Paper No.: 12
Paper Title: FOOD PACKAGING TECHNOLOGY
Module – 33: Migration of toxic substances from package to food product

1. Introduction:

Packaging makes food more convenient. It gives the food greater safety assurance from microorganisms, biological and chemical changes such that the packaged foods can enjoy a longer shelf life. As a result, packaging has become an indispensable element in the food manufacturing process. Flexible plastic packaging was the fastest-growing packaging category in India, achieving a CAGR of 16.6% during 2007-2011. In order to meet the huge demand of the food industry, there was a remarkable growth in the development of food packaging in the past decades. Now, more than 30 different plastics are being used as packaging materials. Also, different types of additives, antioxidants, stabilizers, lubricants, anti-static and anti-blocking agents, have been developed to improve the performance either during processing and fabrication or in use of these polymeric packaging materials. Most concern usually focuses on food additives, both those added intentionally to the foods and those coming in the food from the packaging material. In the area of packaging material, plasticiser migration from food contact materials into food has raised many concerns in communities since the early eighties. This was attributed to the demonstrated carcinogenic effect in rodents and potential estrogenic effect in humans as revealed by toxicological studies of several commonly used plasticisers. Such incidence indicated that the packaging could itself represent a source of hazard through the migration of substances from the packaging material into food.

2. Migration

The term "migration" usually describes a diffusion process, which may be strongly influenced by an interaction of components of the food with the packaging material. This interaction may substantially affect the properties of the packaging material. However, food components, particularly fat, that migrate into plastics, like PE or PP, will considerably increase the mobility of plastic components, thus, enhancing the migration into the contained food.

2.1 Significance of Migration

The migration causes either health effects or it affects quality of food packed. Numerous types of packaging materials have substances capable of migrating to foods and subsequently pose great risk to human health. As migration is a health issue, it has become legal concern in most countries. In an attempt to harmonize legislation, the EU (European Union) and the FDA (Food and Drugs Administration) initiated global control through positive lists of substances that can be used, while restricting substances with toxic potential.

3. Migration from Non-polymeric Materials

3.1 Paper and Paper Boards

Paper and board are widely used as food packaging materials. As public interest in conservation of natural resources is increased in the past several years and the use of recycled paper and board has increased. Recycled fibre materials can be used in certain limits as food contact materials. The safety of recycled fibre-based materials for food contact applications is largely affected by the ability of post-consumer contaminants to be absorbed into recycled materials and later released by the packaging material and trapped on the food. In an accelerated study at 70 and 100°C, it was found that Benzophenone, which is widely used as a photo-initiator for inks that are cured with ultraviolet (UV) light, is a carcinogen at higher levels of exposure and highly fat-soluble compound; whole milk powders in direct contact with paper samples pick up benzophenone at higher level compared to food products with less fat content. Migration is in general rapid and extensive and to keep migration in acceptable limits a low storage temperature should be applied in combination with a suitable barrier layer for indirect contact when recycled paper is used. Certain heavy metals are also found to be transferred from recycled paper to food.

3.2 Metal

Metal food packaging itself covers a wide range of packaging types including food and beverage cans and ends, closures, tubes, trays, drums and pails. Although metal is the defining component of these packages providing strength and integrity, the additional materials required to make a functional package are more often the primary food contact materials in the package. The metals used to manufacture cans, ends and closures are either steel (tin plated) or aluminium. In most cases, they are coated on the food contact surface with a resinous or polymeric protective coating to avoid interaction between the food and the metal. These coatings use Bisphenol A diglycidyl ether (BADGE) as plasticizer. BisphenolA (BPA) may act as an endocrine disruptor, which can cause developmental and neurological impacts. Some studies have investigated BPA release from can linings. The amount of BPA migrated from the can coating into the food during processing (90 min at 121°C) was found to be very high (80% to 100% of the total BPA present in the can coating), indicating that high processing temperatures promote migration.

The nature of the gasket materials used for vacuum closures (PVC plastisols) can lead to significant levels of plasticiser migration when used in contact with fatty foods under sterilisation / pasteurisation conditions. It is not possible to obtain tin with zero lead contamination as the elements coexist in the ore. As a consequence, the tin content of tinplate will always contain traces of lead, but the regulations has been made to limit the lead content in the tin coating of tinplate for food packaging to 100 mg/kg as defined in European Standard EN 10333.

3.3 Glass and Wood

Glass is the most inert packaging material for foods. Several studies in various countries have investigated that glass as packaging material itself is harmless considering migration of heavy metals – lead, cadmium, total chromium and mercury. All results were negative i.e. below the threshold. Using clean lab methods and protocols developed for measuring lead in polar snow and ice, it is found that the greatest lead concentration found in water from a glass bottle (417 ng/L) is well below the maximum allowable concentration for lead in drinking water set by the EU, Health Canada, and the WHO (10 µg/L).

Wood is also an organic material and does not pose serious harm to health if foods are packed in wooden containers. Migrating substances from packaging materials other than polymers to food are shown below.

No.	Packaging Material	Food	Migrated Substance
1	Wooden Packaging	Apples	I-propanol
2	Cans coated with Lacquer	Tomato, Fruits	Epichlorohydrin, BADGE
3	Al - laminated Cartons	Skimmed milk & Stirred Yoghurt	Aluminium
4	Aseptic Packaging	Milk	Hydrogen Peroxide
5	Al - Foil paper laminates	Butter, Margarine	Phthalate esters (DBP, BBP, DEHP)
6	Ceramic containers	Dairy Products	Lead, Cadmium
7	Al - Can	Milk	Aluminium
8	Recycled Paper & Board	-	4,4-bis(diethylaminobenzophenone)

4. Migration from Polymeric Materials

Plastic packaging includes trays and lids, films, pouches, bottles, and so on. Plastic reinforces metals for lining closures, glass to reduce container breakage, and paper for moisture resistance. Multilayer polymeric packaging is made by combining two or more plastic films through co-extrusion, blending, lamination, and coatings to achieve desired features such as gas and moisture barrier properties, UV and visible light transmission, flexibility, stretchability, heat sealability, low glass transition, and other mechanical properties indicative of strength or performance characteristics.

4.1 Hazardous Migrating Components in Plastic Packages (Additives)

Additives enhance the performance of polymers during processing and fabrication. Plasticizers, antioxidants, light stabilizers, lubricants, antistatic agents, slip compounds, thermal stabilizers and printing ink are the most commonly used additives in different types of polymeric packaging materials. Unreacted monomers and oligomers may also migrate from plastics to foods. Table below shows some monomer/oligomers and substances that may migrate from plastics to foods. The restriction has also been applied to the Specific Migration Limits for some metals and primary aromatic amines migrating from plastic packages into food.

No.	Packaging Material	Food	Migrating Substance
1	Polystyrene	Milk, Yoghurt, Water, Instant foods, Beverages	Styrene
2	PVC Films	Cheese	Bis(2-ethylhexyl) adipate (DEHA)
3	LDPE/HDPE	Food simulating liquids	Irganox 1010 (phenolic antioxidant)
4	Microwave packaging	--	cPET (PET monomer)
5	PP Cups	Cheese sauce	2-decanone
6	PS + ABS + Waxed paperboard	Dairy products	Mineral Hydrocarbons
7	LDPE	Milk	Naphthlene
8	ABS	Dairy products	Mineral Hydrocarbons
9	PC	Water	Bisphenol -A
10	Polymers	Milk	Dioctylphthalate

4.1.1 Plasticizers

Plasticizers are the group of compounds used to improve flexibility, workability, and stretchability of polymeric films as a process aid, reducing melt flow. Plasticizers reduce shear during mixing steps in polymer production and improve impact resistance in the final plastic film. Some important plasticizers include phthalic esters, such as di-2-ethylhexyl phthalate (DEHP) used in PVC formulations, comprising about 80% of plasticizer volume for PVC production. Plasticizers have a low molecular weight and can migrate from packaging materials into wrapped food, thus becoming indirect food additives. DEHA (di-(ethylhexyl) adipate), a plasticizer in PVC, can migrate from packaging into fatty foods. The migration of plasticizers from plastics in to food has been reported by in several workers. As a result of these studies, the packaging industry has replaced PVC with regenerated cellulose not associated with plasticizers.

4.1.1.1 Phthalates:

Phthalates or phthalate esters are esters of phthalic acid and are mainly used as plasticizers. Phthalates are known to interfere with the production of male reproductive hormones in animals and likely to have similar effects in humans. Their effects in animal studies are well recognized and include lower testosterone levels, decreased sperm counts and lower sperm quality. Exposure to phthalates during development can also cause malformations of the male reproductive tract and testicular cancer. Young children and developing foetuses are most at risk.

One study investigated phthalate migration from baby bottles under hot-fill conditions of 2 h at 70°C, and found that migration levels for diisobutyl phthalate (DiBP) and dibutyl phthalate (DBP) varied from 50 to 150 µg /kg, while DEHP displayed comparatively lower migration levels (25 to 50 µg/kg). Phthalates showed a high-transfer rate of 350% when used in gasket material for closures in a study with olive oil. This indicates transfer not just from the gasket, but from underneath the seal or rim. Migration of phthalates was determined from a wide range of food-packaging materials to food simulants after 10 days of storage at 40°C. Higher amounts of plasticizers were found released from PE bread-bag as compared to PE film. Low level of phthalates and DEHA migrate from tetra pack packaging materials. The PS packaging for yoghurt showed very little migration. Several Specific Migration Limits are recommended for different plasticizers, such as 1.5 mg/kg for DEHP, 0.3 mg/kg for DBP, 30 mg/kg for BBP.

4.1.1.2 Bisphenol A:

It is a part of the bisphenols group of chemical compounds with two hydroxyphenyl functionalities. It is a colorless solid that is soluble in organic solvents, but poorly soluble in water. In the European Union, the Total Dietary Intake is set at 0.05mg/kg body weight/day and a Specific Migration Limit of 0.6mg/kg food has been regulated.

Since the beginning of the 90's, BPA has been the subject of increased scientific investigation regarding its estrogenicity. Scientists have found BPA to interact with estrogen receptors, both in the nucleus as well as on the cell membrane, to be an androgen receptor antagonist and to reduce the synthesis of some steroids at the molecular level. In vitro studies have found low-dose effects of BPA on adipose, reproductive and mammary tissue, the immune and nervous system, the liver and in pancreatic and pituitary models. In in vivo models, exposure levels below 50 mg/kg body weight/day have been observed to cause changes in brain physiology, brain structure, behavior, sex differences in the brain, puberty in females, the mammary gland, uterus and vagina, ovary oocytes and female fertility as well as metabolism and the immune system. Further, effects such as carcinogenesis, male reproduction and adipogenesis have been also recently added to the list.

Studies have found that foetuses and young children exposed to BPA are at risk for secondary sexual developmental changes, brain and behaviour changes and immune disorders. Infants fed with liquid formula are among the most exposed, and those fed formula from polycarbonate bottles can consume up to 13 µg/kg body weight/day. Yet, consensus regarding the health risks of BPA has not been established in the scientific community and discussion on the risk evaluation of BPA has been ongoing since the 1990s. Some of the scientists proposes that the current Total Dietary Intake for BPA is adequately justified and that the available evidence indicates that BPA exposure represents no noteworthy risk to the health of the human population, including new-borns and babies.

4.1.1.3 Other Plasticizers:

These category include adipates, epoxidized soya bean oil (ESBO) etc. DEHA, an adipate has been demonstrated to induce liver adenomas and carcinomas in mice but not in rats. According to the International Agency for Research on Cancer (IARC), it is "not classifiable as to its carcinogenicity to humans". They can cause eye irritation and skin allergy at very high concentration. Repeated oral administration of ESBO had been shown to affect the liver, kidney, testis and uterus.

In a study with high fat foods like cheese and Ham packed in PVC film and heated in microwave, the migration of all plasticizers increased with increasing fat content and contact time. Adipate plasticizers could easily migrate from the packaging film into these foods with the rate of migration higher for foods with higher fat content.

In general, migration of plasticizers is influenced by food composition, contacting phase, the time–temperature combination of exposure of the food to the packaging film, and the initial concentration of the migrant components in the film. PVC is not suitable for food-contact applications in a microwave oven due to high migration of Di-octyladipate, but Saran may be used if direct contact with high-fat foodstuffs is avoided.

4.1.2 Antioxidants

Under the exposure of UV light and in the presence of air, polymer may undergo degradation through oxidation mechanism. To slow down such oxidation process, antioxidants are added to the polymer by preferentially degrading themselves.

Arylamines are common antioxidants used in plastic food packaging. Butylatedhydroxytoluene (BHT), 2- and 3-*t*-butyl-4-hydroxyanisole (BHA), tetrakismethylene-(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate) methane (Irganox 1010), and bisphenolics such as Cyanox 2246 and 425, and bisphenol A are the most common phenolics used as antioxidants.The arylsubstitutedphosphites are considered as toxic. Nevertheless, some of them are found in the positive lists of many countries, often accompanied by strict purity requirements. This is due to the tri-substituted derivative being much toxic than the mono- and di-substituted ones.

Another class of antioxidants, the organophosphites, reduces hydroperoxides formed during oxidation to alcohols. Tris-nonylphenylphosphite (TNPP) is the most commonly used organophosphite, followed by tris (2, 4-di-*t*-butylphenyl) phosphite, also known as Irgafos 168.Triphenylphosphite can be included among highly toxic substances. Quantification and the specific migration limits of antioxidants are also of interest because these compounds and their degradation products migrate from plastics into food during processing and storage. In a study it was found that migration of antioxidants increased as the fat content of the food and storage temperature increased.

4.1.3 Monomers and Oligomers

Monomers, as well as oligomers, are likely to migrate from packaging materials to food. Monomers are reactive substances, with respect to living organisms, and hence, potentially toxic. Therefore, hygiene regulations aim at restricting the content of residual monomers in the raw or starting materials, plastics and articles made therefrom.

Despite the acute toxicology of styrene is not high, its metabolism involves phenyloxirane, a mutagenic compound. Further, styrene may affect sensory properties at very low levels: 200–500 ppb in yoghurt, and 40–730 ppb in water.

Studies report the migration of styrene into food and estimate the daily styrene exposure of 18.2 to 55.2 μg for individuals, with an annual exposure of 6.7 to 20.2 mg. This level of exposure causes irritation of the human organs and skin, as well as neurological disorders. In a study the migration of styrene from different food-contact PS foam materials (meat trays, egg cartoons, cups, plates, and hinged carry-out containers) to the oil (mixture of canola, sunflower, and other vegetable oil) and 8% ethanol at 21 °C for 10 days, 49 °C and 65.5 °C for 1, 4 and 10 days was studied. Migration increased from 1 to 10 days and found to be proportional to the square root of the increase in time at a specific temperature for all articles except for drink cups. Styrene migration from PS to hot drinks like tea, milk, and cocoa in milk was highly dependent upon temperature of drinks and fat content, with the highest level of migration in hot cocoa with milk.

Vinyl chloride monomer is highly toxic, the levels of which in PVC food packaging materials are closely controlled. Both the residual monomer contents of the polymer and migration levels to foods or food simulants are regulated as well.

In the food packaging industry, isocyanates are used in polyurethane polymers and adhesives. They are toxic compounds, and their health effects are well documented. Also, their use in food packaging materials is regulated by EC Directives. Residual levels in finished plastics must not exceed 1.0 mg/kg.

Finally, polyethylene terephthalate (PET) is commonly used as packaging material for beverages and edible oils. PET has become a widely used polymer because its drawn films have high strength, flexibility, and clarity. PET is known to contain small amounts of low-molecular weight oligomers of cyclic compounds ranging from dimer to pentamer. A PET package that permits 10 μg/kg or less migration of a component is still considered acceptable.

4.1.6 Contaminants

Apart from additives and monomer residues present in the packaging materials, other sources of food contamination have been reported as well. Decomposition products from additives or monomers will also migrate into the food under proper conditions.

The presence of the residues of these chemicals may lead to contamination. Diphenylthiurea is used in the manufacturing of PVC film, benzene, dioxins processing agents (hydrogen peroxide) and other volatiles for some of the most representative residues.

4.2 Overall Migration

The concept of the Overall Migration limit has mainly been used to control the total amount of substance migrating from plastics into food, rather than for determining the toxicological importance of the substances, and also for reducing the Specific Migration experiments. One study examined different polymers under Microwave and oven heating for Overall Migration in olive oil. Materials included PET, PPO/EPS, PPO/HIPS, HIPS, PP/EVOH/PP, PP/PVDC/PP, PA66, PVDC, PET-coated board, PET/steel, PP/aluminum, and PP.

The Overall Migration values obtained using microwave heating were within the Overall Migration limit of 10 mg/dm^2 or 60 mg/kg, as specified in Commission Regulation (EU) No 10/2011. Results showed that microwave heating causes less migration than conventional heating, with the exception of PET-coated boards.

5. Methods for detection of Migration in food

Appropriate analytical methods are needed to determine migration from plastic packaging into food. Regulatory agencies have specified analytical methods for some, but not all, migrants. Official test methods are usually time-consuming, complicated, and impractical for routine or daily controls. Therefore, the EC accepted, in addition to official methods, more practical test methods. The methods used are based mainly on the extraction followed by chromatographic or spectrophotometric analysis.

Mathematical models have been developed and are used frequently to predict the migration of the low-molecular-weight components from plastic packaging and may be suitable for materials with migration data. However, these models do not adjust to different polymeric properties and behaviour, especially in terms of migration from new polymeric materials without well-characterized properties. Therefore, experimental determination of migrating compounds must be conducted to verify the accuracy of the migration results predicted by the developed mathematical models.

A number of gas chromatographic techniques for different plasticizers have been developed.Determinations of styrene monomer in food and food simulants using GC techniques are common.PET oligomers in olive oil and iso-octane have been determined using GC–MS with selective ion monitoring (SIM) and HPLC-UV.

6. Factors affecting Migration of toxic substances in to food

Several factors govern the migration of packaging materials residue in to the foods. This includes: Properties and composition of packaging materials, Properties/state and composition of food materials, surface contact area, head space, period of contact, temperature, light, irradiation, agitation, in-package processing and storage etc. The migration of additives or contaminants from food packaging to food may be separated into three different, but inter-related, stages: diffusion within the polymer, solvation at the polymer-food interface, and dispersion into bulk food.

7. Legislations

Over the past few decades, scientists and regulatory agencies have become concerned about consumer protection from possible food toxicity caused by migration of compounds from food contact materials into food. Hence, many countries have formulated their own guidelines and regulations for testing of those substances and specified the limit of migration. Therefore, various approaches from different countries can be considered.

7.1 European legislation

Recently, Commission Regulation (EU) 10/2011 on plastic materials and articles intended to come into contact with food has replaced Directive 2002/72/EC (Commission Regulation No 321/2011). The 321/2011/EU and 1282/2011/EU amendments have been implemented to the Commission Regulation (EU) No 10/2011 for the restriction of use of BPA in plastic infant bottles, and the correction of regulations for plastic materials, respectively. Commission Regulation (EU) No 10/2011 has specified Overall Migration limits of 10 mg/dm^2 or 60 mg/kg.

7.2 US FDA legislation

The U.S. Food and Drug Administration considers substances that are not added intentionally, and may come in the contact with food materials from packaging or food-contact materials as indirect food compounds. The FDA identifies the types of foods and conditions of use for food-contact substances. The food-contact materials and allied aspects have been described in Parts 174 to 178 in Title 21 under the CFR (Code of Federal Regulation, 2011). The indirect food compounds used in food-contact articles may include adhesive and coating components (Part 175), paper and paperboard components (Part 176), basic components of food-contact surfaces (Part 177), and adjuvant, production aids, and sanitizers (Part 178). Some components are considered as safe and fall under the category "general recognized as safe" (GRAS).

7.3 Legislation in Australia and New Zealand

Food Standard Australia New Zealand (FSANZ) provides standards for general food, food products, food safety, and primary productions. Among these issues, only standard 1.4.1 and 1.4.3 provides information on contaminants and toxicants as well as food-contact materials and articles, respectively. The Standard 1.4.3 provides only basic information on food-contact articles and materials, and does not detail the substances that should be used in production of food-packaging materials. The Australian Standard AS 2070–1999 is also covering plastic materials in contact with food. This standard guides the industry and follows regulations provided by EU and FDA.

7.4 Legislation in India

There are no specified regulations from Food Safety and Standards Authority in India. But, they specify that all the packaging materials used in food packaging should meet BIS standards. Bureau of Indian Standards has published specifications for individual plastics e.g. PE, PS, PVC (IS: 10446-1982, IS: 10142-1982 and IS: 10151-1982) etc with overall migration limit of 60 mg/kg for residual monomer, and specific migration limit of 6 mg/kg for Irganox 1076(antioxidant), 1.2 mg/kg for N,N-bis (2-hydroxyethyl) alkyl amine hydrochlorides. The organization also specifies guidelines on suitability of plastics for food packaging and positive list of constituents of plastics.

8. Conclusion

As packaging of food is inevitable due to several reasons, the concern about health and safety issues raised due to migrants from packaging materials should be addressed with serious remarks to scientific community, regulatory authority and general public. Certain additives and monomers form PS and PVC should be monitored through proper surveillance. More attention should be paid to additives used in polymer manufacturing process. There are other fields such as processing line, cookware in households etc. which may act as route of contamination and hence must be evaluated. The new processing and packaging techniques such as microwave heating, in package high pressure processing, etc. have substantial effects on migration.

Migration is likely to occur in packaged milk and milk products also, and most of the urban market of foods is served with packaged food. So, the utmost care should be taken in selection of packaging materials for food and there is a need to perform research work in this field in India as per Indian atmosphere and conditions.

References

1. Allard P. Colaiacovo MP. 2011. Bisphenol A. In: Reproductive and Developmental Toxicology. R.C. Gupta, ed. Elsevier, München. pp 673-686
2. CEC, Synoptic Document No 7. 1994. Draft of provisional List of Monomers and Additives Used in the Manufacture of Plastics and Coatings Intended to Come into Contact with Foodstuffs. Commission of the European Communities. Directorate-General III. Industry. Industrial Affairs III: Consumer Goods Industries, Brussels
3. CFR (Code of Federal Regulation) 2011. Title 21. Food and Drug, Department of Health and Human Services. Available from: http://cfr.vlex.com/source/code-federal-regulations-food-drus-1070/page/58
4. Coles R, McDowell D, Kirwan MJ. 2003. Food packaging technology. Oxford, U.K.: Blackwell Publishing. p 284
5. Crompton TR. 2007. Additive migration from plastics into food. 1st ed. Shawbury, Shrewsbury, Shropshire, UK: SmithersRapra Technology Limited
6. EFSA Panel. 2005. Opinion of the Scientific Panel on food additives, flavourings, processing aids and materials in contact with food (AFC) related to Bis(2-ethylhexyl)phthalate (DEHP) for use in food contact materials. The EFSA Journal, 243: 1-20
7. EFSA. 2012. Scientific opinion on bisphenol A: evaluation of a study investigating its neurodevelopmental toxicity, review of recent scientific literature on its toxicity and advice on the Danish risk assessment of bisphenol A. The EFSA Journal. Cited from: http://www.foodpackagingforum.org/Food-Packaging-Health/Bisphenol-A
8. European Environment Agency. 2012. Bisphenol A: contested science, divergent safety evaluations. Lessons from health hazards. Cited from: http://www.foodpackagingforum.org/Food-Packaging-Health/Bisphenol-A
9. FSANZ General Food Standards. 2000. Part 1.4. Food Standards, Australia, New Zealand. Available from: http://www.comlaw.gov.au/Series/F2008B00618
10. Kattas L, Gastrock F, Cacciatore A. 2000. Plastic additives. In: Harper CA, editor. Modern plastics. New York, NY: McGraw-Hill. pp 4.1–4.66
11. Sablani SS, Rahman MS. 2007. Food packaging interaction. In: Rahmna MS, editor. Handbook of food preservation. Boca Raton, F.L.: CRC Press, Taylor and Francis. pp 939–956
12. US EPA. 2002. Integrated Risk Information System: Bisphenol A. Cited from: http://www.foodpackagingforum.org/Food-Packaging-Health/Bisphenol-A