306 materials such as laminates. A huge variability of compounds was found among the
307 adhesives studied. Both techniques provided useful information, nevertheless, the HS-
308 SPME-GC-MS was selected for the future study of migration processes, as it was a fast,
309 reliable and very sensitive method and it did not require sample handling.

310

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Table 1: Instrument parameters for the GC-TOF-MS analysis

Instrumentation			
Ionization mode		EI	CI
GC conditions	Gas flow (ml min ⁻¹)	1	1
	Injector (°C)	230,splitless	230,splitless
	Oven	60°C, 5min; 5°C min ⁻¹ ; 220°C 6min	60°C, 5min; 5°C min ⁻¹ ; 220°C 6min
MS conditions	Ionization mode	EI+	CI+
	Mass range	50-800	50-800
	Reaction gas	No	Methane

Table 2. Instrument parameters for the HS- GC-MS and HS-SPME-GC-MS analysis

Instrumentation		
CombiPal HS	Preincubation time (s)	120
	Incubation Temperature (°C)	80
	Volume extracted (mL)	1
CombiPal HS-SPME	Preincubation time (s)	120
	Incubation Temperature (°C)	80
	Extraction time (s)	1500
	Desorption time (s)	60
	Postfiber condition time (s)	1200
GC conditions	Column	DB-5(30 mx0.25 mm,0.25 um)
	Gas flow (ml min ⁻¹)	1.5
	Injector (°C)	250,splitless
	Oven	40°C, 5min; 10°C min ⁻¹ ; 300°C 1min
MS conditions	Mass range	45-400
	Source (°C)	230
	Quadrupole (°C)	150
	Electron energy (eV)	70

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Table 3: Compounds identified in adhesives 1, 2 and 3 by GC-TOF-MS in EI and CI modes, retention times (RT), identification number of the compounds in figures 1 and 2 (No), molecular formula, match factor; main fragment formula, its accurate measured mass and ΔmDa for the EI mode; accurate measured mass of MH and ΔmDa for the CI mode (ΔmDa was calculated referred to the theoretical mass from NIST database)

RT (min)	Compounds	Adhesive	No	Molecular formula	Match factor	EI			CI	
						Main fragment formula	Accurate mass	ΔmDa	Accurate mass (MH)	ΔmDa
5.1	2-propenoic acid, 2-methylpropyl ester	2		C7H12O2	817	C3H3O	55.0160	-2.4		
5.13	2-propenoic acid,methyl ester	2		C4H6O2	748				87.0447	0.1
5.2	4-heptanone	2		C7H14O	926	C4H7O	71.0480	-1.7	115.1131	0.8
5.4	propanoic acid,2-methyl-,butyl ester	2		C8H16O2	786	C4H9O2	89.0600	-0.3	145.1231	0.3
5.83	4-heptanone, 3-methyl	2		C8H16O	856				129.1280	0.1
5.89	2-propanone, 1-bromo	3	1	C3H5BrO	891				136.9687	8.5
5.9	bicyclo[2.2.1]heptan-2-ol, 2-(2-cyclopenten-1-yl)-	1		C12H18O	633	C4H5O	69.0331	-0.9		
6.4	butanoic acid,butyl ester	2		C8H16O2	932	C4H7O	71.0452	-4.5		
6.46	butanoic acid,butyl ester	2		C8H16O2	911				145.1248	2.0
6.7	pyrazine,2,6-dimethyl-	2		C6H8N2	758	C6H8N2	108.0678	-0.9		
7.2	4-methoxy-oxazolidin-2-one	2		C4H7NO3	685	C4H6O2	86.0359	-0.9		
7.7	1-butoxy-2-ethylhexane	1		C12H26O	847	C4H9	57.0700	-0.4	187.2049	-1.3
8.4	2-butenic acid, butyl ester	2		C8H14O2	852	C4H7O2	87.0410	-3.6	143.1106	3.4
9.1	cyclohexanol, 1-butyl-	1		C10H20O	632	C7H15	99.1187	1.3		
9.1	1-hexanol-2-ethyl-	1/3	2	C8H18O	795	C6H11	83.0753	-10.8	131.1377	-5.9
9.1	6-dodecanone	3	3	C12H24O	631	C4H10	58.0779	-0.4		
9.1	cycloheptanol	3	4	C7H14O	561	C3H5O	57.0375	3.5		

9.1	1-decanol	3	5	C10H22O	807	C6H11	83.0757	-10.4		
9.1	1-hexene,2,5-dimethyl-	3	6	C8H16	740	C4H8	56.0598	-2.8		
9.7	acetic acid,2-ethylhexyl ester	1/3	7	C10H20O2	864				173.1552	1.1
9.7	1-pyrrolidinyloxy,3-amino-2,2,5,5-tetramethyl-	3	8	C8H17N2O	644	C4H8N	70.0659	0.2		
9.9	benzaldehyde	1/2		C7H6O	844	C7H5O	105.0341	0.1	107.0504	0.7
10.1	2-fluorobenzoic acid, heptadecyl ester	1/3	9	C24H39FO2	791	C9H17O	141.1276	-0.3		
10.3	2-butoxyethyl acetate	3	10	C8H16O3	901	C4H7O2	87.0446	0.0	161.1207	3.0
10.5	guanidine	1/2		C24H39FO2	949				60.0481	-8.0
10.8	2-fluorobenzoic acid, undecyl ester	1		C18H27FO2	767	C9H17O	141.1272	-0.7		
10.9	benzene, 1,3,5-triethyl-	1		C12H18	939	C10H13	133.1008	-0.9	163.1497	1.0
11.5	propanoic acid, octyl ester	1/3	11	C11H22O2	754	C5H10	70.0689	-9.4	187.1695	-0.3
11.8	2-propenoic acid,2-ethylhexyl ester	3	12	C11H20O2	856				185.1541	0.0
12.3	hexanoic acid, 2-ethyl-,2-methylpropyl ester	1		C12H24O2	829				201.1835	-1.9
13.0	2,5-pyrrolidinedione, 1-(benzoyloxy)-	2		C11H9NO4	964				220.0610	0.0
13.4	n-butyric acid 2-ethylhexyl ester	1/3	13	C12H24O2	859	C4H7O	71.0498	0.1	201.1805	-4.9
13.8	octane, 3-ethyl-	1		C10H22	828	C8H16	112.1238	-1.4		
14.4	cyclopentane,(2-methylbutylidene)-	1		C10H18	691	C8H13	109.1011	-0.6		
15.2	ethanol2(2butoxyethoxy)	3	14	C8H18O3	800				163.1243	-9.1
15.9	3-hydroxypropanoic acid 1-butyl ester	2		C7H14O3	588	C3H5O3	89.0229	-1.0		
16.2	decane,1-bromo-	3	15	C10H21Br	900	C4H8[81Br]	136.9800	1.1		

16.2	undecane,1-bromo	3	16	C11H23Br	813				235.1120	5.8
18.5	ethanol,2(2-butoxyethoxy) acetate	3	17	C10H20O4	913				205.1325	-11.5
19.1	2-butanone,4-(acetyloxy)-	3	18	C6H10O3	709	C4H7O2	87.0447	0.1		
19.2	5-chloro-2-methyl-3(2H)-isothiazolone	1/3	19	C4H4ClNOS	835	C4H4NOS[35Cl]	148.9703	0.1	149.9791	1.1
19.3	1-dodecanol	2		C12H26O	879	C6H11	83.0857	-0.4	187.2096	3.4
20.5	2,4,7,9-tetramethyl-5-decyn-4,7-diol	3	20	C14H26O2	792				227.2011	0.0
20.9	3(2H)-isothiazolone, 2-methyl-	1/3	21	C4H5NOS	881	C4H5NOS	115.0019	-7.3	116.0137	-3.3
21.4	cyclopentane,1,2,3-trimethyl-, (1a,2a,3a)-	3	22	C8H16	718	C5H10	70.0753	-3.0		
21.4	3,7-dioxo-4,8-dioxa-10-ethyl-1-tetradecanol	3	23	C14H26O5	712	C3H5O2	73.0237	-5.3		
22.2	2-[2-(2-ethoxyethoxy)ethoxy]ethyl acetate	3	24	C10H20O5	844	C4H7O2	87.0441	-0.5	221.1389	0.0
23.1	2-butenedioic acid (z)-, dibutyl ester	3	25	C12H20O4	886	C4H3O3	99.0080	-0.2		
23.2	phenol 2,4-bis(1,1-dimethylethyl)	3	26	C14H22O	883				207.1749	0.0
23.2	pentanoic acid, 5-hydroxy-,2,4-t-butylphenyl esters	3	27	C19H30O3	886	C13H19O	191.1444	0.8		
23.4	benzoic acid,4-ethoxy-,ethyl ester	3	28	C11H14O3	872	C7H5O2	121.0291	0.1	195.1021	0.0
25.3	2-[2-(2-butoxyethoxy)ethoxy]ethyl acetate	3	29	C12H24O5	816	C4H7O2	87.0444	-0.2		
25.5	hexanedioic acid, 3-methyl-,dibutyl ester	2		C15H28O4	670	C7H11O3	143.0709	0.1		
25.8	4,4'-bi-1,3,2-dioxaborolane, 2,2'-diethyl-, (R*,S*)-	1		C8H16B2O4	722	C5H7O2	99.0439	-0.7		
27.2	phenol, 4-(1,1,3,3-	1		C14H22O	932	C9H11O	135.0804	-0.6		

	tetraamethylbutyl-							
27.6	benzophenone	3	30	C ₁₃ H ₁₀ O	913	C ₇ H ₅ O	105.0337	-0.3

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Table 4. Compounds identified by HS-SPME-GC-MS in adhesives 1, 2 and 3, retention times (RT) and identification number of the compounds in figure 3 (No).

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RT (min)	Compounds	Adhesive	No
9.2	benzaldehyde	2	
10.72	1-hexanol- 2-ethyl	1/3	1
11.9	undecane	2	
12.3	benzene ,1,3,5-triethyl	1	
12.8	acetic acid, 2-ethylhexyl ester	1/3	2
13.4	2-ethylhexylacrylate	3	3
13.6	1-butoxy-2-ethylhexane	1	
14.0	ethanol, 2-2(butoxyethoxy)	3	4
14.1	dimethyl adipate	3	5
15.3	n-butyric acid, 2-ethylhexyl ester	1	
16.0	ethanol, 2-2(butoxyethoxy) acetate	3	6
16.1	propanoic acid, 2-methyl-,hexyl ester	2	
16.1	3-hydroxypropanoic acid 1-butyl ester	2	
16.7	2,4,7,9-tetramethyl-5-decyne-4,7-diol	3	7
17.3	1-dodecanol	2	
22.97	butanoic acid, butyl ester	2	
23.25	hexanedioic acid, 3-methyl-,dibutyl ester	2	

Table 5. Concentration of the compounds found in PE from migration experiments expressed as $\mu\text{g}/\text{dm}^2$ of PE and as $\mu\text{g}/\text{g}$ of PE, limits of detection (LOD) expressed as ng/dm^2 of PE and RSD (%) of the analytical method.

	lamine PP side ($\mu\text{g}/\text{dm}^2$)	lamine PP side ($\mu\text{g}/\text{g}$)	lamine paper side ($\mu\text{g}/\text{dm}^2$)	lamine paper side ($\mu\text{g}/\text{g}$)	LOD (ng/dm^2)	RSD (%)
1-hexanol-2-ethyl	0.04	0.11	0.34	0.93	0.79	5.5
2-ethylhexylacetate	0.05	0.13	1.2	3.3	0.39	6.2
Ethanol-2(2 butoxyethoxy)	0.17	0.46	3.2	8.7	0.59	6.7
2-ethylhexylacrylate	0.04	0.11	0.58	1.5	0.39	5.3
Dimethyladipate	0.07	0.18	0.27	0.74	0.79	5.4
Ethanol 2(2- butoxyethoxyacetate)	1.6	4.4	28	75	0.39	8.3
<u>2,4,7,9-tetramethyl-5- decyne-4</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	0.59	6.0

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n.d. non detected in the migration experiment

Figure 1. Chromatogram of adhesive 3 obtained by GC-TOF-MS and EI mode. Identification numbers explained in table 3.

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Figure 2. Chromatogram of adhesive 3 obtained by GC-TOF-MS and CI mode. Identification numbers explained in table 3.

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Figure 3. Chromatogram of laminate 3 obtained by HS-SPME-GC-MS with a polyacrylate fiber
[Identification numbers explained in table 4.](#)

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