Eur Food Res Technol (2008) 226:1399–1407
DOI 10.1007/s00217-007-0670-4

ORIGINAL PAPER

Migration from the gaskets of lids into oily foods: first results on polyadipates

Maurus Biedermann · Katell Fiselier · Giuseppe Marmiroli · Giampietro Avanzini · Ernst Rutschmann · Susanne Pfenninger · Koni Grob

Received: 21 February 2007 / Revised: 25 April 2007 / Accepted: 7 May 2007 / Published online: 7 June 2007
© Springer-Verlag 2007

Abstract The migration from the gaskets of plasticized PVC in metal closures usually far exceeds the legal limits if the packed food contains some free oil. If the gaskets continue to consist of PVC, polyadipates seem to be the only acceptable plasticizers, although difficult to work with: they render the plastisol highly viscous and make it difficult to place a uniform ring into the lid. This suggests dilution with plasticizers of low viscosity. Results from simulating tests (olive oil in direct contact) confirm that the migration of polyadipates is far lower, but also that even the migration of minor portions of diluting plasticizers is critical for the overall migration. The first tests with 11 packed foods, stored and repeatedly shaken for up to 2 years, show migration of polyadipate clearly below the limits. It was lower than that determined by simulating tests, whereas the migration of ESBO was several times higher, questioning the suitability of presently applied testing.

Keywords Gaskets for metal closures · Migration of plasticizers · Polyadipates · Oily foods · Simulating migration testing

M. Biedermann · K. Fiselier · E. Rutschmann · S. Pfenninger · K. Grob (✉)
Official Food Control Authority of the Canton of Zürich, P.O. Box, 8032 Zurich, Switzerland
e-mail: Konrad.Grob@klzh.ch

G. Marmiroli · G. Avanzini
IN.CAM, Via Brodolini, 42040 Campegine, Italy

List of abbreviations

AHCM	Acetylated, hydrogenated castor oil monoglyceride
ATBC	Acetylated tributyl citrate
DEHP	Di-(2-ethylhexyl) phthalate
Da	Dalton
DBS	Dibutyl sebacate
EA	Erucamide
EE190	Acetylated monolaurate
ELSD	Evaporative light scattering detection
ESBO	Epoxidized soy bean oil
OA	Oleamide
OML	Overall migration limit
PA	Polyadipate
SEC	Size exclusion chromatography
SML	Specific migration limit
TDI	Tolerable daily intake

Introduction

Metal closures for glass containers are equipped with a gasket sealing against the rim of the jar, presently consisting of plasticized polyvinyl chloride (PVC). A lid contains nearly 1 g of gasket material, of which typically 250–350 mg is in direct food contact, i.e. on the food-oriented side of the seal [1]. As the PVC usually contains 35–45% plasticizer, mostly more than 100 mg plasticizer is exposed to the food. A small amount of free oil (typically on top of the food) is sufficient to extract the plasticizers from the gasket to an extent approaching completeness after a longer storage period. There is negligible migration, however, if the food is purely aqueous, like marmalade or pickles, or if the food is sufficiently firm not to get into contact with the lid (as often the case for, e.g. mustard).

The migration of plasticizers into oily food was typically in the range of 100–1,000 mg/kg, far exceeding the European overall migration limit (OML) of 60 mg/kg or 10 mg/dm^2 and often even further exceeding the specific migration limits (SMLs) or limits derived from tolerable daily intakes [2, 3]. Migration reaches worrying levels: di(2-ethylhexyl) phthalate (DEHP) was found in concentrations up to 1,130 mg/kg [4]. A child of 20 kg body weight reaches the tolerable daily intake (TDI, 0.05 mg/kg body weight) with less than 1 g of such a product per day, which means that the content of a single jar (300 g) is sufficient to bring exposure to the TDI for almost 1 year (provided other sources of DEHP are neglected). It must be assumed that such products were marketed and consumed for many years.

The frequent and drastic infringement of legal requirements became public in autumn 2004. As there were no lids respecting the legal limits for oily products, the Swiss authorities lifted the legal restrictions for epoxidized soy bean oil (ESBO) [5] in order to provide a way out for the food industry, but also to prevent the use of plasticizers more toxic than ESBO. At first, the EU Commission insisted on complying with the rules, but then reacted by declaring that the gaskets are no longer considered to be within the scope of the plastic directive 2002/72 (although the blowing agent azodicarbonamide and the ESBO for infant food were regulated within this directive and its amendments 2004/1 and 2005/79). The Commission intended to introduce a new regulation on lids in order to enable a temporary lifting of existing restrictions, such as the overall migration limit (OML). However, this approach had to be abandoned because of legal problems, and the lids were re-introduced into the plastic regulation by the 4th Amendment of Directive 2002/72. An additional regulation (working title "Transitional Regulation") temporarily increases the tolerated migration for some plasticizers until the 4th Amendment is implemented.

More than 2 years after the first actions were taken (summer 2004), two technical solutions became public. Metropak (Hvidovre, Denmark) introduced a metal closure with a polyethylene ring replacing the PVC gasket. So far, its application seems to be limited to products not requiring treatment at elevated temperature. In Summer 2005, IN.CAM. (Campegine, Italy) started the production of lids for pasteurized products with a PVC gasket plasticized only with polyadipate (PA).

Polyadipates

Polyadipates are used as plasticizers in numerous PVC applications, including cling films for wrapping foods. They are also called polymeric additives, as they consist of oligomers based on adipic acid linked by a diol. Numerous PAs are marketed for food contact. They vary in the molecular mass distribution, the link unit (diol) and in their termination (adipic acid, alcohol or a mixture of both). Acid-terminated PAs are end-capped with octanol and/or decanol. Alcohol-terminated PAs may be end-capped with acetic acid or fatty acids.

For applications in food contact, Directive 2002/72/EC specifies PAs as polymeric materials consisting of "1,2-propanediol and/or 1,3- and/or 1,4-butanediol and/or polypropyleneglycol esterified with adipic acid, also end-capped with acetic acid or fatty acids C10–C18 or n-octanol and/or n-decanol". With its amendment 2004/19/EC, the range of accepted fatty acids was reduced to C12–C18. The directive sets an SML of 30 mg/kg, whereby only the part with a molecular mass below 1,000 Da is taken into consideration (Practical Guide [6]).

For containers of less than 500 ml content, Article 7 of Directive 2002/72 permits the recalculation of the specific migration through the internal food contact surface area of the container, and a transformation of the SMLs listed in terms of mg/kg assuming 6 dm^2 being in contact with 1 kg of food, i.e. dividing them by 6 dm^2/kg. This significantly increases the tolerated migration into small packs. Article 2, ruling on the overall migration, is similar, but excludes caps and lids from this recalculation, i.e. the OML always applies as 60 mg/kg. The 4th Amendment of Directive 2002/72 will change this, giving this bonus also to lids. The "Transitional Regulation" defines the relevant food contact surface area as "total food contact surface of lid and sealed container".

Table 1 illustrates the recalculation to migration related to food contact surface area for some real jar sizes. The first columns specify the jar and its total internal surface. Using the OML as a numeric example, maximum legally tolerated migration is calculated in terms of amount related to the lid (mg/lid), which is equivalent to the amount in the jar content. When applied as concentration in the jar content (60 mg/kg), the lids may release up to between 5.4 mg (90 g jar) and 18 mg (300 g) material. If the limit is applied in terms of quantity per contact surface area (10 mg/dm^2), the tolerated migrate increases to 12–27 mg/lid, and the legally accepted concentration in the jar content increases up to 130 mg/kg (second last column), which corresponds to an extra tolerance (bonus) by up to a factor of 2.2.

The relatively high molecular weight of PAs causes the migration to be substantially lower than that of monomeric plasticizers. The <1,000 Da fraction relevant for the SML gets smaller with increasing mean molecular mass and ranges between about 5 and 35% (extremes shown in Fig. 1 by their size exclusion chromatograms, as shown in [7]). Further, migration rapidly decreases for components exceeding 1,000 Da, and because the high molecular mass PA contains less material closely above 1,000 Da, overall migration also decreases.

Table 1 Effect of recalculating the OML from concentrations (mg/kg) in the jar content to migration per contact surface area (mg/dm^2) as discussed in the text

Jar size				mg/lid at OML in terms of		OML in mg/dm^2 as mg/kg	Bonus OML as mg/dm^2
W (g)	Ø (mm)	*h* (mm)	*a* (dm^2)	60 mg/kg	10 mg/dm^2		
90	43	65	1.2	5.4	12	133	2.2
125	55	48	1.3	7.5	13	104	1.7
190	53	100	2.1	11	21	111	1.8
300	63	107	2.7	18	27	91	1.5

The same extra-tolerance (bonus) applies to SMLs

W weight of jar content, *Ø* diameter of jar, *h* height of jar, *a* total internal surface area

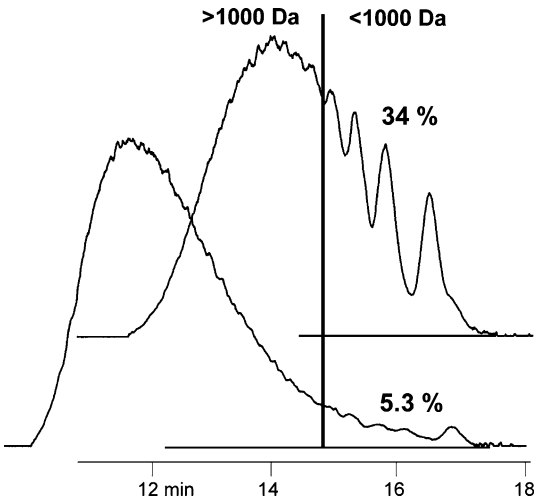

Fig. 1 Size exclusion chromatograms with evaporative light scattering detection (ELSD) and segmental linearization [7] of PAs of low and high molecular mass, containing a large (34%) or a small (5.3%) fraction of <1,000 Da components, respectively

For the manufacture of gaskets in lids, PAs are difficult to work with: when mixed into PVC powder, highly viscous plastisols are obtained. With the common technology involving a pistol it is difficult to deposit these such that a uniform gasket is obtained. The viscosity increases with the molecular mass, i.e. the PA with the lowest migration is most difficult to apply. This calls for a compromise and is also the reason why several producers attempt to mix the PA with less viscous monomeric plasticizers (see later).

Analytical methods

The proportion of the <1,000 Da components was determined for 13 commercial PAs using size exclusion chromatography (SEC) and ELSD with segmental linearization [7]. It is an approximation because SEC separates by size and shape rather than by molecular mass. Furthermore, the different components do not have equal response per unit mass, and the application of response factors is not possible in practice.

The determination of PA concentrations in food or simulant D (olive oil) starts with the determination of the total amount of PA to check compliance with the OML. If the overall migration exceeds the SML, but remains below the OML, also compliance with the SML must be tested, which means isolation of the <1,000 Da fraction by SEC.

The method used to obtain the results reported below was described in [8]. It is based on determining adipate, as described by Castle et al. [9, 10], although by alkali transesterification and formation of the dibutyl ester. The calculation of the PA material presupposes a conversion factor (CF) taking into account the other constituents of PA, such as the diol linker and possibly groups introduced for end-capping. The CF was derived from the stoichiometric proportion of adipic acid in the PA components of a molecular mass below 1,000 Da, because this is the material relevant for the specific migration and also the major portion in the overall migrate [11]. It was calculated for each compound present in the PA at a relevant amount. The weighed mean proportion was determined taking into account the relative concentrations of the components in the PA. The CF ranged between 1.1 and 2.5.

Adequate migration testing

For the development of new gaskets, accelerated migration testing is an essential tool to answer the question whether migration will remain below the legal limit up to the end of the shelf life of the packed food, which may be as much as 5 years. For oily foods, simulant D (olive oil) is used, brought into contact with the relevant part of the gasket by applying the lid to a jar and keeping the jar on its head. The testing conditions specified by the EU Directive 82/711 provide the thermal treatment for pasteurization or sterilization plus exposure at 40 °C for 10 days. However, because legal limits must be respected in the real products (EU framework regulation 1935/2004), the testing conditions must be adjusted to correctly simulate migration into the food, even if this causes them to deviate from those legally specified.

An attempt was made to extrapolate the long-term migration of PAs from that of plasticizers used in the past [1]: the amount of migrated ESBO and phthalate was determined in products from the market and compared to results obtained from simulated migration testing of similar unused lids. To compensate for varying amounts of gasket material and plasticizer exposed to food, migration was calculated as percentage of the plasticizer present in the gasket in direct food contact (food-oriented part of the seal). The age of the samples was unknown; it was probably far below the shelf life for most samples.

Migration of ESBO into real products reached 90% of the amount present in the gasket in food contact. The highest migration of phthalates far exceeded 100%, indicating that phthalates diffused into the food also from within and even outside the seal. Also lids with several plasticizers being combined in the gasket showed that the migration of ESBO is several times lower than that of phthalates and other frequently used plasticizers, pointing out the importance of the molecular mass for diffusion processes. ESBO was considered pertinent for comparison, as the molecular mass is around 1,000 Da, i.e. in the range of main interest for PAs. Migration testing at 100 °C during 1 h plus at 40 °C for 10 days only caused 13% of the ESBO to migrate, i.e. simulation at the conditions specified by law severely underestimated migration into food. After 20 days at 60 °C, ESBO migration reached 58% of the amount present in the gasket, i.e. these conditions seemed to better reflect reality, but still not to simulate the worst case.

This paper summarizes the results on the migration of PAs obtained up to the end of the year 2006. The results are not considered conclusive and important inconsistencies have not been clarified, but in the interest of rapid progress towards lids for oily foods complying with legislation it seemed useful to present them now.

Experimental

The determination of PA in foods or simulant D (olive oil) was described in [8]. Briefly, 1 g of sample or 100 mg of olive oil from simulation was suspended/dissolved in 10 ml tetrahydrofuran (THF) containing the internal standard and some verification standards. To 100 µl of the supernatant/solution, 2 ml of 5% 1-butoxide/1-butanol was added, and the PA allowed to transesterify during 60 s at ambient temperature. The reaction was stopped by admixture of 4 ml aqueous disodium hydrogen citrate (15 g/100 ml). In the resulting 2-phase system, the esters are in the supernatant butanol. To reduce the water content of the butanol, 400 µl heptane containing further verification standards was added. This solution was analyzed for dibutyl adipate by gas chromatography (GC)–mass spectrometry (MS).

The CF for calculating the adipate into PA was determined for the product used in the gasket, either using a sample of the PA if available or an extract from the gasket. The PA components <1,000 Da were identified by silylation and GC–MS with a short column minimizing degradation at high oven temperature [12]. Quantitative compositional analysis involved GC-FID with response factors calculated from effective carbon numbers. From each component, the amount of DMA formed was stoichiometrically calculated. The sum of the concentrations of the PA components divided by summed contributions to DMA yielded the CF. The detection limit of the method was around 1 mg/kg, the limit of determination about 3 mg/kg, determined by interferences, i.e. varying with the sample matrices. The measuring uncertainty was below 20%.

The PAs were characterized by the percentage of <1,000 Da components, using SEC-ELSD on a 300 × 7.8 mm i.d. column packed with Phenogel 5 µm/500 Å (Phenomenex, Brechbühler AG, Schlieren, Switzerland) and THF free of stabilizer and peroxides as mobile phase [8]. The same SEC was used for preseparation of samples to determine the migrates <1,000 Da.

ESBO was determined in foods or simulant D (olive oil) by on-line coupled high performance liquid chromatography (HPLC)-GC-flame ionization detection (FID) [12]. The other plasticizers were measured by GC–MS with injector-internal thermal desorption using programmed temperature vaporizing (PTV) injection [13].

Migration was simulated with simulant D (refined olive oil; Fluka, Buchs, Switzerland) according to the official method EN 1186 of the Comité Européen de Normalization (CEN). 10 ml oil was added into a jar and the lid mounted loosely. The jar was heated to 100 °C for 15 min before manually screwing down the lid to a deformation of the gasket equivalent to that resulting from industrial closure. Then the jar was turned on its lid and the migration experiment started with heating corresponding to pasteurization (1 h/100 °C) or sterilization (1 h/130 °C) followed by 10–20 days at 40 or 60 °C. The olive oil extracted from the gasket was transesterified with methoxide/methanol [14] to avoid esterification of free fatty acids expected in the gaskets from the Zn/Ca stabilizers. Since the ratio of methyl palmitate/methyl oleate was increased in the extract from the gasket as compared to the olive oil used, the olive oil absorbed into the gasket was calculated from methyl palmitate and stearate only.

The amount of gasket material in direct food contact was determined gravimetrically by cutting the gasket along the inner side of the seal against the jar rim and removal with wood-carving tools as described in [1].

Results

Plasticizer composition

First experiments primarily aimed at investigating the potential for reducing the viscosity of a PA plastisol by admixture of less viscous plasticizers. Table 2 shows results from migration testing of lids of 53 mm diameter with olive oil for 1 h at 100 °C (pasteurization) plus 10 or 36 days at 40 °C. Migration in terms of mg/dm^2 was calculated for a 190 g jar with an internal surface area of 2.1 dm^2. The lid in the first line had a gasket containing 34% of PA1 containing about 16% components <1,000 Da and 10% ESBO. After testing for 10 days, 6.3 mg PA migrated, of which 3.7 mg (59%) were components <1,000 Da. Together with 3.7 mg ESBO, the total migration of plasticizers amounted to 10 mg/lid. After 36 days, the sum of the migrated plasticizers reached 16.5 mg/lid or 7.9 mg/dm^2, which is still clearly below the OML (10 mg/dm^2). With 2.7 mg/dm^2, the PA < 1,000 Da remained below the SML (5 mg/dm^2).

Dilution of PA2 (about 14% <1,000 Da) with 8% ESBO and 11 or 5% EE190 (acetylated monolaurate) resulted in migration exceeding the OML for the 190 g jar at least after 36 days. The gasket exclusively with PA2, however, showed substantially lower migration, suggesting that the OML would be respected down to small jars.

A next experiment (Table 3) primarily compared various PAs and mixtures thereof, in three cases with an addition of ESBO. The PAs are characterized by the percentage of components <1,000 Da. PA1 and PA2 correspond to those in Table 2. Migration testing involved 1 h/100 °C plus 10 days/40 °C. In two cases also the slip agents oleamide (OA) and erucamide (EA) were analyzed. As their content was equal in all gaskets, the same values were assumed for the other lids (in italics) to enable summing up the main migrants and approximating overall migration.

The PAs are listed in the sequence of decreasing percentage of <1,000 Da components. Indeed, the migration of whole PA as well as of the components <1,000 Da decreased correspondingly, as shown in terms of milligrams per lid in the center of the table and in the percentage referring to the PA material contained in the gasket in direct food contact at the right. For the lid of the top line, 4.1% of the PA in the gasket was transferred, while it was 11% of the ESBO and about 30% of the slip agents. For PA5 with

Table 2 Migration testing for experimental lids

Plasticizers (% in gasket)				Migration 1 h 100 °C + 10 days 40 °C						Migration 1 h 100 °C + 36 days 40 °C					
				mg/lid				Sum		mg/lid				Sum	
PA1	PA2	ESBO	EE190	PA	PA < 1000	ESBO	EE190	mg/lid	mg/dm^2	PA	PA < 1000	ESBO	EE190	mg/lid	mg/dm^2
34		10		6.3	3.7	3.7		10	4.8	11	5.9	5.2		17	7.9
	25	8	11	2.8	2.4	2.2	17	22	10	4.3	2.1	3.5	21	28	13
	31	8	5	3.9	3.4	2.7	9.5	16	7.7	5.6	2.9	4.0	15	24	11
	44			5.6	3.8			5.6	2.7	8.3	3.9			8.3	4.0

EE190, acetylated monolaurate; PA < 1,000, PA components below 1,000 Da

Table 3 Migration experiments (olive oil, 1 h/100 °C + 10 days/40 °C) for experimental 63 mm lids containing various PAs

Gasket components (% in plastisol)								Migration (mg/lid) 1 h/100 °C + 10 days/40 °C						Transfer from gasket in food contact (%)			
PA1	PA2	PA3	PA4	PA5	ESBO	OA	EA										
% <1,000 Da																	
16	14	10	9	5				PA		ESBO	OA	EA	Sum	PA	ESBO	OA	EA
								Tot.	<1,000					Tot.			
20				13	11	0.93	0.93	4.3	3.0	3.9	0.8	1.0	10.0	4.1	11	27	34
14.6	14.6			14.6		*0.93*	*0.93*	5.1	3.3		*0.8*	*1.1*	7.0	3.6			
	22			22		0.93	0.93	3.7	2.7		0.8	1.1	5.6	2.6		27	37
		33			11	*0.93*	*0.93*	5.1	2.2	5.1	*0.8*	*1.1*	12.1	4.9	14		
		20		20	4	*0.93*	*0.93*	3.7	1.6	2.3	*0.8*	*1.1*	7.9	2.9	18		
			44			*0.93*	*0.93*	3.0	2.3		*0.8*	*1.1*	4.9	2.1			
				44		*0.93*	*0.93*	2.3	1.7		*0.8*	*1.1*	4.2	1.6			

the lowest percentage of <1,000 Da components, the transfer amounted to only 1.6%.

Under the simulating testing conditions, the SML for PA (5 mg/dm^2) was well respected by all lids (even for a 90 g jar, 6 mg/lid would be tolerated, see Table 1). The migration of the sum of the additives was between 4.2 and 7 mg/lid for the gaskets exclusively containing PAs as plasticizers and 10–12 mg/kg for those with 11% ESBO. Even the latter comply with the OML for most of the jar sizes, but the margin is small and the OML could easily be exceeded if the simulated testing had underestimated real migration. The migration of the slip agents alone amounted to nearly 2 mg/lid, i.e. almost reached that of PA5 present at 25 times higher concentration.

Table 4 shows results from two lids of unknown manufacturers (composition determined analytically [15]). Migration was tested by heating to 100 °C/1 h followed either by 40 °C/10 days or 60 °C/20 days. Lid 1 contained 20% of a PA with about 20% <1,000 Da components, 8% dibutyl sebacate (DBS) and 8% acetylated and hydrogenated castor oil monoglyceride (AHCM; Danisco Grindsted Soft-N-Safe). Even with 40 °C/10 days, migration was high (sum, 27 mg/lid), primarily because of the diluting plasticizers. In fact, at 40 and 60 °C testing conditions, 47 and 123%, respectively, of the DBS in the gasket in direct food contact was transferred into the oil, but only 7 and 18%, respectively, of the PA.

Lid 2 contained 10% of a polyadipate of rather low molecular mass, combined with 20% acetyl tributyl citrate (ATBC) and a small amount of DBS. Although the molecular mass of ATBC is modest (402 Da), its migration in terms of percent in direct food contact was only 16 and 50% at 40 and 60 °C testing conditions, respectively, and surprisingly little above that of the polyadipate.

Adequate simulation

Most of the above results were obtained using the testing conditions laid down in the EU Directive 82/711. However, as shown in [1], migration into foods may be higher and it is the migration into food that finally has to comply with the legal limits. To predict long-term migration, conditions for simulation were adjusted such that the percentages of migration observed in products from the market were reached for ESBO and di-(2-ethylhexyl)-phthalate (DEHP). At least 20 days at 60 °C were required. Since no such experiments were possible with PA, these conditions were, as a first approach, assumed to be appropriate also for PA.

Figure 2 compares the migration of PA with that of ESBO and DEHP in standard migration testing after an initial heating to 100 °C for 1 h followed by 40 or 60 °C for varied periods of time. Results are expressed in terms of percent of the component in the gasket in direct food contact, distinguishing between the <1,000 Da fraction and the total of the PA. Different lids were used, with PA, ESBO or DEHP as the only plasticizer in the gasket. For ESBO it was shown that among five lids from different manufacturers the migration at 60 °C for 10 days varied from 37 to 88% [1], i.e. significant variation must be taken into account.

The PA corresponded to PA4 in Table 3 with 9% of <1,000 Da components. The migration of the PA < 1,000 Da largely corresponded to that of ESBO and was lower than that of DEHP (390 Da). Migration of the total PA was far lower. From the difference between the total and the <1,000 Da PA migrate it is calculated that for 20 days at 60 °C merely 3.6% of the 91% material >1,000 Da migrated into the oil. From this it might be concluded that the migration of PA would be little above that

Table 4 Simulated migration (olive oil, 1 h/100 °C + 10 days/40 °C or 20 days/60 °C) for lids with gaskets containing various plasticizers (Composition gasket) reducing the viscosity of the PA

	Lid 1					Lid 2				
	Composition gasket (%)	Migration				Composition gasket (%)	Migration			
		mg/lid		%			mg/lid		%	
		40 °C	60 °C	40 °C	60 °C		40 °C	60 °C	40 °C	60 °C
PA	20	4.8	12.5	7	18	10	2.5	8.5	10	33
DBS	8	13	34	47	123	1.5	1.6	4.8	41	122
AHCM	8	7.0	21	25	76					
ATBC						20	8.2	26	16	50
EA	1.2	0.8	2.2	19	52	1.3	0.7	2.1	21	62
OA	1.2	1.0	2.8	23	66	1.1	0.8	1.9	28	66
Sum		27	72				14	43		

DBS dibutyl sebacate, *AHCM* acetylated and hydrogenated castor oil monoglyceride, *ATBC* acetyl tributyl citrate, *EA* erucamide, *OA* oleamide

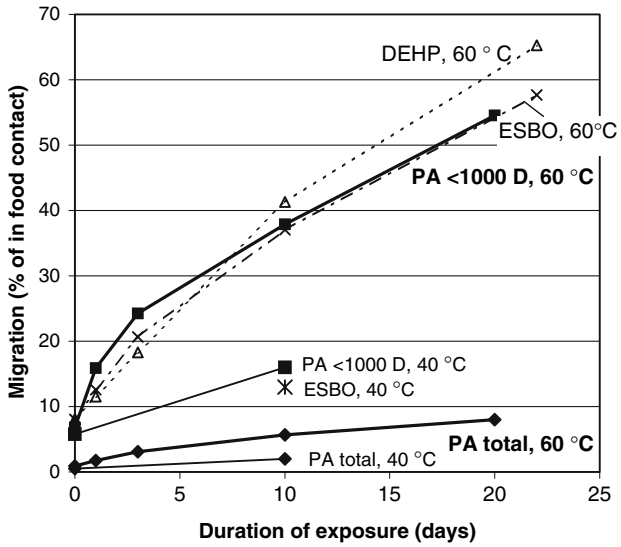

Fig. 2 Migration of PA4 containing 9% components <1,000 Da into oil during various periods of time; total PA material (*PA total*) and the fraction <1,000 Da (*bold lines* for 60 °C). Comparison with ESBO and DEHP migration applying the same conditions. Values at time 0 correspond to the migration after the initial heat treatment

of ESBO (for which 20 days/60 °C seemed adequate) when calculating only with the part <1,000 Da.

Overall migration

Overall migration was determined for 63 mm lids with PA2 intended for pasteurization as well as with PA4 (and a different PVC) for sterilization. Testing was performed with olive oil in a jar turned on the lid and an initial heating for 1 h at 100 °C (pasteurization) or 130 °C (sterilization) followed by either 10 days/40 °C or 20 days/60 °C. In the oil from the migration test, also the specific migrations of PA and the slip agents were determined.

For the lid with PA2, testing at standard conditions of 10 days/40 °C caused an overall migration of 12.5 mg/lid (Table 5) slightly exceeding the OML for the 90 g jar in Table 1, but respecting it for the 125 g jar. 6.5 mg/lid or 52% of this migrate was from the PA. The slip agents contributed 18%, whereas 30% originated from non-identified sources, such as the PVC stabilizers, PVC raw material and the coating. With PA4, containing 9 rather than 14% <1,000 Da components, overall migration was below the OML even for extremely small jars.

Testing at 60 °C for 20 days increased overall migration by a factor of almost 2.5. For the lid with PA2, the OML was exceeded even for 300 g jars. Migration of the PAs and the amides OA and EA increased more strongly than that of the unidentified other components, i.e. increased also in relative terms. For the lid with the higher molecular PA4, the OML was respected for jars of at least 190 g content.

Migration into real products

For a long-term migration test, critical real foods (Pesto, various sauces, vegetables in oil, all >10% oil) were industrially packed between November 2004 and September 2005. They were stored at ambient temperature and gently shaken every 1–2 months, imitating agitation in reality. The gaskets were plasticized with PA1 or PA2. Periodically a jar of each product was analyzed for PAs, i.e. the data refers to different jars of the same product. Migration was calculated as concentration in food (center in Table 6) as well as in terms of mg/dm^2 (to compare with the legal limits). The migration data shows scattering clearly exceeding the measurement uncertainty, presumably reflecting that the exchange between the lid and the food is not well reproduced (for instance, of sauces major lumps may adhere to the lid).

In November 2004, an olive paste in oil and an oily tomato sauce were packed into 190 g jars using 63 mm lids with PA1 containing 16% components <1,000 Da. After 2 years, migration of the total PA was still clearly below the OML (7.7 and 6.3 mg/dm^2) and probably also below the SML (the material <1,000 Da was not determined).

Lids produced later contained the somewhat higher molecular PA2 with clearly lower migration. After 19 months, the migration remained far below the legal limits: the highest migration of total PA was 2.7 mg/dm^2, i.e. even total PA migration was clearly below the SML. As the PA makes up more than half of the overall migrate, the OML was also well respected.

Table 5 Overall migration from a lid for pasteurization with PA2 and a lid for sterilization with the higher molecular mass PA4

	Migration (mg/lid)								Composition (%)					
	Overall		PA		OA + EA		Sum		PA		OA + EA		Others	
	40 °C	60 °C	40 °C	60 °C	40 °C	60 °C	40 °C	60 °C	40 °C	60 °C	40 °C	60 °C	40 °C	60 °C
PA2	12.5	30	6.5	21	2.3	5.1	8.8	26	52	71	18	17	30	12
PA4	8.3	20	4	12	1.5	3.2	5.5	15	48	60	18	16	34	24

Migration per lid and composition of the migrate (right)

Table 6 Critical oily products packed in jars with gaskets plasticized with PA1 and PA2 (1 and 2)

Product in jar	Lid Ø (mm)	Jar size (g)	Area (dm^2)	PA	Filling date	Migration of total PA									
						in mg/kg food/analysis date					in mg/dm^2/analysis date				
						11/05	1/06	5/06	8/06	12/06	11/05	1/06	5/06	8/06	12/06
Olive paste	63	190	2.1	1	Nov 04	35	60		40	85	3.2	5.4		3.6	7.7
Tomato sauce	63	190	2.1	1	Nov 04	35	45		55	70	3.2	4.1		5.0	6.3
Pesto genovese	53	190	2.1	2	May 05	15	10		20	25	1.4	0.9		1.8	2.3
Sugo	63	190	2.1	2	July 05	15	15	20	20	30	1.4	1.4	1.8	1.8	2.7
Basil paste	53	190	2.1	2	Aug 05	20	15	20	15	20	1.8	1.4	1.8	1.4	1.8
Tomato paste	53	190	2.1	2	Aug 05	20	20		20	15	1.8	1.8		1.8	1.4
Garlic in oil	53	190	2.1	2	Aug 05	20	20		25	30	1.8	1.8		2.3	2.7
Italian sauce	63	190	2.1	2	Aug 05	15	15	25	25	25	1.4	1.4	2.3	2.3	2.3
Vegetables in oil	63	300	2.7	2	Sep 05	10	10	5	15	20	1.1	1.0	0.5	1.6	2.2
Pesto Genovese	53	190	2.1	2	Sep 05	10	15	10	25	10	0.9	1.4	0.9	2.3	0.9
Vegetables in oil	63	190	2.1	2	Sep 05	20	20	15	15	15	1.8	1.8	1.4	1.4	1.4

Characterization of the pack (left). Storage between filling date and date of analysis. Migration in terms of concentration in the homogenized food and related to the total internal contact surface of the pack

Table 7 Migration from lids containing PA mixed with other plasticizers into oily products from the market

	PA	ESBO	DBS	AHCM	OA	EA	Total
1. Dry tomatoes in oil, 340 g							
Contents in gasket (%)	10	22	8	4			
Migration into food (mg/kg)	5	22	35	10			72
Migration into food (mg/dm^2)	0.5	2.1	3.3	0.9			6.7
Migration (%)	6.5	11	50	28			
2. Vegetables in oil, 280 g							
Contents in gasket (%)	20	12	4.3		1.1	1.1	
Migration into food (mg/kg)	18	25	70		4	3	113
Migration into food (mg/dm^2)	1.9	2.6	8.3		0.4	0.3	12
Migration (%)	7	14	106		24	18	
3. Tomato sauce, 370 g							
Contents in gasket (%)	20	12	4.3		1.1	1.1	
Migration into food (mg/kg)	8	11	25		5	3	52
Migration into food (mg/dm^2)	0.7	1.0	2.3		0.5	0.3	4.7
Migration (%)	3	6	38		30	18	

Lids of unknown origin and an analytically determined composition given in the first line. Lids of products 2 and 3 are the same

The migration of 20–30 mg/kg PA2 into the food after 15–19 months corresponds to 3.8–5.7 mg/lid, which is less than that determined by conventional migration testing at 10 days/40 °C conditions and the jar on its head (6.5 mg/kg for 63 mm lid in Table 5 and 5.5 mg/lid for a 53 mm lid in Table 2). This is in contrast to the finding that migration of ESBO simulated at 10 days/40 °C was about 4–7 times lower than that observed in real food [1].

In the end of 2006, still only few products with PA-containing lids from other manufacturers were marketed. Table 7 lists three, whereby the second and third were with the same type of lid. The products were merely a few weeks old. The lid of the dry tomatoes in oil contained 10% PA, much ESBO, DBS and some AHCM (the amides were not determined). DBS was the predominant migrant, although present only as a minor component. Despite being a rather large jar, the product is unlikely to respect the limits up to the end of its shelf life, with the risk that DBS, for which the "Transition Regulation" does not provide an exception, exceeds the OML.

The lids of the products 2 and 3 contained 20% PA as well as 12 and 4.3% of ESBO and DBS, respectively. In the vegetables in oil, the migration already exceeded the OML, the DBS being responsible for more than 60% of the sum of the determined migrants. DBS must have started migrating from underneath the seal against the jar rim, because more than 100% of the amount in the gasket in food contact was transferred. As in the dry tomatoes, the migration of ESBO

was lower than expected when considering that the PA used contained about 20% of <1,000 Da components. It is also far below that of DBS. The tomato sauce contained 4% fat and the migration was substantially lower.

Conclusions and discussion

Polyadipates could be the only chance to produce metal closures with PVC gaskets of present geometry complying with the legal limits in oily foods. The results confirm that the SML for PA and the OML can be respected for all jar sizes, but also suggest that the margin is narrow and the testing procedure all but clear. The above data can be summarized by the following conclusions:

1. The migration of PAs is many times lower than that of other PVC plasticizers. Simulated testing suggests that the migration of the <1,000 Da PA components is similar to ESBO and that the migration of components above 1,000 Da is low.
2. Migration decreases with increasing molecular mass (or decreasing percentage PA <1,000 Da), but because the viscosity of the plastisol increases, it also renders the deposition of the gasket more difficult.
3. Dilution of the PA with less viscous plasticizers produced non-uniform results: the migration of added DBS was high, causing a strong increase of overall migration, whereas that of ESBO was remarkably low (below that from a gasket exclusively plasticized with ESBO).
4. Overall migration tests at standard conditions of 10 days/40 °C with the jars on their head suggest that lids with PAs of intermediate molecular mass comply with the limits down to small jars; using tests involving 20 days/60 °C, as appropriate for ESBO, only high molecular PAs seem suitable and still critical for small jars.
5. The summed migration of the PVC additives makes up most of the overall migration.
6. Monitoring of 11 real products during up to 19 months with lids exclusively containing PAs as plasticizer showed migration clearly below the legal limits.
7. After 19 months at ambient temperature, PA migration into food was below that determined by simulation at 10 days/40 °C and far below that at 20 days/60 °C considered adequate for ESBO.
8. Using mixtures of plasticizers reducing the high viscosity of PA plastisols, migration into real products was close to the legal limits or exceeded them already after a short storage time, confirming that this approach is critical.

Migration testing of lids needs improvement: standard 10 days/40 °C severely underestimated the migration of ESBO into food [1]. Conversely the testing conditions found to reasonably simulate the migration of ESBO (20 days/60 °C) seem to strongly overestimate the migration of PAs. Perhaps testing with the jar on its head does not adequately reproduce the transfer into the food.

References

1. Fankhauser-Noti A, Grob K (2006) Trends Food Sci Technol 17:105–112
2. Fankhauser-Noti A, Fiselier K, Biedermann S, Biedermann M, Grob K, Armellini F, Rieger K, Skjevrak I (2005) Eur Food Res Technol 221:416–422
3. Fankhauser-Noti A, Biedermann-Brem S, Grob K (2006) Eur Food Res Technol 223:447–453
4. European Commission, SANCO, Rapid Alert System for Foods and Feeds (Rasff) News 06-314 from 18 Aug 2006
5. Bundesamt für Gesundheit, Weisung 3, ESBO in Lebensmitteln. Bern, 5 Nov 2004. http://www.bag.admin.ch/verbrau/aktuell/d/Weisung_051103_FINAL.pdf
6. Practical Guide, European Commission, DG SANCO, p. 138. http://www.cpf.jrc.it/webpack/downloads/PRACTICAL%20GUIDE%20(2003.04.15).pdf
7. Biedermann M, Grob K (2006) J Sep Sci 29:114–122
8. Biedermann M, Grob K (2007) Chromatographia 64:543–552
9. Castle L, Mercer AJ, Gilbert J (1988) J AOAC Int 71:394–396
10. Castle L, Mercer AJ, Gilbert J (1988) Food Addit Contam 5:277–282
11. Biedermann M, Grob K (2006) Packag Technol Sci 19:159–178
12. Fankhauser-Noti A, Fiselier K, Biedermann-Brem S, Grob K (2005) J Chromatogr A 1082:214–219
13. Fankhauser-Noti A, Grob K (2006) J Sep Sci 29:2365–2374
14. Suter B, Grob K, Pacciarelli B (1997) Z Lebensm Unters Forsch 204:252–258
15. Biedermann-Brem S, Biedermann M, Fiselier K, Grob K (2005) Food Addit Contam 22:1274–1284