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Safety of Packaging Materials for Seafoods

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Plastics and plastic based materials are increasingly used in fish industry either as containers or crates for storage of raw materials in semi-rigid and other flexible forms for processed fish and fish products. The finished plastics contain impurities such as left over monomer residues, additives, stabilizers, odorous adjuvants, colorants and antioxidants. These may leach into the foodstuffs affecting the quality of seafoods. For regulating their use many developed countries after considerable studies have formulated their own standards and codes of practice for packaging materials for food contact applications. As the migration of the chemical constituents and additives of the packaging materials into fish and fish products is likely to render the seafood unsafe for human consumption, it is absolutely necessary to test for global migration. The overall migration residue gives a fair estimate of safety. This paper deals with different safety aspects of packaging materials for fish and fishery products.

Key words: Packaging materials, seafood safety

Seafood export from India has now crossed Rs. 6000 crores, and the major share of trade is with quality and environmentally conscious nations like Japan, European Union and USA. Success in entering into these markets lies in the hygienic preparation of the product and adopting packaging meeting the health, safety and environmental requirements of these countries. There is a widespread concern on the increasing presence of packaging materials in the waste stream and their effect on environment in the industrialized nations. Environmental legislations concerning packaging are being enacted aimed at their reduction at source or facilitate their recycling or reuse through incentives, penalties, voluntary and mandatory restraints. Hazardous substances migrating or permeating from the packaging materials and their components into the foodstuffs coming in contact with them and affecting the health and safety of the consumer are also of equal concern. Plastics are increasingly used as packaging media for fish products and migration of left over residual monomers and additives may impair the quality of packed products. Hazardous metals, volatiles, etc., in printing inks and

can solders if permeating beyond acceptable limits endanger health of consumers. There are laws regulating the limits of these hazardous substances in packaging materials and ingredients in food products and there are complete bans on certain packaging materials in some countries. These laws and restrictions vary territorially and the exporter of marine products has to be aware of these, so that his products are not rejected or held up at destination due to unacceptable packaging.

Nearly 95% of exports of marine products are in the frozen condition and the balance includes minor items like live/fresh, chilled/dried fish etc. The packaging materials/packages used in fish industry are both modern as well as traditional types, ranging from bamboo baskets, jute bags, leaf mats to corrugated fibre board boxes, duplex board cartons, metal containers of aluminium and tin plate, plastic films and their laminates, thermoformed trays, polypropylene and high density polythene crates, expanded polystyrene insulated boxes, glass bottles, etc. Of all these types of packaging materials, flexible packaging materials come in direct contact with food in majority of cases. While most of the packaging materials are made indigenously some plastics are imported to meet the exporters' obligations. The consumption of packaging materials used in fish industry is estimated to be worth US $ 50 million.

Plastics and plastic based materials are increasingly used in fish industry either as containers/crates for storage of raw materials and processed fish at factories or final packaging in semi-rigid and other flexible forms. Some of the plastics commonly used for fish packaging are low-density polythene (LDPE), high-density polythene (HDPE), linear low-density polythene (LLDPE), high molecular weight high-density polythene, polypropylene (cast and oriented polypropylene), polyester (PET), polyamide (PA), polystyrene (PS), ethylene acrylic acid (EAA) and polyacrylonitrile (Gopal, 1999). All plastics, apart from the basic polymer, contain several non-polymeric components, either inherent or deliberately added to plastics, which are classified in three categories, viz., polymerisation residues (residual monomers, catalyst remnants, polymerization solvent, etc.), processing aids and end use additives (Mahadeviah & Gowramma, 1996). Use of processing aids such as plasticizers, stabilizers, antioxidants, slip agents, lubricants and antistatic agents are unavoidable End use additives such as antioxidants, brightners, blowing agents, mould release agents, colourants and UV stabilizers are deliberately added to the polymer either during manufacture

or subsequently to achieve the desired end properties of the finished plastic material. The useful properties of plastics are not manifested without the use of such additives.

Polymers themselves being of high molecular weight are inert and have limited solubility in aqueous and fatty systems. But the non-polymeric components may leach out from plastics to foods whenever direct contact occurs between food and plastics thereby contaminating the food product with the consequent risk of toxic hazard to the consumer (Murthy & Raju, 1989; Crosby, 1981; Crompton, 1979). The awareness in this matter has led the national and international regulatory authorities in the formation of guidelines for proper use of plastics for food packaging application. Such guidelines are necessary to restrict the indiscriminate use or abuse of plastics in food packaging.

Different countries like India, USA, UK, Europe and Japan have laid down specifications and codes of manufacture for the safety in use of plastics for food contact applications (BPF, 1981; IS: 10146-1982; IS: 10151-1982; FDA, 1983; Anon, 1984; IS: 10910, 1984; IS: 11434, 1985; IS: 11435, 1985; IS: 11704, 1986; IS: 11705, 1986; IS: 12229, 1987; IS: 12252, 1987; IS: 12247, 1988; IS: 12248, 1988 EC, 1992; IS: 10142, 1999). This relates principally to the use of various ingredients, additives and other processing aids used by the manufacturer in the formulations of plastics composition. These recommendations are based on the existing toxicological data. In India, agencies like Bureau of Indian Standards (Bureau of Indian Standards) and Prevention of Food Adulteration Act (PFA) have formulated code of practice and specifications for a number of food grade plastics. In this regard, Bureau of Indian Standards has laid down positive list of constituents, which are generally regarded as safe (GRAS) and specifications for safe use of plastics commonly used in food packaging. The residual monomer content and heavy metal content in different plastics specified by different countries and limits of heavy metals in colours used are presented in Table 1 and Table 2, respectively (Anon, 1984).

The other regulations on food packaging materials comprise of regulations for adjuvants such as antioxidants, colorants and plasticisers, used in food packaging materials. Only cited materials must be used and within given limits i.e., the amount of the adjuvant which can be used and the kinds of plastic in which it can be used are prescribed in Table 3 (Crosby, 1981; Till *et al.*, 1982; Castle *et al.*, 1989).

Table 1. Limits of monomer and heavy metals in plastics

Country	Monomer	Heavy metals
BIS, India	VCM in PVC-1 ppm; in food migration-10 ppb, styrene in polystyrene-2000 ppm	Lead 1 ppm and others 0.01 ppm in PVC
EEC-Europe	VCM in PVC-1 ppm	Nil
BPF-UK	VCM in PVC-1 ppm, styrene in PS-5000 ppm	Nil
Japan	VCM in PVC-1 ppm. Volatile component in polystyrene-5000 ppm	i) Lead, Cadmium & Barium 100 ppm each in PVDC
	Vinylidine chloride in PVDC-6 ppm, Caprolactum in Nylon-15 ppm.	ii) 0.05 ppm Antimony & 0.1 ppm Germanium in PET.
FDA-USA	VCM not specified styrene in PS-10000 ppm, Acrylonitrile in ABS plastics-11 ppm	Nil

VCM – Vinyl chloride monomer; PVC – Polyvinyl chloride; PVDC – Polyvinylidene chloride

Table 2. Limits of heavy metals in colors used in plastic manufacture

Heavy Metal	Limit (%)
Lead	0.01
Arsenic	0.005
Mercury	0.005
Cadmium	0.20
Selenium	0.20
Barium	0.01

The third aspect is the extractive limits for the final food contact article. Here the limitations would thus include the contributions from all the adjuvants and processing aids used in making the food contact packaging material, etc. These regulations spell out the time/temperature/solvent conditions for the short term extraction experiments (migration tests) used to test compliance.

Migration tests for adjuvant transfer into foods should be conducted with each type of food in a given package under normal conditions of use for an expected contact time. However, apart from being economically prohibitive, this type of evaluation with actual foods is analytically difficult

Table 3. Permitted additives in finished packaging materials (BIS)

Additive type	LDPE/ LLDPE	HDPE	PVC	PS	IONOMER	EAA
Polymerisation residues	0.2%	0.2%	-	-	0.2%	<0.5%
Calcium, Aluminium, Silicon, Titanium	-	0.2%	-	-	-	-
Chromium	-	50 ppm	-	-	-	-
Emulsifying agents	0.3%	0.3%	3%	-	-	-
Catalyst	0.2%	0.2%	0.25%	0.2%	-	-
Lubricants	2.0%	2.0%	-	-	2.0%	1.0%
Stearyl ethylene diamine	-	-	-	-	-	0.2%
Fatty acid amides	0.2%	0.2%	0.3%	0.3%	-	-
Microcrystalline waxes, paraffin or oil	0.1%	-	-	-	-	-
Octoates, oleate, palmitate & stearate of Zinc	2.0%	-	-	2.0	-	-
Poly 1,2 propylene glycol	0.1%	-	-	0.1%	-	-
Pthalates of monovalent alcohols	0.2%	-	3.0%	-	-	-
Polyethylene glycol	-	-	-	0.1%	-	-
Stearyl erucamide	-	-	-	-	-	0.2%
N, N-Bureau of Indian Standards-stearyl/palmityl ethylene diamine Fatty alcohols	1.0%	1.0%	-	-	-	-
	-	-	3.0%	-	-	-
Antioxidants	1.5%	1.5%	-	-	2.0%	1.5%
4,4-thio-BIS (6-tbutyl-n-cresol)	0.25%	0.25%	-	-	-	-
4,4-butylidine-BIS (6-tert-butyl-n-cresol)	0.3%	0.3%	-	-	-	-
1,3,5-trimethyl-2, 4,6-tris (3,5-ditert butyl-4-hydroxy-benzyl) benzene	0.5%	0.5%	-	-	-	-
2,4, dinonyl phenyl, di (4-monononylphenyl) phosphite	0.3%	0.3%	-	-	-	-
2.2-methylene-BIS 6- (1 methyl-cyclohexyl) p-cresol	0.2%	0.2%	-	-	-	-
Thio-BIS (6-tert-butyl-n-cresol)	0.25%	0.2%	-	-	-	-
Antistatic agent	0.5%	0.5%	-	-	0.5%	0.5%
Tri-iso-propanolamine	0.5%	-	-	-	-	-
N-N-Bureau of Indian Standards (2-hydroxyethyl) alkyl amines	0.3%	0.3%	-	-	-	-
	0.4%	0.4%	-	-	-	-
Cetyl pyridinium chloride N, N-Bureau of Indian Standards (Polyhydroxyethyl) alkyl amine	-	0.3%	-	-	-	-

because of their complex nature. Foodstuffs vary in composition from place to place and more importantly they are unstable and decompose fairly rapidly. Further, the duration involved makes long-term tests with foodstuffs impractical. Food simulating liquids have been recommended to be used in place of actual foodstuffs and are as follows (Crosby, 1981).

i. Distilled water

ii. 3% acetic acid (w/v) in aqueous solution

iii. 8% ethanol (v/v) in aqueous solution for foodstuffs having alcohol less than 8%

iv. 50% ethanol (v/v) in aqueous solution for foodstuffs having alcohol more than 8% and less than 50%

v. n-Heptane – shall be redistilled before use.

Foods are divided into several types (Robertson, 1983) in order to determine the over all migration residue (Table 4)

Table 4. Food categorization

Category	Description
I	Non - acid (pH>5.0), aqueous products, may contain salt or sugar or both and including oil-in-water emulsions of low or high fat content.
II	Acidic (pH<5.0), aqueous products may contain salt or sugar or both and including oil-in-water emulsions of low or high fat content.
III	Aqueous, acid or non acid products containing free oil or fat; may contain salt and including oil-in-water emulsions of low or high fat content.
IV	Dairy products and modifications:
	A. Water-in-oil emulsion, high or low fat
	B. Oil-in-water emulsion, high or low fat
V	Low moisture fats and oils
VI	Beverages:
	A. Containing upto 8% alcohol
	B. Non alcoholic
	C. Containing more than 8% alcohol
VII	Bakery products
	A. Moist bakery products with surface containing free fat or oil
	B. Moist bakery products with surface containing no free fat or oil
VIII	Dry solids with the surface containing no free fat or oil (no end test required)

Method for determination of migration residue depends on the type of food, simulating solvents, time and temperature (IS: 9845-1981; Anon, 1983; Anon, 1978) (Table 5). Limits for migration residues are given in Table 6.

Table 5. Simulating solvents for different types of food and time temperature conditions in global migration tests

Condition of use	Types of food (see Table 4)	Food simulating solvents			
		Water	Heptane	8% Alcohol	50% Alcohol
A. High temp. Heat sterilised (eg. over 100°C)	I, IV-B, VII-B	121°C, 2 h	-	-	-
	III, IV-A, VII	121°C, 2 h	66°C, 2 h	-	-
B. Boiling water sterilised	II, VII B	100°C, 30 min			
	III, VII A	100°C, 30 min	49°C, 30 min	-	-
C. Hot filled or pasteurised above 66°C	II, IV-B	Till boiling, cool to 38°C			
	III, IV-A	Till boiling, cool to 38°C	49°C, 15 min	-	-
	V	-	49°C, 15 min	-	-
D. Hot filled or pasteurised below 66°C	II, IV-B, VI-B	66°C, 2 h	-	-	-
	III, IV-A	66°C, 2 h	38°C, 30 min		
	V	-	38°C, 30 min	66°C, 2 h	
	VI- A	-	-	-	66°C, 2 h
E. Room temp. Filled and stored (no thermal treatment in the container)	I, II, IV-B, VI-B	49°C, 24 h	-	-	-
	III, IV-A	49°C, 24 h	21°C, 30 min	-	-
	V, VII	-	49°C, 24 h	-	-
F. Refrigerated storage (no thermal treatment in the container)	III, IV-A, VII A	21°C, 48 h	21°C, 30 min	-	-
	I, II, IV-B, VI-B, VII B	-	-	-	
	VII A			49°C, 24 h	
	VI- C				49°C,24 h
G. Frozen storage (no thermal treatment in the container)	I,II,III, IV-B,VII	21°C, 24 h	-	-	-
H. Frozen or refrigerated storage: Ready-prepared foods intended to be reheated in container at the time of use:					
i. Aqueous or oil-in-water emulsion of high or low fat.	I, II, IV-B, VII B	100°C, 30 min.		-	-
ii. Aqueous, high or low free oil or fat.	III, IV-A, VII A	100°C, 30 min.	49°C, 30min.	-	-

Table 6. Global Migration Limits (GML) in various specifications

Standard (Country)	GML
BIS (India), BPF (UK), EEC (Europe)	60 $mg.kg^{-1}$ or 0.1 $mg.cm^{-2}$ for all polymers for which specifications are available
FDA (USA)	a. 50 $mg.l^{-1}$ or 0.75 $mg.cm^{-2}$ for resinous and polymeric coatings b. 21-197 $mg.in^{-2}$ for rubber articles c. 0.15 $mg.in^{-2}$ (water) for phenol formaldehyde moulded article d. 0.02-0.5 $mg.in^{-2}$ for polyesters (depending on use and conditions) e. 0.2-2.5 wt. percent for various nylons depending in extractive solvent
JIS (Japan)	a. 150 $mg.l^{-1}$ for PE and PP b. 30 $mg.l^{-1}$ for containers to be used at >100°C c. 15-30 $mg.l^{-1}$ for PA

Considering the importance of seafoods in the economy of our country, it is very important to devote attention to produce and market good quality seafood products for both export and internal markets. Even though we have implemented strict quality control practices for ensuring food safety for the export trade, there are no proper guidelines and strict quality control with reference to packaging materials used. Most of the packaging materials used are not being tested for safety aspects. In order to make the packaging materials safe, testing should be made mandatory for parameters like overall and specific migration for residual monomer content and other toxic components.

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