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ORIGINAL PAPER

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Overall migration from commercial coextruded food packaging multilayer films and plastics containers into official EU food simulants

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Abstract The overall migration from a wide range of commercial five-layer coextruded packaging films into aqueous food simulants (distilled water, 3% aqueous acetic acid) and alternative fatty food simulant (iso-octane) was studied. The overall migration from commercial plastics cups (PS, HIPS, and PP) used for ice-cream or yogurt packaging into distilled water and 3% aqueous acetic acid was also studied. Test conditions for packaging material/food simulant contact and method of overall migration analysis were according to the EU directives and CEN-standards. The results showed that for all tested five-layer films and plastics (PS, HIPS, and PP) cups values of overall migration into aqueous simulants (0.11–0.79 mg/dm^2, 2.3–15.9 mg/l) and (<0.10–0.41 mg/dm^2, <0.80–3.1 mg/l) were significantly lower than the upper limit (10 mg/dm^2) for overall migration from plastic packaging materials and articles into food and food simulants set by the EU Directive 90/128/EEC and their revisions. The overall migration values from five-layer materials into iso-octane were significantly higher (0.94–8.23 mg/dm^2, 18.8–164.7 mg/l) than the above values but are still lower than the upper limit for overall migration. Global migration values of five-layer films into aqueous food simulants seems to be independent of material thickness. In contrast, overall migration into iso-octane increases with film thickness.

Keywords Overall migration · Food simulants · Plastics packaging materials

Abbreviations PA Polyamide · Tie Adhesive material · Surlyn Ionomer · PE Polyethylene · LDPE Low density polyethylene · LLDPE Linear low density polyethylene · HDPE High density polyethylene · PS Polystyrene · HIPS High impact polystyrene · PP Polypropylene · EVOH Ethylene-vinyl alcohol

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Introduction

Multi-layer structures (laminates and coextrusions) are one of the more significant developments of recent packaging technology. These materials are produced by combination of various types of plastics film materials or plastics plus non-plastics materials (paper, aluminum foil, and regenerated cellulose) and possess properties which are a combination of individual material properties. The multilayer material is usually an excellent barrier to moisture, oxygen, carbon dioxide, and nitrogen while they provide adequate mechanical protection to the contained product. These barrier materials are flexible enough to allow pouches to be manufactured or rigid enough to assure thermoforming. Use of these multilayer materials significantly increases the shelf life and quality of various packaged foods such as meat, fish, poultry, cheese, snacks, coffee, and ready-made meals [1, 2, 3].

Coextruded LDPE is widely used as one of the components in multilayer structures because of its unique properties of moisture-barrier and heat sealability [4]. PP and PS are two of the most widely used polymers in food packaging and were third and fourth consumption in Europe in 1995 after LDPE/LLDPE and HDPE [4]. PS accounts for 600,000 tons of packaging materials in Europe – thermoformed containers (320,000 tons), molded containers and lids (240,000 tons), trays and boxes (40,000 tons) [2]. Primary food-contact applications of thermoformed PS are containers (cups) for yogurt, ice-cream, cream, cottage cheese, and single-serving cups [4, 5]. These containers are formed mainly from high impact Polystyrene (HIPS) [1, 2, 3, 4]. The most thin-walled containers such as those used for butter, margarine, and increasingly for yogurt are made from molded PP [4].

A subject of utmost importance is the migration of low molecular weight components from the above packaging materials into foods or food simulants. It should also be pointed out that substances used for lamination, i.e., adhesives, organic solvents, may also migrate into the foodstuffs through thin plastics layers [6].

The European Union (EU) has published a number of Directives setting the basic rules for migration testing of packaging materials intended to come into contact with foodstuffs, laying down the list of simulants, test conditions, and test methods to be used for testing overall migration of constituents from packaging materials [7, 8, 9].

According to Directive 90/128/EEC the overall migration limit is 10 mg for all transferred substances per dm^2 of the food contact material surface. Testing with aqueous simulants involves evaporating the simulants to dryness and determining the residue gravimetrically. Testing with fatty food simulants (olive oil or approved alternatives: sun flower oil or synthetic triglyceride HB 307) involves weighing of the plastic before and after simulant contact. The amount absorbed into the plastic oil is determined by extraction and GC analysis [9, 10].

The use of vegetable oils as food simulants presents a number of difficulties and is a time-consuming procedure [6, 11, 12]. Some alternative fatty food simulants have been proposed – mainly solvents which can be evaporated such us iso-octane or heptane and ethanol-water mixtures. Many of the problems encountered in applying fat migration testing can be overcome by using the above alternative solvents because overall migration can been determined directly by weighing a residue after evaporation of a solvent [13, 14, 15, 16].

Practical Guide N. 1 of the Commission of EU [17] and Directive 97/48/EC [18] refer to iso-octane as one of the alternative fatty food simulants.

There are a number of published studies using iso-octane as an alternative fatty food simulant: The results of a comparison study of global migration into iso-octane over 2 days at 20 °C with olive oil over 10 days at 40 °C from 130 commercial polymer samples showed that iso-octane and olive oil had similar results with regard to migration data [19]. De Kruijf and Rijk [13] reported that iso-octane is a suitable alternative food simulant for overall migration testing under various time and temperature conditions. Hamdani and Feigenbaun [16] found that the affinities of iso-octane and sunflower oil to all migrants were similar and iso-octane can be considered as an alternative fatty food simulant for plasticized PVC.

In previous work we have studied some parameters about specific migration of plasticizers from food-grade PVC and PVDC/PVC films into different fatty foods and olive oil [20, 21, 22, 23].

The objectives of this work were (1) to determine the overall migration from a wide range of commercial multilayer polymer samples into the aqueous food simulants distilled water and 3% aqueous acetic acid, and into the fatty food simulant iso-octane, (2) to determine the overall migration from commercial PS, HIPS, and PP cups for yogurt or ice-cream into distilled water and 3% acetic acid, and (3) to study extent of migration as a function of packaging material thickness.

Materials and methods

Materials

Coextruded five-layer commercial samples of food packaging materials (film forms), and PS, 98% HIPS, 100% HIPS, and PP cups supplied by Greek industrial companies supporting the study are listed in Tables 1, 2, 3 and 4. The total thickness of film samples was between 40 μm and 300 μm. Analytical grade acetic acid and iso-octane were supplied by Merck (Darmstadt, Germany). Water used was double distilled.

Migration experiments

Overall migration from coextruded packaging materials into aqueous and alternative fatty food simulants. Rectangular strips of each film sample (surface area 100 cm^2) were placed in two side contact (total contact surface area 200 cm^2) with 100 ml of food simulant (distilled water, 3% aqueous acetic acid, or iso-octane) in glassy beakers. Beakers were covered by parafilm so as to avoid evaporation of simulant during contact period and kept in a thermostatically controlled chamber at 40±0.5 °C for ten days. For iso-octane the temperature/time of plastic/simulant contact was 20±0.5 °C for two days [18]. The film samples were removed and the simulant was placed in a 250-ml preweighed Erlenmeyer flask and evaporated on a rotary evaporator with double distilled water in the heating bath. The Erlenmeyer flask containing the residue of evaporation was kept in a thermostatically controlled chamber at 105±1.0 °C for 1 h followed by 1 h in a desiccator and then weighed. An analytical balance Sartorius BP221S capable of weighing to 0.1 mg was used. The overall migration was calculated in mg/dm^2 of film surface area taking into account the exposed surface area of the test sample and in mg/l of simulant. Blank samples were run simultaneously and corrected migration values were calculated for each simulant. For each plastics sample three determinations were performed and final migration value was the mean of the three determinations.

Overall migration from plastic cups into aqueous food simulants. Five different plastics cups of different capacities were used. Two of the cups were intended for yogurt packaging and the three other cups were intended for ice-cream packaging. Packaging materials including experimental details are given in Table 3. The cup samples were filled (one side contact) with corresponding simulant and refrigerated at 5±0.5 °C for ten days. Each cup was covered by parafilm as previously described. The migration values were determined using the above-mentioned method. For each cup three determinations were performed and final migration value was the mean of the three determinations.

Results and discussion

Overall migration from coextruded packaging materials into aqueous food simulants

Overall migration values from coextruded five-layer films into aqueous food simulants (distilled water and 3% aqueous acetic acid) after ten days contact at 40± 0.5 °C are given in Table 1.

The results show that the overall migration values from all studied coextruded materials into distilled water (0.11–0.72 mg/dm^2, 2.3–14.4 mg/l) and 3% aqueous acetic acid (0.2–0.79 mg/dm^2, 3.9–15.9 mg/l) were much lower than the upper limit for migration set by the EU (10 mg/dm^2).

Table 1 Overall migration into aqueous simulants from five-layer coextruded films after ten days contact at 40±0.5 °C

Sample No	Sample	Individual layer thickness (μm)	Total thickness (μm)	Overall migration[a] into:			
				Distilled water		3% aqueous acetic acid	
				mg/dm²	mg/l	mg/dm²	mg/l
1	PA/tie/Surlyn/ Surlyn/Surlyn	20/5/21/21/21	88	0.11±0.02	2.3±0.3	0.20±0.03	3.9±0.5
2	PA/tie/Surlyn/ Surlyn/Surlyn	21/5/28/28/28	110	0.14±0.01	2.9±0.2	0.23±0.02	4.6±0.4
3	LDPE/tie/PA/tie/LDPE	17/5/17/5/17	61	0.50±0.06	10.0±1.1	0.43±0.06	8.6±1.1
4	LDPE/tie/PA/tie/LDPE	20/5/20/5/20	70	0.52±0.04	10.4±0.8	0.52±0.05	10.5±0.9
5	LDPE/tie/PA/tie/LDPE	35/5/30/5/35	110	0.60±0.09	12.0±1.8	0.56±0.04	11.2±0.8
6	PA/tie/LDPE/LDPE/LDPE	16/5/13/13/13	60	0.39±0.05	7.8±1.0	0.47±0.03	9.4±0.6
7	PA/tie/LDPE/LDPE/LDPE	25/5/20/20/20	90	0.53±0.07	10.6±1.4	0.54±0.04	10.8±0.9
8	PA/tie/LDPE/LDPE/LDPE	40/5/35/35/35	150	0.54±0.06	10.8±1.2	0.62±0.08	12.4±1.6
9	PA/tie/LDPE/LDPE/LDPE	40/5/40/40/40	165	0.48±0.07	9.6±1.4	0.45±0.09	9.0±1.8
10	PA/tie/LDPE/LDPE/LDPE	25/5/50/50/50	180	0.43±0.09	8.6±1.8	0.46±0.08	9.2±1.6
11	PA/tie/LDPE/LDPE/LDPE	46/5/83/83/83	300	0.62±0.07	12.4±1.4	0.58±0.10	11.6±2.0
12	LDPE/tie/EVOH/tie/LDPE	13/5/5/5/13	41	0.26±0.04	5.2±0.9	0.52±0.06	10.4±1.3
13	PA/EVOH/tie/LLDPE/LDPE	15/5/5/50/50	125	0.58±0.08	11.6±1.6	0.60±0.09	12.2±1.8
14	PE/tie/PA/tie/PE	45/5/45/5/50	150	0.72±0.10	14.4±1.9	0.79±0.07	15.9±1.4

[a] Values represent the mean of three determinations ± the standard deviation

As shown in Table 1, under present experimental conditions there are no statistically significant differences in overall migration values from all studied materials between distilled water and 3% aqueous acetic acid.

There are also no statistically significant differences in overall migration values between same five-layered films of varying thickness. Migration into aqueous simulants seems to be independent of film thickness. All the above results can be explained in terms of the quite low solubility of the polymer constituents and additives in water and thus the very low penetration capability of aqueous simulants into polymers. Migration can be directly correlated to the chemical nature of the migrant, the polymer and the food simulant. Polymers as compared to water are usually a lot less polar in nature and thus water does not affect polymer structure. In turn polymer constituents and additives remain in the polymer when the latter comes in contact with water [6, 15].

Garde et al. [24] studied overall migration from different thickness PP films (thickness: 50 μm, 100 μm, and 200 μm) into distilled water and 3% aqueous acetic acid and observed that the migration values into two aqueous simulants were very low (0.2–0.4 mg/dm²) independent of film thickness. They also found no significant differences in migration values between distilled water and 3% aqueous acetic acid. Czerniawski and Pogorzelska [25] studied overall migration from various plastics films and laminates (HDPE, LLDPE, PA/PE, polyethylene terephthalate (PET)/aluminum/PE, paper/PE) and observed that the migration values into aqueous food simulants are very low (0.2–1.0 mg/dm²) with no significant differences in migration values between distilled water and 3% aqueous acetic acid. The above results are in agreement with the results of the present work.

Overall migration from coextruded packaging materials into iso-octane

Overall migration values from coextruded five-layer films into iso-octane after two days contact at 20±0.5 °C are given in Table 2. These results show that the overall migration values from all studied coextruded materials into iso-octane (0.94–8.23 mg/dm², 18.8–164.7 mg/l) were lower than the upper limit for migration set by the EU (10 mg/dm²). They are, however, significantly higher compared to the corresponding overall migration values into aqueous simulants. This can be explained by the capability of iso-octane to penetrate into the plastics packaging materials, causing swelling of the polymer and thus change in its structure. The consequence is an increase in the diffusivity of the potential migrants and a resulting increase in the rate of migration [14, 26, 27].

Piergiovanni et al. [28] studied diffusion of di-*n*-butyl phthalate dissolved in iso-octane through LDPE film and observed that iso-octane quickly penetrated the LDPE film (70 μm thickness).

The partition coefficient (k) between the polymer and liquid phase is expressed as the concentration in the polymer (c_p) at equilibrium divided by the concentration in the liquid at equilibrium (c_L) [15]:

$$k=c_p/c_L \quad (1)$$

For aqueous simulants k is much higher than one and migration is much more lower than that in organic solvents (k value near to one).

Another interesting observation from results presented in Table 2 is that the overall migration from the same five-layer films having different thickness increases with film total thickness. Figure 1 gives migration amount from (PA/tie/LDPE/LDPE/LDPE) film into iso-octane as a function of film total thickness (60–300 μm). The results in Fig. 1 (samples No. 6–11, Table 2) indicate that a relationship exists between the total thickness of five-

Table 2 Overall migration into iso-octane from five-layer co-extruded films after two days contact at 20±0.5 °C

Sample No	Sample	Individual layer thickness (μm)	Total thickness (μm)	Overall migration[a]	
				mg/dm²	mg/l
1	PA/tie/Surlyn/ Surlyn/Surlyn	20/5/21/21/21	88	0.94±0.12	18.8±2.4
2	PA/tie/Surlyn/ Surlyn/Surlyn	21/5/28/28/28	110	1.27±0.26	25.4±5.2
3	LDPE/tie/PA/tie/LDPE	17/5/17/5/17	61	2.91±0.21	58.2±4.2
4	LDPE/tie/PA/tie/LDPE	20/5/20/5/20	70	3.17±0.20	63.4±4.0
5	LDPE/tie/PA/tie/LDPE	35/5/30/5/35	110	4.12±0.32	82.4±6.4
6	PA/tie/LDPE/LDPE/LDPE	16/5/13/13/13	60	2.94±0.21	58.8±4.2
7	PA/tie/LDPE/LDPE/LDPE	25/5/20/20/20	90	4.10±0.46	81.9±9.2
8	PA/tie/LDPE/LDPE/LDPE	40/5/35/35/35	150	5.71±0.28	114.2±5.6
9	PA/tie/LDPE/LDPE/LDPE	40/5/40/40/40	165	6.31±0.20	126.3±4.0
10	PA/tie/LDPE/LDPE/LDPE	25/5/50/50/50	180	6.84±0.60	138.4±12.1
11	PA/tie/LDPE/LDPE/LDPE	46/5/83/83/83	300	8.23±0.67	164.7±13.4
12	LDPE/tie/EVOH/tie/LDPE	13/5/5/5/13	41	2.16±0.24	43.2±4.8
13	PA/EVOH/tie/LLDPE/LDPE	15/5/5/50/50	125	5.38±0.49	107.6±9.8
14	PE/tie/PA/tie/PE	45/5/45/5/50	150	7.45±0.75	149.1±15.0

[a] Values represent the mean of three determinations±the standard deviation

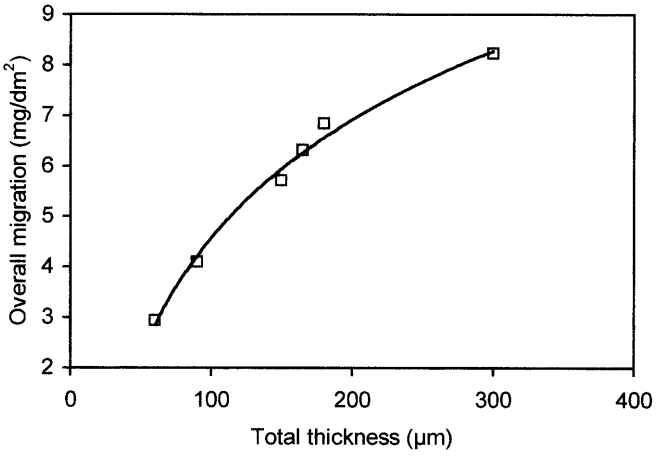

Fig. 1 Overall migration into iso-octane from five-layer coextruded film (PA/tie/LDPE/LDPE/LDPE) after two days contact at 20±0.5 °C as a function of film total thickness

layer film and the corresponding migration amount. As film thickness increases overall migration values increase but this relationship is not proportional to thickness increase. This can be explained in terms of decrease penetration capability of iso-octane into five-layer films as film thickness increases. Table 2 shows that as total thickness of each film increases, there are simultaneously increases in the thickness of outer layers of each film which were in direct contact with iso-octane (two side contact). Thickness of the two outer layers of each film is about half of the total thickness.

Application of the T-test to overall migration data (mg/dm², Table 2) showed that for samples No 6–11 the migration differences are statistically significant (confidence level 90–99%). Figge [29] studied the dependence of the migration of antioxidant Irganox 1076 from LDPE specimens of varying thickness (50–2000 μm) into HB 307 (fatty food simulant) and observed that migration initially increased with the thickness of the specimen while migration remained practically independent of sample thickness beyond a thickness value of 600 μm. Garde et al. [24] studied the overall migration from dif-

Table 3 Approved food simulants and test conditions according to Directives 85/572/EEC and 97/48/EC for migration testing of plastic cups intended to come into contact with yogurt and ice-cream

Sample No	Material	Food intended to come into contact with	Simulant	Contact area (cm²)	Volume of simulant (ml)	Conditions of contact in actual use		Test conditions	
						Time (h)	Temp. (°C)	Time (d)	Temp. (°C)
1	PS	Yogurt	3% aqueous acetic acid	156	200	>24	5	10	5
2	PP	Yogurt	3% aqueous acetic acid	390	500	>24	5	10	5
3	PS	Ice-cream	iso-octane	112	160	>24	–30	10	5
4	98% HIPS	Ice-cream	iso-octane	170	200	>24	–30	10	5
5	100% HIPS	Ice-cream	iso-octane	135	180	>24	–30	10	5

Table 4 Overall migration from plastics cups into aqueous food simulants

Sample No	Material	Overall migration[a] into:			
		Distilled water		3% aqueous acetic acid	
		mg/dm²	mg/l	mg/dm²	mg/l
1	PS	–	–	0.25±0.03	2.0±0.2
2	PP	–	–	0.41±0.07	3.1±0.5
3	PS	0.23±0.05	1.6±0.4	–	–
4	98% HIPS	0.14±0.03	1.2±0.3	–	–
5	100% HIPS	<0.10	<0.8	–	–

[a] Values represent the mean of three determinations±the standard deviation

ferent thickness PP films (50 µm, 100 µm, 200 µm) into fatty food simulants (olive oil and *n*-heptane) and observed that the migration amount per unit area increased with film thickness. The above results are in agreement with our present results.

Overall migration from plastic cups into aqueous food simulants

The overall migration values from different commercial plastics cups (PP, PS, 98% HIPS, 100% HIPS) into distilled water or 3% aqueous acetic acid after 10 days contact at 5±0.5 °C are given in Tables 3, 4. The choice of each simulant was made according to the real commercial use of each container (ice-cream or yogurt packaging). The results show that the overall migration values from all studied cups into distilled water (<0.10–0.23 mg/dm², <0.8–1.6 mg/l) and 3% aqueous acetic acid (0.25–0.41 mg/dm², 2.0–3.1 mg/l) were a lot lower than the upper limit for migration set by the EU (10 mg/dm²). The 100% HIPS cups showed a non detectable migration amount (<0.10 mg/dm²).

Nerin et al. [5] studied specific migration of styrene from PS cups in yogurt and observed a low concentration of styrene in yogurt despite the high concentration of styrene in the packaging material. Tawfik and Huyghebaert [30] studied specific migration of styrene from PS cups into different foods and simulants and observed low migration (maximum 0.025–0.37% of the total styrene from cups into foods and foods simulants respectively). These observations are in agreement with our present results.

Conclusions

The results obtained in this work show that overall migration values from five-layer coextruded films in official EU aqueous food simulants (distilled water and 3% aqueous acetic acid) are a lot lower than the upper limit for overall migration set by the EU (10 mg/dm²) and are independent of film thickness.

In contrast there is clear correlation between five-layer film thickness and overall migration value into the fatty food simulant iso-octane. This can be explained by the similarity in chemical nature and interaction propensity between plastics and iso-octane compared to aqueous food simulants. A result of this interaction is polymer penetration by iso-octane. This penetration increases migration.

Overall migration values from five-layer films into iso-octane are lower than the upper limit for overall migration set by the EU. Similarly all studied commercial PS, HIPS, and PP cups show migration values into aqueous simulants a lot lower than the above upper migration limit.

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