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Migration aspects for food contact materials with aqueous food simulating solvents as per different international standards

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Abstract

Plastic packaging materials coming in food contact applications are evaluated for overall migration as per USFDA, EEC, and BIS. In latest modification of EEC directives distilled as aqueous food simulant has been replaced by 10% ethanol. Hence, in the present study we have investigated the difference between distilled water & 10% ethanol as aqueous food simulant with respect to overall migration of commercial packaging films LDPE, HDPE, PP, PET & PS under all the conditions of the time and temperature as per USFDA, EEC, and BIS standards. Overall migration values for aqueous foods under simulating test conditions from frozen to boiling/retort condition, varied differently for specific packaging films: LDPE (0.35-0.57 mg/dm^2), HDPE (0.36-0.61 mg/dm^2) PP (0.13-1.23 mg/dm^2) PET (0.26-1.35 mg/dm^2) & PS (0.25-0.46 mg/dm^2) respectively. All these values were significantly lower than the specified maximum limit (10 mg/dm^2) as per international standards. The results suggest that there was statistically significant difference ($p \leq 0.05$) under frozen condition to boiling/retort temperature between distilled water & 10% ethanol. The obtained overall migration values for all samples as per different standards can be attributed to the influence of the solvent and time-temperature used conditions. Further IR of the migration additives proved to be same component in distilled water and 10%ethanol. Our results clearly suggest that either of the above two simulant will be suitable for aqueous non-acidic food.

Keywords: Polypropylene (PP), High density polyethylene (HDPE), Low density polyethylene (LDPE), Polyethylene terephthalate (PET), Polystyrene (PS), United States Food and Drug Administration (USFDA), Bureau of Indian Standards (BIS) and European Commission (EEC).

1. Introduction

In recent years plastics are being used tremendously as food contact materials in various forms and shapes. Each plastic has its unique properties for its application in food contact applications. In general plastics used in food contact applications are Low density polyethylene (LDPE), High density polyethylene (HDPE), Polypropylene (PP), Polyethylene terephthalate (PET), and Polystyrene (PS).

They are used in various forms, shape and sizes like films/laminates/coextruded converted into pouches or bags and as rigid containers in the form of bottles, cans, drums, pipes etc.,. PP and PS are two of the widely used polymers in food packaging and were third and fourth consumed packaging materials in Europe after LDPE and HDPE [1].

These materials are being increasingly used for packaging, storing and transporting aqueous foods including potable water.

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These plastics should conform to their respective international specifications for food compatibility. PE, PP and PET bottles are also being used for storing pharmaceutical syrups which are water and low alcoholic based. Such versatile use of plastics is due to a host of advantageous properties like light weight, strength, flexibility, barrier properties towards moisture, flavour and gasses, crack resistance, availability in attractive shapes and sizes and low cost. Plastics is not an inert material and is able to interact with the surrounding environment, allowing food-packaging interactions, such as sorption, permeation and migration. Migrations of additives from packaging materials into foods have been major concern in recent years worldwide. Migration of such additives requires to be controlled for their limits. In general plastics polymers are evaluated for their food compatibility by overall/specific migration of additives, using food simulants and simulating used test conditions of time and temperature. Different countries, have laid down different specifications like USFDA, EEC, and BIS for their safe use in food contact simulants such as distilled water (aqueous foods pH $\geq$5), 3% acetic acid (acidic beverages pH$\leq$5), 10-50% ethanol (alcoholic beverages) and n-heptane (oils/fats and fatty foods) have been specified by different standards. For aqueous food, USFDA and BIS have specified distilled water as simulant and EEC directives (ECC10/2011) specifies 10% ethanol. With regard to the EEC, water is considered now as a food and not as a food Simulant. EEC regulation introduces separate sets of standardized testing conditions for overall migration test by using 10% ethanol for aqueous food instead of distilled water [2]. Similarly for aqueous acidic foods, USFDA doesn't differentiate in acidic and non acidic foods simulant, where water has been suggested for both these foods [3]. For the compatibility studies, various international standards have specified different test conditions of time and temperature, based on types of food, coming in contact and used for filling and storing conditions. Hence, the current study was aimed to evaluate and compare the difference between distilled water and 10% ethanol by overall migration on various polymers like LDPE, HDPE, PP, PET & PS from frozen condition to retort temperature.

2. Materials and Methods

2.1. Materials

i. Films samples: LDPE (43.5μm), HDPE (39.5μm) and PP (42μm) received from Indian Oil Corporation Limited, Product Application and Development Centre (PADC) Panipat, New Delhi.
ii. PET bottles (1.5 lt Capacity, 2.28mm) received from M/s Reliance Industries, Rasayani, Maharashtra
iii. PS thermoformed container with thickness of 2.25mm received from Supreme Petro chem. Ltd, Maharastra.

2.2. Chemicals. Potassium bromide (KBr) Sigma Aldrich (Bangalore, India).Water and ethanol were freshly distilled before use.

2.3. Equipments. Fourier Transforms Infrared Spectroscopy (RAMAN Nicolet 5700), Analytical balance, Hot air oven, Thermometer, Hot plate, Water bath and Autoclave.

2.4. Overall migration from packaging materials into aqueous food simulants; Distilled water and 10% ethanol. Rectangular strips of each sample (surface area 500 cm^2) were exposed with both sides (total contact surface area 1000 cm^2) in 1000 ml of food simulant (distilled water and 10% ethanol) in glass beakers in triplicates. Beakers were covered by glass petri dishes, so as to avoid evaporation of simulant during contact period and kept in a thermostatically controlled chamber/water bath at stipulated test condition of time and temperature. At the end of test period, the sample was removed and the extracted solutions were concentrated on a hot plate. The concentrated solution was further transferred to a clean stainless steel dish and further evaporated to dryness in a thermostatically controlled chamber at 100±5^{0}C. The dish was cooled for 30 min in a desiccators and residue was weighed to nearest 0.1mg. The amount of extractive obtained was calculated and expressed (mg/in^2 & ppm) as per USFDA and (mg/dm^2 & ppm) as per BIS and EEC. 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 [4]. Food simulant and test conditions selected for the experiment are shown in Table 1.

2.5.Fourier Transforms Infrared Spectroscopy (FTIR). All samples were analyzed using FTIR. Migrated additive of each sample was finely pulverized and mixed with KBr at a ratio of approximately 1:10. The mixture was compressed into an evacuable pellet die in conjunction with a 15 ton manually operated hydraulic press (Graseby Specac, Kent, UK). The produced KBr pellet was placed in the cell of the spectrometer and scanned within the frequency range of 4000–400 cm^{-1}. All measurements were carried out at 20°C in anhydrous conditions [5].

2.6. Statistical analysis. All determinations were carried out in triplicate and the data were subjected to one-way ANOVA followed by Tukey's multiple comparison test for significant differences using SPSS14.0 software.

3.Results and Discussion

3.1. Overall migration from food contact materials. Overall migration studies were carried on various plastic food contact materials like LDPE, HDPE, PP, PET & PS under various simulating storage conditions of time and temperature as per USFDA, EEC directives and BIS as shown in the Table 1. The overall migration value for all the samples tested for frozen condition (no thermal treatment in container) ranged from minimum of 0.13 mg/dm^2 (1.30) ppm in PP at distilled water for 21°C/ 48h, to maximum of 0.41 mg/dm^2 (4.16) ppm in HDPE at 10% ethanol for 20°C/10 days shown in the Table 2a. At Room temperature filled and stored, which also includes refrigerated condition (as per BIS) the overall migration values ranged from minimum of 0.18 mg/dm^2 (1.8) ppm in PP with distilled water for 40°C/ 10 days, to maximum 0.42 mg/dm^2 (4.23) ppm in HDPE at 10% ethanol for 40°C/ 10 days shown in the Table 2b. Whereas in high temperature hot filled or pasteurized below 66°C/ 70°C, all the tested samples values ranged from minimum of 0.23 mg/dm^2 (2.3) ppm in PP at distilled water at 66°C/ 2h, to maximum of 0.46 mg/dm^2 (4.63) ppm in HDPE at 10% ethanol at 70°C/ 2h, as shown in the Table 2c, and Hot filled or pasteurized above 66°C/ 70°C, below 100°C all the tested samples values ranged from minimum of 0.36 mg/dm^2 (3.66) ppm in PP at distilled water at 100°C/ 0.5h, to maximum of 0.61 mg/dm^2 (6.10) ppm in HDPE at 10% ethanol at 100°C/ 1h shown in the Table 2d. only PP & PET which can withstand at high temperature, hence, test were conducted for overall migration at retort conditions of high temperature heat sterilized. The value ranges from minimum of 1.18 mg/dm^2 (11.86) ppm in PP at distilled water at 121°C/ 2h, to maximum of 1.35 mg/dm^2 (13.5) ppm in PET at 10% ethanol at 121°C/ 1h shown in the Table 2e. The PET bottle showed shrinkage at 100°C and above temperature. For all the tested materials in different specified conditions the overall migration values ranged from a minimum of 0.013 mg/in^2 (1.3ppm) in PP at distilled water for 21°C/ 48h, to maximum of 1.3 mg/in^2 (13.5ppm) in PET at 10% ethanol at 121°C/ 1h as shown in Table 2. All the above values were well within the specified limit of (0.5 mg/in^2 & 50 ppm) as per USFDA (expressed USFDA values of mg/in^2 were converted into mg/dm^2, i.e. 0.5 mg/in^2 ≈7.75 mg/dm^2) and as per EEC and BIS (10 mg/dm^2 & 60 ppm). In the case of coloured plastic materials, colour migrated to simulant or decolourised coconut oil from food contact material shall not be apparent to the naked eye. If the colour migrated is clearly visible, such materials are not suitable for food contact applications, even though the extractive value is within the limits specified [6]. In our studies, no colour migration was observed in all test materials during all conditions. Hence, all tested materials were found to be suitable for packaging of aqueous food contact application at frozen condition to retort temperature as per different standards. Under present experimental conditions the statistical analysis of obtained migration results by ANOVA showed a significant difference ($p \leq 0.05$) in distilled water and 10% ethanol from frozen condition to retort temperature. The migration values were in increasing order with increasing temperature from frozen condition to retort temperature as shown in Table 2a-e. This increase in migration values is expected due to loosening of the matrix of polymer for higher migration in food products with increase in temperature.

In general, migration of additives into the simulants shows that the amount of migration is directly proportional to the square root of time. The migrated quantity increases fast with time initially and then tends towards a limiting value that is the migration maxima (E_m). The time required to reach E_m depends on the nature of the system, thickness of the plastic and co-efficient of diffusion [7]. In our studies, the migrants into distilled water simulants seems to be less when compared with 10% ethanol. Type of food simulants may influence the migration. Migration can be directly correlated to the chemical nature of the migrant, the polymer and the food simulant [8, 9].

Table 1. Specified food simulants and test conditions for overall migration for aqueous food as per USFDA, EEC, and BIS standards

Sl. No	CONDITION OF USE	SIMULANT AND TEST CONDITIONS		
		USFDA	**EEC**	**BIS**
1	Frozen condition (no thermal treatment in container)	Dist.water (21°C/48 h)	10% Ethanol (20°C/10 days)	Dist.water (40°C/10 days)
2	Room temperature filled and stored and also in refrigerated	Dist.water (49°C/24 h)	10% Ethanol (40°C/10 days)	Dist.water (40°C/10 days)
3	Hot filled or pasteurized below 66°C/70°C	Dist.water (66°C/2h)	10% Ethanol (70°C/2h)	Dist.water (70°C/2h)
4	Hot filled or pasteurized Above 70°C, below 100°C	Dist.water (100°C/0.5h)	10% Ethanol (100°C/1h)	Dist.water (100°C/1h)
5	High temperature heat sterilized (Retorting)	Dist.water (121°C/2h)	10% Ethanol (121°C/2h)	Dist.water (121°C/2h)

Table 2. Overall migration studies were carried on various plastic food contact materials under various simulating storage conditions of time and temperature as per USFDA, EEC directives and BIS

a)	**Overall migration in Frozen condition (no thermal treatment in container)**						
		US-FDA: Dist.Water (21°C/48 hrs)		BIS:Dist.Water (40°C/10 days)		EEC: 10% Ethanol (20°C/10 days)	
Sample No	**Sample**	**mg/dm²**	**(ppm)**	**mg/dm²**	**(ppm)**	**mg/dm²**	**(ppm)**
1	LDPE	$0.35^a\pm0.10$	3.53	$0.37^b\pm0.05$	3.76	$0.38^a\pm0.12$	3.86
2	HDPE	$0.36^a\pm0.11$	3.66	$0.40^b\pm0.05$	4.00	$0.41^c\pm0.15$	4.16
3	PP	$0.13^a\pm0.05$	1.30	$0.22^b\pm0.1$	2.20	$0.15^c\pm0.05$	1.50
4	PET	$0.26^a\pm0.11$	2.66	$0.36^b\pm0.05$	3.63	$0.32^b\pm0.09$	3.20
5	PS	$0.25^a\pm0.10$	2.50	$0.34^b\pm0.05$	3.43	$0.25^a\pm0.10$	2.50

b)	**Overall migration in Room temperature filled and stored and also in refrigerated**						
		US-FDA: Dist.Water (49°C/24 hrs)		BIS:Dist.Water (40°C/10 days)		EEC: 10% Ethanol (40°C/10 days)	
Sample No	**Sample**	**mg/dm²**	**(ppm)**	**mg/dm²**	**(ppm)**	**mg/dm²**	**(ppm)**
1	LDPE	$0.34^a\pm0.05$	3.46	$0.37^b\pm0.05$	3.76	$0.41^c\pm0.05$	4.13
2	HDPE	$0.38^a\pm0.05$	3.83	$0.40^b\pm0.05$	4.00	$0.42^c\pm0.11$	4.23
3	PP	$0.18^a\pm0.1$	1.86	$0.22^b\pm0.1$	2.20	$0.22^c\pm0.05$	2.23
4	PET	$0.32^a\pm0.05$	3.23	$0.36^b\pm0.05$	3.63	$0.38^c\pm0.05$	3.83
5	PS	$0.30^a\pm0.05$	3.06	$0.34^b\pm0.05$	3.43	$0.36^c\pm0.05$	3.66

c)		Overall migration in Hot filled or pasteurized below 66°C /70°C					
		US-FDA: Dist.Water (66°C/2 hrs)		BIS:Dist.Water (70°C/2hrs)		EEC: 10% Ethanol (70°C/2hrs)	
Sample No	**Sample**	**mg/dm^2**	**(ppm)**	**mg/dm^2**	**(ppm)**	**mg/dm^2**	**(ppm)**
1	LDPE	$0.38^{a}\pm0.05$	3.86	$0.40^{b}\pm0.05$	4.06	$0.42^{c}\pm0.05$	4.26
2	HDPE	$0.42^{a}\pm0.05$	4.26	$0.44^{b}\pm0.05$	4.46	$0.46^{c}\pm0.05$	4.63
3	PP	$0.23^{a}\pm0.05$	2.33	$0.24^{b}\pm0.05$	2.46	$0.26^{c}\pm0.05$	2.63
4	PET	$0.35^{a}\pm0.05$	3.53	$0.36^{b}\pm0.05$	3.63	$0.39^{c}\pm0.05$	3.93
5	PS	$0.32^{a}\pm0.05$	3.26	$0.34^{b}\pm0.05$	3.43	$0.36^{c}\pm0.05$	3.66

d)		Overall migration in Hot filled or pasteurized above 70°C, below 100°C					
		US-FDA:Dist.Water (100°C/0.5 hrs)		BIS:Dist.Water (100°C/2hrs)		EEC: 10% Ethanol (100°C/1hrs)	
Sample No	**Sample**	**mg/dm^2**	**(ppm)**	**mg/dm^2**	**(ppm)**	**mg/dm^2**	**(ppm)**
1	LDPE	$0.51^{a}\pm0.10$	0.51	$0.54^{b}\pm0.11$	5.43	$0.57^{c}\pm0.12$	5.76
2	HDPE	$0.57^{a}\pm0.12$	5.71	$0.58^{b}\pm0.13$	5.83	$0.61^{c}\pm0.14$	6.10
3	PP	$0.36^{a}\pm0.06$	3.66	$0.40^{b}\pm0.07$	4.06	$0.39^{c}\pm0.05$	3.93
4	PET	$0.47^{a}\pm0.09$	4.73	$0.48^{b}\pm0.09$	4.83	$0.49^{b}\pm0.09$	4.90
5	PS	$0.46^{a}\pm0.08$	4.63	$0.45^{b}\pm0.08$	4.56	$0.46^{c}\pm0.08$	4.66

e)		Overall migration in High temperature heat sterilized (Retorting)					
		US-FDA: Dist.Water (121°C/2hrs)		BIS:Dist.Water (121°C/2hrs)		EEC: 10% Ethanol (121°C/2hrs)	
Sample No	**Sample**	**mg/dm^2**	**(ppm)**	**mg/dm^2**	**(ppm)**	**mg/dm^2**	**(ppm)**
1	PP	$1.18^{a}\pm0.05$	11.86	$1.20^{b}\pm0.05$	12.03	$1.23^{c}\pm0.05$	12.33
2	PET	$1.32^{a}\pm0.05$	13.23	$1.31^{b}\pm0.05$	13.16	$1.35^{c}\pm0.05$	13.5

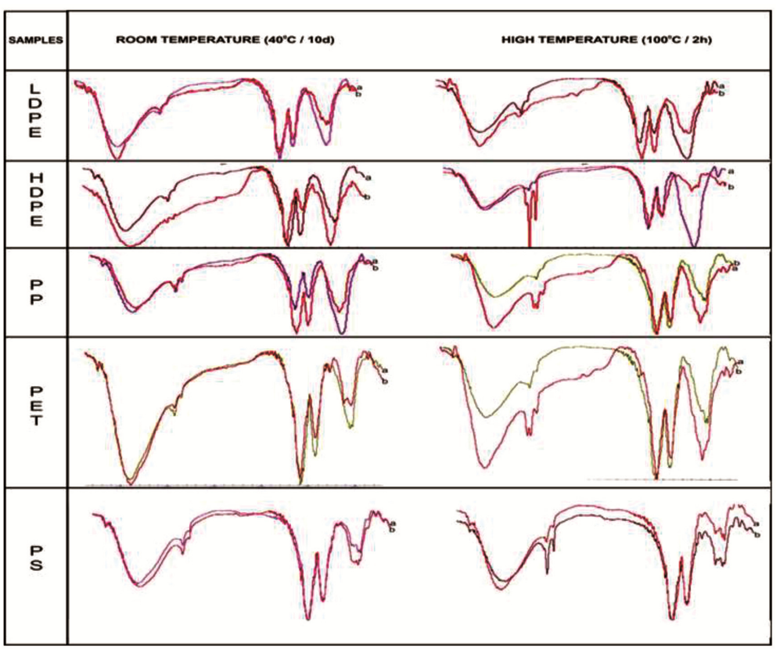

Figure 1. FT-IR: Compare the difference between Distilled water and 10% ethanol of migrated additives under Room temperature and high temperature. a: Distilled water and b: 10%Ethanol.

Further, the additives migrated from distilled water and 10% ethanol at low temperature (40°C/ 10 days) and high temperature (100°C/ 2h) were analyzed by using FT-IR. IR spectra of additives migrated from each tested material for both the lowest and highest temperature are same and showing the super imposable image of spectra justifying the same identity of specific additives as shown in Figure 1. All the above results can be explained in terms of the quite low solubility of the polymer additives in distilled water and thus the very low penetration capability of distilled water simulants into polymers. It is clear that 10% ethanol may act as better solvent for extraction compared to water.

4.Conclusion

Overall migration studies were conducted on food contact materials to understand the difference between distilled water and 10% ethanol specified as aqueous food simulant as per USFDA, BIS and EEC directives. Overall migration values of all food contact materials LDPE, HDPE, PP, PET & PS used for aqueous food were well below the safety limits as per different international standards.

The migration values results suggest that there was a significant difference between distilled water and 10% ethanol ($p \leq 0.05$) for aqueous food under frozen condition to high temperature. Distilled water and 10% ethanol as aqueous simulant act in similar way for migration of additives. However 10% ethanol shows slightly higher migration compared to distilled water. The obtained values for different standards for all samples can be attributed to the influence of the solvent and time-temperature used conditions. However, our results suggested that either of the above two simulant can be used for aqueous food under all the condition. Further investigation is needed regarding analysis of specific migration of additives like IRGAFOS-168, ADB-215, DHT-4A, NX-800 and Ca-St used in the polymer.

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Compliance with Ethics Requirements:

Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human and/or animal subjects (if exists) respect the specific regulations and standards.

References

1. Dele Raheem., Application of plastics and paper as food packaging materials – An overview, *Emirates Journal of Food and Agriculture,* **2012***, 25*(3), 177-188
2. Explanatory views on Regulation (EU) No. 10/2011 on plastic materials and articles intended to come into contact with food Plastics Europe and CEFIC FCA November 2011. (http://ec.europa.eu/food / food/chemicalsafety/foodcontact/documents_en.ht)
3. Code of Federal Regulations. *Food And Drug Administration*, Revised as of April 1, **2013**, *3* (CITE: 21CFR175.300)
4. BIS (1998) (2004). IS:9845, *Determination of overall migration of constituents of plastics materials and articles intended to come i contact with foodstuffs* – Method of analysis, New Delhi/, 2004, India.
5. http://www.epa.gov/ttnemc01/ftir/FTIRProtocol.pdf
6. Colourants for polymers. 178.3297, *Code of Federal Regulations*, 21, parts 170-179, Food and drugs. Revised as of April, *1*, 2004
7. Vijayalakshmi, N.S.; Baldev Raj.; Ravi, P. ; Mahadeviah, M., Effect of time temperature on the overall migration of additives from plastics into food simulants, *Deutsche lebensmittel – rundschau* **1999**, *95*(1), 22-26
8. Antonios, E.; and Goulas., overall migration from commercial coextruded food packaging multilayer films and plastics containers into official EU food simulants, *European Food Research Technology* **2001**, *212*, 597–602
9. Alin, J.; and Hakkarainen, M., Migration from polycarbonate packaging to food simulants during microwave heating, *Polymer Degradation and Stability* **2012**, *97*(8), 1387-1395.