

Migration of Chemical Compounds from Packaging Polymers during Microwave, Conventional Heat Treatment, and Storage

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Abstract: Polymeric packaging protects food during storage and transportation, and withstands mechanical and thermal stresses from high-temperature conventional retort or microwave-assisted food processing treatments. Chemical compounds that are incorporated within polymeric packaging materials to improve functionality, may interact with food components during processing or storage and migrate into the food. Once these compounds reach a specified limit, food quality and safety may be jeopardized. Possible chemical migrants include plasticizers, antioxidants, thermal stabilizers, slip compounds, and monomers. Chemical migration from food packaging is affected by a number of parameters including the nature and complexity of food, the contact time and temperature of the system, the type of packaging contact layer, and the properties of the migrants. Researchers study the migration of food-packaging compounds by exposing food or food-simulating liquids to conventional and microwave heating and storage conditions, primarily through chromatographic or spectroscopic methods; from these data, they develop kinetic and risk assessment models. This review provides a comprehensive overview of the migration of chemical compounds into food or food simulants exposed to various heat treatments and storage conditions, as well as a discussion of regulatory issues.

Introduction

Food Packaging is a rapidly evolving field. Besides keeping foods safe from contamination and retaining the nutritional properties and sensory characteristics of foods, packaging provides additional features that are important to consumers. These include resealability, tamper evidence, and the display of product information, as well as reuse or recycling features. The use of both flexible and rigid polymeric packaging is growing rapidly, and is driven by new developments in bio-plastics, and the desire to reduce the bulk and weight of metal and glass containers. Polymer packaging incorporated with chemical compounds is commonly referred to as plastics. Incorporation of low-molecular-weight chemical compounds improves functional properties of plastics. However, the potential influence these substances on product safety and quality remains in question when amount of these migrating compounds in food exceed their specified limits. The term “migration” refers to the diffusion of substances from a zone of higher concentration (the food-contact layer) to one of a lower concentration (usually the food surface). This process is often influenced by food-packaging

interactions (Arvatoyannis and Bosnea 2004) and the temperature of the system.

Diffusion of chemical substances from polymers is a very complex process, and is dependent on several parameters, such as concentration of substances in packaging film and food, nature of the foods, temperature, and the time period over which duration of contact occurs. During the process of diffusion, these compounds enter into another matrix (such as film or food), which changes their concentration in both the packaging and food. Although chemical compound migration is mainly a diffusion-controlled process, it is equally important to consider the mechanism of convection and chemical reactions. The degree of solvent stirring, polymer-solvent partition coefficients, swelling of solvents, and concentration-dependent diffusivity play a key role in the diffusion process (Reid and others 1980). For example, in a liquid, viscous, or solid food, diffusivity may change since the interface between plastics and food material would be different in each of these cases.

The migration process can be divided into 4 major steps: diffusion of chemical compounds through the polymers, desorption of the diffused molecules from the polymer surface, sorption of the compounds at the plastic-food interface, and desorption of the compounds in the food (Ferrara and others 2001). The mass diffusion process is usually governed by Fick's law. The steady state diffusion process indicates no change in concentration over the time ($\frac{\partial C_p}{\partial t} = 0$); however, most of the interactions between the packaging and food are influenced by nonsteady state conditions.

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$$\text{Fick's first law: } N_A = -D_p \frac{\partial C_p}{\partial x} \quad (1)$$

$$\text{Fick's second law: } \frac{\partial C_p}{\partial t} = -D_p \frac{\partial^2 C_p}{\partial x^2} \quad (2)$$

N_A is the steady state flux; C_p is the concentration of migrant in the polymer; D_p is the diffusion coefficient of migrant in polymer. For practical purposes, diffusion and partition coefficients are assumed to be constant. In polymers such as polyethylene (PE) and polypropylene (PP) with low glass transition temperatures (T_g), it can be assumed that migration of substances made from these materials obey Fick's laws (Brandsch and others 2000). The partition coefficient (k_p) that determines the migration at the polymer-solvent boundary can be written as:

$$k_p = \frac{C_s}{C_p} \quad (3)$$

C_s is the migrant concentration in food/food simulant/solvent phase. The lower the k_p value, the more the migrant is absorbed into the food from the polymer. When fatty foods come in contact with these polymers, this value is low ($k_p < 1$); for water, it is very high ($k_p > 1000$) (Piringer 2007). However, the coefficients can vary with concentration and time, leading to non-Fickian diffusion, resulting from the solvent penetration-induced swelling phenomenon (Piringer 2007), which is often accelerated by the temperature of these processes. Changes in temperature may influence the partition coefficient, as the solubility of the migrant changes both in the polymer and food phases at equilibrium. The temperature dependence of partition coefficient is also described with the Arrhenius equation (Bastarrachea and others 2010).

The process of diffusion is also influenced by temperature. The fundamental equation correlating diffusion coefficient and temperature is the Arrhenius type equation (Bastarrachea and others 2010):

$$D_p = D_0 e^{-\frac{E}{RT}} \quad (4)$$

where D_0 is the pre-exponential factor, E is the activation energy for diffusive molecules, R is the gas constant, and T is the absolute temperature of the system. Several approaches have been carried out to develop a new model for predicting diffusion of compounds, where $D_p = f$ (molecular mass of migrant, absolute temperature). This correlation was developed by Brandsch and others (2000):

$$D_p = D_0 \exp \left(A_p - 0.1351 M_r^{2/3} + 0.003 M_r - \frac{10454}{RT} \right) \text{ cm}^2/\text{s} \quad (5)$$

where $A_p = A'_p - \tau/T$, M_r is the relative molecular mass of the migrant, and A'_p and τ are specific parameters of the polymer matrix.

The diffusion process is also influenced by the state of the polymer matrix, whether they exist in the rubbery or glassy state at storage temperature. Diffusion in glassy polymers is much slower than in rubbery polymers.

The likelihood of monomer and oligomer migration increases when a plastic is exposed to high temperatures during thermal processing or when food is stored for extended periods. Transfer of chemical compounds from plastics into food has raised concerns about the potentially adverse effects of food products on human health. Much of the initial work in this area was conducted in the 1980s, when microwaveable food packaging specifically adhesives

and newly developed foil susceptors was first being developed for consumer applications. A susceptor is a lightly metalized polyethylene terephthalate (PET) that absorbs electromagnetic waves such as microwave (MW) radiation, converting this energy to heat, which is then transferred from the susceptor to the food product by conduction, creating localized areas of high temperature on the product surface. These new MW-specific packaging materials facilitated the development of foods such as microwaveable popcorn and required testing of packaging materials under conditions that were completely new to the food industry.

To analyze the overall migration (OM) from the food-contact plastic layer, 4 food simulants are most commonly used to simplify testing for regulatory compliance purposes since the simulants are less chemically complex (Grob 2008) than foods. The simulants recommended for migration testing are: water (simulant A) to represent aqueous foods (pH > 4.5); 3% aqueous acetic acid (simulant B) to represent acidic aqueous foods (pH < 4.5); 10% aqueous ethanol (simulant C) to simulate alcoholic food products, and olive oil (simulant D) for fatty foods.

Recent regulations on food simulants provided by EU 10/2011 have replaced and modified the formulation of the old food simulants as follows: Ethanol 10% (v/v) for aqueous food (simulant A); acetic acid 3% (w/v) for acidic food (simulant B); 20% (v/v) ethanol for alcoholic product (simulant C); for fatty food, 50% (v/v) ethanol (simulant D1) and vegetable oil (simulant D2), and lastly, Tenax (PPPO) for dry food (simulant E). However, the U.S. Food and Drug Administration recommends 10% ethanol for aqueous and acidic foods (type I, II, IVB, VIB, and VIIB in Table 1); 10% to 50% ethanol for low- and high-alcoholic foods (type VIA, VIC), and food oil, HB307 or Miglyol 812 for fatty foods (type III, IVA, V, VIIA, IX). HB307 is a mixture of synthetic triglycerides, and Miglyol 812 is the derivative product from coconut oil. HB307 is the product of NATEC, Hamburg, Germany. Miglyol 812 is a fractionated coconut oil that is composed of saturated C_8 (50–65%) and C_{10} (30–45%) triglycerides with boiling point range of 240 to 270 °C. This product is made by Dynamit Nobel Chemicals, HULS America Inc., Piscataway, NJ. Table 1 shows the classification of types of food and food simulants recommended for FCM (Barnes and others 2007).

Testing the migration of chemical compounds from food packaging into food simulants involves 2 steps (Castle 1996, 2007). The first step is to expose the polymer packaging to the food simulant(s) and allow substances from the packaging material to migrate into the simulant(s). The second is to quantify the migrants transferred to a food simulant in terms of OM or specific migration (SM). Determining OM is a regulatory requirement in European Union countries that have established migration limitations for substances from food-contact materials. Migration of chemical substances is highly dependent upon processing and storage conditions, the nature of the packaging material, and the compounds it may contain, as well as the chemical properties of the food.

OM represents the total amount of nonvolatile substances transferred from the food-contact plastic to the food (EU 10/2011). EU Directive 10/2011 limits the OM to 10 mg/dm² on a contact area basis or 60 mg/kg in the simulant or food (for plastics). The OM of all chemicals that could possibly migrate during heat exposure or other type of physical stress is determined by a simple gravimetric method. In this process, the residue is weighed after the evaporation of the volatile simulants such as alcohol (simulant C), or the mass loss of the plastic specimen is measured before and after exposure (for example olive oil and nonvolatile fat simulants) to obtain the amount of OM (Bradley and others 2009).

Table 1—Classification of food types and food simulants for food-contact materials recommended by FDA (reproduced from chemical migration and food-contact materials by Barnes and others 2007).

Type	Description	Classification	Recommended simulant
I	Nonacid, aqueous products; may contain salt, sugar, or both (pH > 5)	Aqueous	10% ethanol
II	Acid, aqueous products; may contain salt, sugar, or both, and including oil-in-water emulsions of low- or high-fat content	Acidic	10% ethanol
III	Aqueous, acid or nonacid products containing free oil or fat; may contain salt, and including water-in-oil emulsions of low- or high-fat content	Fatty	Food oil, HB307, Miglyol 812
IV	Dairy products and modifications A. Water-in-oil emulsions, high or low fat B. Oil-in-water emulsions, high or low fat	Fatty Aqueous	Food oil, HB307, Miglyol 812 10% ethanol
V	Low-moisture fats and oils	Fatty	Food oil, HB307, Miglyol 812
VI	Beverages A. Containing up to 8% alcohol B. Nonalcoholic C. Containing more than 8% alcohol	Low alcohol Aqueous High alcohol	10% ethanol 10% ethanol 50% ethanol
VII	Bakery products (other than those under types VIII or IX) A. Moist bakery products with surface containing free fat or oil B. Moist bakery products with surface containing no free fat or oil	Fatty Aqueous	Food oil, HB307, Miglyol 812 10% ethanol
VIII	Dry solids with the surface containing no free fat or oil	Dry	Tenax
IX	Dry solids with the surface containing free fat or oil	Fatty	Food oil, HB307, Miglyol 812

Table 2—Standardized testing conditions for overall migration (EU 10/2011).

Intended food-contact condition	Simulated contact time and temperature
Food at frozen and refrigerated conditions	10 d at 20 °C
Long-term storage at or below room temperature, including 15 min of heating up to 100 °C or 70 °C for up to 2 h	10 d at 40 °C
Any food heated up to 70 °C for up to 2 h, or up to 100 °C for up to 15 min, not followed by long-term room or refrigerated temperature storage	2 h at 70 °C
High-temperature application up to 100 °C for all food stimulants	1 h at 100 °C
High-temperature applications up to 121 °C	2 h at 100 °C or at reflux or alternatively 1 h at 121 °C
Any food-contact conditions with food simulants A, B or C, at temperature exceeding 40 °C.	4 h at 100 °C or at reflux
High-temperature applications with fatty foods exceeding the conditions heating up to 121 °C	2 h at 175 °C

Several standard testing conditions for OM are recommended by EU Directive 10/2011 (Table 2). The specific migration (SM) is the amount of a specific compound that has migrated from the food-contact plastic into the food or simulant(s). A specific migration limit (SML) is set for each potential migrant using the simulants described above for compliance testing (García and others 2006). Another concept is SML(T), which indicates the total moiety or substance(s) in terms of the SML in food or food simulants.

Although several testing conditions have been suggested, a further complication is the nature of simulant-packaging interactions. Absorbent packaging material poses a particular problem for accurate OM or SM testing. For example, oil simulants are absorbed by a susceptor paperboard (Mountfort and others 1996), making gravimetric analysis with simulant D impractical. In this case, isooctane can be used as a substitute of simulant D. However this substitution makes comparison of data difficult.

This article provides a comprehensive review of the scientific literature on the most common polymers used in food-packaging materials, including the chemical compounds incorporated in packaging polymers, the influence of thermal processing on the level of additive migration into different foods and food simulants from food-contact materials, the migration occur during long-term storage of thermally processed food, and finally, the analytical methods used to identify and quantify additive and monomer migrants.

Polymers Used in Food Packaging

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 (Coles and others 2003). Multilayer polymeric packaging is made by combining 2 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. Small hydrocarbon monomers such as ethylene (C₂H₄) are the basic materials for forming plastic polymers using different manufacturing processes including: addition polymerization, condensation polymerization, or synthesis of copolymers. Their basic classification includes elastomers, thermoplastics, and thermosets (Piringer and Baner 2000).

There are hundreds of plastics, but only very few are utilized in food packaging. The most common are polyolefin, copolymers of ethylene, substituted olefins, polyesters, polycarbonate, and polyamide (nylon). PET/polypropylene (PP) laminates with different barrier materials such as polyvinylidene chloride (PVDC), ethylene-vinyl alcohol (EVOH), or polyethylene (PE) to provide improved structures (Table 3). Susceptor materials are also used in food packaging for MW applications (Ozen and Floros 2001). Table 4 displays some important properties of the polymers frequently used for food packaging. The following section provides a brief discussion of the properties and applications of the most frequently used polymers, copolymers, and their blends relevant to the food industry.

Polyolefins

Polyolefins are produced from ethylene or propylene. Typical examples are low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and polypropylene (PP). According to the American Chemistry Council (2013), PP and HDPE amount to 19.4% and 17.8% out of resin produced in 2012, respectively. The branched-chain structure of LDPEs prevents close packing of monomeric units within

Table 3—Chemical structures of some selected polymers and chemical substances.

Polymer/chemical substances	Structure	Polymer/chemical substance	Structure
PET		PVDC	
PE		DEHA	
PS		BPA	
PP		Caprolactam	
Nylon 6		Chimassorb 81	
EVOH		Irganox 1076	
PC		BHT	
PVC		ESBO	

Table 4—Properties of some polymers frequently used for food packaging.

Polymer	Properties							
	T_g (°C)	T_m (°C)	k (W/m·K)	Density (kg/m ³)	OTR at 25 °C and 0% RH (cc/m ² d)	WVTR at 38 °C and 90% RH (g/m ² d)	Tensile strength (MPa)	Young's modulus (MPa)
LDPE	-125	110	0.32 to 0.40	910 to 940	7750	16 to 31	8 to 12	200 to 400
HDPE	-110	126 to 135	0.38 to 0.51	941 to 965	1550 to 3100	6	10 to 60	600 to 1400
EVOH	72	191	0.35	1200	0.08 to 0.19	22 to 124	71.6	3138
PA	47 to 57	265	0.23	1140	15 to 30	155	36 to 79	2300 to 2500
PET	67 to 80	267	0.15 to 0.24	1400	50 to 90	16 to 23	55	1700
PVC	87	212	0.19	1220 to 1360	465 to 9300	31 to 465	55.5 to 55.6	276 to 7584
PVDC (Saran)	-35	198	0.13	1600 to 1700	2 to 16	0.8 to 5	73	483
PC	150	220	0.192	1200	2480	139.5	62.1	2380
PS	100	240	0.033	1050	3100 to 4500	109 to 155	26 to 48	3200 to 4200
PP	-18	176	0.22	900	1550 to 2480	6	30 to 38	1100 to 150

The data are based on 25- μ m film thickness.

Source: Robertson (2006), Zhang and others (2001), Mark (1999).

the polymer chain, resulting in a relatively low molecular weight (density often ranges from 910 to 940 kg/m³) and low degree of crystallinity (55% to 70%) (long-chain entanglement prevents crystallization upon cooling). LLDPE is another form of LDPE in which the polymer structure has no long-chain branches; the molecules are linearly oriented, resulting in a stiffer and more crystalline structure. PP has a saturated linear polymeric structure with a lower density (900 kg/m³) and higher softening points (140 to 150 °C) than the other PEs. HDPE has a relatively high density (941 to 965 kg/m³) and higher degree of crystallinity (up to 90%) due to its nonpolar, linear, and relatively simple structure.

The higher softening point of PP and HDPE allows it to withstand high temperatures, such as exposure during steam-sterilization. Unlike LDPE, HDPE has high water vapor and gas barrier properties due to its high crystallinity. Oriented polypropylene (OPP), a type of PP, is in demand for food packaging because its bidirectional orientation facilitates diverse applications such as snack food packaging, candy-bar overwraps, beverage bottles, and soup wrappers (Robertson 2006).

Polytetrafluoroethylene

The reaction between hydrofluoric acid and chloroform, subsequent pyrolysis, and polymerization yields polytetrafluoroethylene (PTFE). The film made from PTFE can be used in high-temperature food processing applications such as retort-sterilization since it is stable over a wide range of temperature and has a melting temperature of 327 °C. The commercial name of this high-performance fluoropolymer is Teflon, which is best known for its nonstick properties, used in cookware.

Vinyl plastics

Polyvinyl chloride (PVC) is the second most widely used synthetic polymer in food packaging (Robertson 2006). PVC is produced through the polymerization of the vinyl chloride monomer. Different properties of PVC can be achieved by altering the plasticizer content and orientation of the polymer. Plasticizer is added to the material to make the base plastic soft and flexible during formation of the plastic packaging. However, it often imparts rigidity, stretchability, and tackiness to the final material

(Robertson 2006; Crompton 2007). Stabilizers are a necessary additive to unplasticized PVC films in order to limit degradation at high temperatures. Common stabilizers include lead, cadmium, barium, calcium or zinc with epoxides, and salts of tin. Obviously, many of these are toxic and cannot be incorporated into food packaging. The major advantage of PVC over polyolefins is its lower gas permeability for packaging of wine, beer, and fatty foods. However, PVC film has higher water vapor permeability than polyolefin, which limits its application in dehydrated food products.

PVDC

Homo polymers and copolymers of vinylidene chloride (VDC) are good barriers to moisture, gases, aromas, and solvents (Piringer and Baner 2000). The high-barrier properties of PVDC polymer can be attributed to its dense and close packing polymer structure without branching, as well as its stable crystalline form. However, PVDC homopolymer's melting temperature lies slightly below its decomposition temperature, making it unsuitable for food-packaging applications (Robertson 2006). Saran is soft but tough, and can be produced through copolymerization of PVDC and 5% to 50% of vinyl chloride.

The oxygen permeability of high-barrier PVDC is about 0.08 cc.mil/100 in²/d/atm at 23 °C (Brown 1986). The gas barrier properties of PVDC are not affected by moisture, and PVDC itself has a relatively low water vapor transmission rate (WVTR). In packaging, PVDC films are used as the barrier layer in laminates, since it can withstand hot filling and the high temperatures of the retort process.

Polystyrene

Polystyrene (PS) is substituted olefin, made through the addition polymerization of styrene. Styrene is produced through the catalytic dehydrogenation of ethylbenzene. PS films are hard and transparent, and tend to be very brittle. High-impact polystyrene (HIPS) is an improved type of PS, formed by incorporating synthetic rubbers (typically 1,3-butadiene isomer CH₂=CH-CHCH₂) during polymerization to reduce the brittleness of PS. The rubbers block the formation of microcracks in plastics during impact loading. Another important type of PS, general purpose polystyrene (GPPS), is an unmodified homopolymer of styrene. It is glassy and noncrystalline at storage temperature, since the *T_g* ranges from 90 to 100 °C (Robertson 2006). PS has a high permeability to gases and vapors, making it suitable for food products with short shelf-lives. Another form of PS is the expanded type, which has a lower thermal conductivity value (*k* = 0.033 W/m·K); its main application is transportation of frozen food. Low-fat content foods such as coffee, ice cream, yogurt, creamers, honeys, and syrup are commonly packaged in PS. PS is also used to make trays, and divider for egg and fruit packaging (Piringer and Baner 2000; Crompton 2007).

Copolymers of ethylene

Ethylene copolymers are derived from ethylene and another compound with a polar functional group such as vinyl alcohol (VOH), vinyl acetate (VA), or ethyl acetate (EA), or with another alkene such as propene, butene, or octane. EVOH, ethylene vinyl acetate (EVA), ethylene acrylic acid (EAA), and ionomers are the most frequently used as food-packaging polymers. However, EVOH has the most promising gas-barrier properties. EVOH is a semicrystalline copolymer of ethylene and VOH monomer units (Iwanami and Hirai 1983). It is extremely high barrier to

gases, odors, and aromas. EVOH has shown better barrier properties than other polymeric films, including PVDC at 0% relative humidity (RH) (Mokwena and Tang 2012). Data from EVAL Americas (Houston, Tex., U.S.A.) shows that the oxygen permeability of EVOH (EVAL[®] resin with 27 mol% ethylene) is about 0.006 cc.mil/100 in²/d/atm at 23 °C and 0% RH. The ethylene concentration in an EVOH polymer plays a major role in determining barrier properties. For example, an EVOH of 42% ethylene offers a barrier to oxygen 10 times less than one with 27 mol% ethylene (EVAL Americas). However, EVOH polymers are hydrophilic and absorb moisture due to the presence of hydroxyl groups. Gas barrier properties change as the amount of moisture content increases. Thus, the barrier performance of EVOH as food packaging depends on the processing and storage conditions of the packaging (Mokwena and Tang 2012). EVOH is used as the main functional barrier layer in rigid and semirigid containers, including bottles, trays, bowls, flexible films, and paperboard beverage cartons (Robertson 2006). EVA is the random copolymer of ethylene and vinyl acetate. The properties of EVA are dependent upon the VA content and molecular weight of the polymer (Robertson 2006). As the molecular weight increases, the viscosity, toughness, and heat seal strength of the polymer also increase.

EVA has poor barrier properties to gases and moisture. The main advantage of EVA over other polymeric films including PVC is the absence of leachable plasticizer, making it useful for some food-packaging applications, since few migrants can enter the food. The chemical structure of EVAs makes it highly flexible, delivering high-cohesive strength and compatibility with many substrates, and ensuring excellent adhesion to a wide range of materials, forming seals with high resistance to rupture.

Ionomers are ethylene-based polymers with ionized carboxyl group, in which ethylene is polymerized with 1% to 10% of unsaturated organic acid through a high-pressure process, and treated with magnesium, sodium, or calcium salt such as magnesium acetate. Surlyn A is a commercially produced ionomer containing carboxylate groups that provide high-heat stability. Surlyn A has excellent oil and grease resistance, high-abrasion resistance, and higher moisture vapor permeability than LDPE due to lower crystallinity. Ionomers are suitable for composite films. These polymers will also heat-seal, even if food particles are trapped between layers during the filling process (Robertson 2006).

Polyesters

Polyesters are made by condensation-polymerization of carbonyl groups forming carbon-oxygen-carbon links. Probably the most important polyester use in food packaging is polyethylene terephthalate (PET) produced by reacting ethylene glycol with terephthalic acid (TPA). Commonly, a dimethyl ester of TPA is usually used to ensure a more controllable reaction. Linear-saturated PET is hard, semicrystalline, and transparent. It is stable over a wide temperature range (-60 to 220 °C), with a high crystalline melting temperature (*T_m*) of 267 °C and *T_g* ranging from 67 to 80 °C. PET has excellent tensile strength, chemical resistance, and is light weight. In its glassy state, PET is stiff, ductile, and tough, making it a polymer of choice for rigid packaging. Its elastic properties can be further modified through molding and extrusion.

PET is highly impermeable to aromas and gases, but has little resistance to water vapor (Piringer and Baner 2000). PET films can reduce the WVTR and oxygen permeability by the order of 40 and 300, respectively, compared to some other low-barrier polymers (Massey 2004). PET is used to make bottles, films, and

ovenable trays for frozen foods. PET can also be used as a component of foil trays, since it can withstand high electromagnetic fields during microwave (MW) heating. Two-layer polymeric trays comprised of crystalline polyethylene terephthalate (CPET) to provide rigidity and amorphous polyethylene terephthalate (APET) for low-temperature impact strength (Selke 1997) are popular for refrigerated food storage.

Polycarbonates (PC)

Polycarbonates (PC) are linear polyesters of unstable carbonic acid that are produced by reacting phosgene (carbonyl chloride [COCl_2]) with bisphenol A. These polymers are amorphous, with a T_g of 150 °C and T_m values ranging from 220 to 250 °C. PCs are used as components in containers exposed to hot filling or hot processing after filling (Brown 1992). The polymer is also used in the manufacture of many consumer items, including reusable beverage containers, ovenable trays for frozen food and prepared meals, since the low-temperature impact strength enhances the durability of the packaging and its toughness. Other applications of PCs include boil-in-bag packs, retort pouches, and MW-oven cookware due to their stability at high temperatures (Robertson 2006; Crompton 2007). A recent controversy over the safety of BPA (2,2-bis(4-hydroxyphenyl)propane) has led to market removal of PC infant feeding bottles, and the reduction and removal of BPA from food containers and from surface treatments for metallic, plastic, and glass containers that are thermally processed.

Polyamide (PA)

Polyamides are formed by condensation of amine monomers and carboxylic acid. As a result, polymers with amide linkages with high-mechanical strength and barrier properties have been developed. Several polyamides are used in food-packaging applications, including nylon 6, 10, and 11, as well as nylon 6, 6, and nylon 6, 10. In the United States, packaging films are usually produced from nylon 6, while European films are usually produced from nylon 11 due to the lower raw material costs in these markets until recently (Robertson 2006). Nylon 6 has better high temperature, grease and oil properties than nylon 11. Nylons have a T_g below room temperature, but very high T_m values (nylon 6 = 215 °C; nylon 6, 6 = 264 °C; nylon 6, 10 = 215 °C; nylon 11 = 185 °C). Due to the presence of the polar amine group in the polymeric structure, PAs are highly permeable to water vapor, and also absorb water. Absorbed water provides plasticizing effects to the material, increasing impact strength but reducing tensile properties. Their oxygen and other gas barrier properties are excellent compared to other films, but only when the films are dry.

Biaxially oriented PAs (BOPA) have received a great deal of attention for laminate films due to higher flex-crack resistance, mechanical strength and barrier properties than that of other PAs (Piringer and Baner 2000; Robertson 2006). Combining BOPA with PE improves water vapor barrier properties. Applications of PAs in food packaging include vacuum packaging of cheese, bacon (Robertson 2006; Crompton 2007), fresh and processed meats, and frozen foods (Robertson 2006).

Migrating Components in Plastic Packages

Additives enhance the performance of polymers during processing and fabrication. Plasticizers, antioxidants, light stabilizers, lubricants, antistatic agents, slip compounds, and thermal stabilizers are the most commonly used additives in different types of polymeric packaging materials. Plastic additives also reduce the scission and cross-linking of macromolecular chains caused by

thermo-oxidative deterioration (Dilettato and others 1991). Unreacted monomers and oligomers may also migrate from plastics to foods. Table 5 shows some chemical substances that may migrate from plastics to foods. The restriction has also been applied to the SML for some metals and primary aromatic amines migrating from plastic packages into food (EU 10/2011).

Plasticizers

Plasticizers are the group of compounds used to improve flexibility, workability, and stretchability (Page and Lacroix 1995; Cano and others 2002) of polymeric films as a process aid, reducing melt flow. Plasticizers also give a material the limp and tacky qualities usually found in “cling” films (Robertson 2006; Sablani and Rahman 2007). Plasticizers reduce shear during mixing steps in polymer production and improve impact resistance in the final plastic film. Selection of plasticizers depends upon important parameters, such as compatibility with other components in the plastic matrix, low volatility, and lack of coloration (Crompton 2007). 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 for PE include dipentyl phthalate (DPP), di-(2-ethylhexyl) adipate (DEHA), di-octyladipate (DOA), di-ethyl phthalates (DEP), diisobutylphthalate, and di-*n*-butyl phthalate (DBP). Acetyltributyl citrate (ATBC) is a plasticizer for PVDC-based cling-films. Other common plasticizers include di-*n*-butyl phthalate (DBP), dicyclohexyl phthalate (DCHP), di(2-ethyl)hexyl phthalate (DEHP), butyl benzyl phthalate (BBP), diheptyl adipate (DHA), heptyl adipate (HAD), and heptyl octyl adipate (HOA) (Sablani and Rahman 2007). DEHA (di-(ethylhexyl) adipate), a plasticizer in PVC, can migrate from packaging into fatty foods, and exposure is restricted to keep the total daily intake (TDI) below 0.3 mg/kg body weight (Petersen and others 1997; Hammarling and others 1998).

Antioxidants

Antioxidants are added to a variety of polymer resins to slow the onset of oxidative degradation of plastics from exposure to UV light (Arvanitoyannis and Bosnea 2004; Sablani and Rahman 2007). Polymer degrades due to the action of highly reactive free radicals generated by heat, radiation, and mechanical shear that is often enhanced by the presence of metallic impurities. In food packaging, oxidation increases at high temperatures, including contact with hot foods or exposure to infrared heating, retort processing, and, potentially, MW heating.

Arylamines are common antioxidants used in plastic food packaging. Butylated hydroxytoluene (BHT), 2- and 3-*t*-butyl-4-hydroxyanisole (BHA), tetrakis(methylene-(3,5-di-*t*-butyl-4-hydroxyhydrocinamate) methane (Irganox 1010), and bisphenols such as Cyanox 2246 and 425, and bisphenol A are the most common phenolics used as antioxidants (Kattas and others 2000). Another class of antioxidants, the organophosphites, reduces hydroperoxides formed during oxidation to alcohols. Tris-nonylphenyl phosphite (TNPP) is the most commonly used organophosphite, followed by tris (2, 4-di-*tert*-butylphenyl) phosphite, also known as Irgafos 168.

Heat stabilizers

Heat stabilizers are added to plastics to prevent thermal degradation of resins from exposure to elevated temperatures during thermal processing of foods. PVC, PVDC, vinyl chloride copolymers (for example, vinyl chloride/vinyl acetate), and PVC

Table 5--Chemical and physical properties of selected chemical compounds.

Migrant	CAS no.	SML (mg/kg)	Formula	Molecular weight	Density (g/cm ³)	Bp/Fp (°C)	Mp (°C)	Solubility	Water solubility (mg/L)	Application
Styrene (ethenylbenzene)	100 to 42 to 5	NA	C ₈ H ₈	104	0.90	145 to 146/32	-31	Slightly soluble in water, soluble in ether, alcohol, acetone, and carbon di-sulfide	310	Monomer for HIPS and GPPS
Lauro lactam (aza-2 cyclotridecanone)	947 to 04 to 6	5	C ₁₂ H ₂₃ NO	197	NA	-	149 to 153	Water	290	Monomer
Limonene (1 methyl-4-(1 methyl-ethenyl) cyclohexene)	138 to 86 to 3	NA	C ₁₀ H ₁₆	136	0.84	178/46	-95	Insoluble in water; soluble in carbon tetrachloride; miscible in ethanol and diethyl ether	7.6	
1-Octene	111 to 66 to 0	15	C ₈ H ₁₆	112	0.71	121	-101	Insoluble in water; slightly soluble in carbon tetrachloride; soluble in diethyl ether, acetone, benzene; very soluble in organic solvents; miscible in ethanol	4.1	Monomer
Bisphenol A (2,2'-bis(4-hydroxyphenyl) propane)	80 to 05 to 7	0.6	C ₁₅ H ₁₆ O ₂	228	NA	250	153	slightly soluble in water; soluble in acetic acid; very soluble in ethanol, diethyl ether; benzene, alkali	120	Monomer
BHT (2,6-di-tertbutyl-p-cresol)	128 to 37 to 0	NA	C ₁₅ H ₂₄ O	220	0.89	265	71	Insoluble in water, alkali; soluble in ethanol, acetone, benzene, petroleum ether	0.6	Antioxidant
Di-isopropyl naphthalene bis (1-methylhexyl) naphthalene (DIPN)	38640 to 62 to 9	NA	C ₁₆ H ₂₂	212	NA	NA	NA	insoluble in water	0.11	-
Triacetin (glycerol triacetate (GTA))	102 to 76 to 1	NA	C ₉ H ₁₄ O ₆	218	1.16	259/138	-78	soluble in water, ligroin; very soluble in acetone; miscible in ethanol, diethyl ether, benzene, chloroform;	58000	Antifungal agent
ATBC	77 to 90 to 7	NA	C ₂₀ H ₃₄ O ₈	402	1.05	170	>330	Soluble in ethanol, acetone, DMSO and Toluene	20	Plasticizer
Iganox 1076	2082 to 79 to 3	6	C ₃₅ H ₆₂ O ₃	531	NA	273	50 to 55	g/100g solution: Benzene: 57 Acetone: 19 Methanol: 0.6C: 57 Toluene: 50 Ethanol: 1.5 Cyclohexane: 40 Ethyl acetate: 38 n-Hexane: 32	<0.03	Antioxidant and thermal stabilizer blend
DPBD	538 to 81 to 8	NA	C ₁₆ H ₁₄	206	-	350	153	Very soluble in Benzene, ethanol, and ether	0.5 to 1.2	Fluorescent additive
Chimassorb 81	1843 to 05 to 6	6	C ₂₁ H ₂₆ O ₃	326	-	>400/>200	48 to 49	g/100mL solution: Acetone: 43 Benzene: 72 Chloroform: 61 Ethanol: 3.5 Ethyl acetate: 44 n-Hexane: 1.2 Methanol: 1.7 MEK: 6.5 Methylene chloride 6.7 Toluene: >50	< 0.03	UV absorber /stabilizer
ε-Caprolactam	105 to 60 to 2	NA	C ₆ H ₁₁ NO	113	1.022	267/125	70 to 72	Soluble in ethanol, benzene, cyclohexane, chloroform, and dimethylsulfoxide	4560000	Monomer in PA

blends (for example, PVC) require the addition of heat stabilizers to retain functionality. LDPE and polyamides usually do not require the incorporation of heat stabilizers, since these polymers remain stable under severe heat conditions (Crompton 2007).

There are 3 major types of primary heat stabilizers: mixed metal salt blends, organotin compounds, and lead compounds, and 3 secondary heat stabilizers: alkyl organophosphites, epoxy compounds, and beta diketones (Kattas and others 2000). Generally, epoxy stabilizers are derived from epoxidized soybean oil (ESBO), linseed oil, and sunflower oil and are used in a various food-packaging plastics as heat stabilizers, and also as lubricants and plasticizers (Kattas and others 2000; Arvanitoyannis and Bosnea 2004; Boussoum and others 2006). Other heat stabilizers, although more effective, are not suitable for use in food-contact plastics due to their potential toxicity.

Slip agents

Slip compounds significantly reduce the coefficient of friction of the surface of a polymer. Besides providing lubrication to the film surface, slip agents also impart lower surface resistivity (antistatic properties), reduced melt viscosity, better mold release, and antisticking properties (Sablani and Rahman 2007). Common slip compounds are fatty acid amides (primary erucamide and oleamide), fatty acid esters, metallic stearates (for example, zinc stearate), and waxes.

Unreacted monomers and oligomers

The macromolecular structure of plastic is formed through the chemical reaction of monomers. Monomers and oligomers both tend to migrate from packaging materials into foods (Lau and Wong 2000). Serious health risks may arise when the amount of unreacted monomers or low-molecular-weight substances in food reaches to a specified limit and thus absorbed by the human body (EU 10/2011). The use of high volume of PS food packaging (Arvanitoyannis and Bosnea 2004) may pose health concern as residual styrene can migrate from PS. Epoxy resins of BPA, also known as bisphenol A diglyceride ether (BADGE), have cytotoxic effects in living tissues, and have been shown to increase the rate of cell division (Lau and Wong 2000). However, recent FDA (food-contact application) studies in collaboration with the National Center for Toxicological Research (NCTR) state that the use of BPA in containers and other food-packaging materials is safe (BPA: use in FDA 2012, updated April 2013).

The fractional concentration of unreacted epoxy groups decides the degree of toxicity of the compounds. According to Commission Regulation (EU) No 10/2011, the vinyl chloride monomers in PVC plastic can pose acute toxicity in the human body. Therefore, the materials and articles contacting food must not contain vinyl chloride monomers exceeding 1 mg/kg. The isocyanates used in polyurethane polymers and adhesives carry a low risk of oral toxicity, but a high risk of toxicity from dermal or inhalation exposure.

BADGE is a monomer and the main component of epoxy resins for internal can linings. Unreacted BPA in the plastic lining of the cans or containers can migrate into foods during heating and storage. BADGE is added to the polymers to serve as an antioxidant, but may contain unreacted BPA. It is not harmful to humans, as long as the amount of substances is below the specified limit.

PET contains small amounts of low-molecular-weight oligomers and the oligomer may vary from dimers to pentamers.

Cyclic compounds were found in the range of 0.06% to 1% depending on the type of PET (Lau and Wong 2000).

Chemical Compound Migration into Food and Food-Simulating Liquid (FSL)

Migration of chemical compounds from packaging polymers into foods should be evaluated to ensure that the amount of migrating components meet compliance standards set by regulatory agencies. This migration is influenced by several parameters, such as temperature of contact, duration of contact, surface area of contact, types of components in packaging material, and more importantly, type of foodstuff (fatty, acidic, or aqueous) (Barnes and others 2007; Veraart and Coulier 2007; Khaksar and Ghazi-Khansari 2009). As temperature increases, the diffusion of monomers, oligomers, and other compounds increases, and it can result in higher diffusion or rates of migration from packaging materials. The diffusion coefficient of packaging material components increases 6- to 7-fold when packages are exposed to extreme temperature fluctuations (for example, from freezer temperatures to cooking temperature). This effect may be exacerbated when polymer temperature exceeds T_g (Begley and others 1995).

Migration of specific components

Plasticizers. Plasticizers have a low molecular weight and can migrate from packaging materials into wrapped food, thus becoming indirect food additives (Goulas and others 1998). Plasticizers such as phthalate and adipate are commonly used in PVC, PVA, and PE, and their migration to food/food simulants under different study conditions have been reported (Castle and others 1990; Lau and Wong 1996; Goulas and others 2000; Fankhauser-Noti and Grob 2006; Goulas and others 2007; Biedermann and others 2008; Wei and others 2009; Guo and others 2010; Fasano and others 2012).

Migration studies are commonly conducted with food simulants, providing uniform contact of the packaging with the food. One study investigated phthalate migration from baby bottles ($n = 277$) under hot-fill conditions of 2 h at 70 °C (Simoneau and others 2011), and found that migration levels for diisobutyl phthalate (DiBP) and dibutyl phthalate (DBP) varied from 50 to 150 $\mu\text{g}/\text{kg}$, while DEHP displayed comparatively lower migration levels (25 to 50 $\mu\text{g}/\text{kg}$). Migration of 7 plasticizers (ESBO, DEHP, DINP, DIDP, DEHA, DEHS, and ATBC) from PVC gaskets in the closures of glass jars has been reported for contact with oily foods (Fankhauser-Noti and Grob 2006; Ežerskis and others 2007). The average transfer rate was calculated by comparing the amount of plasticizers in direct food contact with gasket material and plasticizers found in food. The average transfer was 46%, with the highest transfer of 90% observed for ESBO. Phthalates showed a high-transfer rate of 350% when used in gasket material for closures in a study with olive oil (Fankhauser-Noti and Grob 2006). This indicates transfer not just from the gasket, but from underneath the seal or rim. Fasano and others (2012) determined the migration of phthalates (PAEs), alkylphenols, BPA, and DEHA from a wide range food-packaging materials to food simulants (3% acetic acid, distilled water, and 15% ethanol) after 10 d of storage at 40 °C. Higher amounts of plasticizers released from PE bread-bag compared to PE film. Low level of PAEs and DEHA migrated from tetra pack packaging materials. The PS packaging for yogurt showed very little DMP migration, but higher amounts of DEHA. Several SMLs are recommended for different plasticizers, such as 1.5 mg/kg for DEHP, 18 mg/kg for DEHA, 0.3 mg/kg for DBP, 30 mg/kg for BBP (EU 10/2011). Divinyl

esters of adipic acid should not exceed 5 mg/kg of final product, and can only be used as comonomer.

In another study, Xu and others (2010) evaluated the migration of 8 PAE compounds (DMP, DEP, BBP, DBP, DEHP, DINP, DOP, and DIDP) from plastics to cooking oil and mineral water under different storage conditions (Table 7). Storage times were up to 2 mo under static conditions (20, 40, and 60 °C) and under a “dynamic” state (20 °C). For the dynamic state, the packaged food simulant was treated at a frequency of 50 times/min for 5 min daily for 2 mo. The PAE content was always higher in cooking oil than in mineral water. DBP and DINP showed the highest migration into the mineral water. DEHP and DBP displayed the highest level of migration into cooking oil at 20 °C after 2 mo. The dynamic process facilitates the migration of the compounds more than in the static state. PAE migration into cooking oil (fatty food 1% to 14%) was found to be higher than into mineral water (aqueous food < 0.35%).

Lau and Wong (1996) evaluated the effect of fat content and contact time after MW heating on the migration of 3 plasticizers: DHA, HOA, and HDA from “cling” film (0.02 mm thick PVC film plasticized with DHA, 2240 $\mu\text{g}/\text{dm}^2$; HOA, 2680 $\mu\text{g}/\text{dm}^2$; and HDA 2550 $\mu\text{g}/\text{dm}^2$) into cheese and ham. Cheese with different fat contents (8.2%, 12.5%, 21.3%, and 32.8%) and ham slices were analyzed in this study. 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 (Hirayama and others 1991; Lau and Wong 1996, 2000; Tsumura and others 2002; Freire and others 2006; Goulas and others 2007).

Badeka and Kontominas (1996) studied the effect of MW heating on the migration of dioctyladipate (DOA), acetyltributylcitrate (ATBC) from food-grade PVC, and PVDC/PVC (Saran) films into olive oil and distilled water (See Table 6 for conditions). Migration of DOA into olive oil reached equilibrium (604.6 mg DOA/L) after heating for 10 min at full power (about 700 W). Plasticizers (DOA and ATBC) migrated during MW heating was always higher for olive oil compared to water under similar treatment conditions. Migration was also observed at room temperature (22 °C) after 20 min of contact without MW treatment (145.7 mg DOA/L or 15.3 mg/dm²) for olive oil, which is above acceptable levels for global migration (60 mg/L) set by the EU (Castle and others 1990). 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 (Badeka and Kontominas 1996). PVC is not suitable for food–contact applications in a MW oven due to high migration of DOA, but Saran may be used if direct contact with high-fat foodstuffs is avoided.

Antioxidants. Quantification and the SML of antioxidants are also of interest because these compounds and their degradation products migrate from plastics into food during processing and storage (Gao and others 2011). Several studies have quantified the migration of antioxidants and their degraded product from different polymers under various conditions (Jickells and others 1992; Garde and others 2001; Dopico-García and others 2003; Alin and Hakkarainen 2010, 2011; Gao and others 2011; Beldi and others 2012; Reinas and others 2012). Antioxidant migration has been widely studied in PP and polyolefins (LDPE) (Goydan and others 1990; Jeon and others 2007; Beldi and others 2012). Garde and others (2001) characterized the migration of antioxidants from PP films of different thicknesses into *n*-heptane and 95% ethanol at 20, 37 and 60 °C, and found that the swelling of polymer in

n-heptane greatly increased migration rates compared to ethanol. Alin and Hakkarainen (2011) observed that prolonged heating (1 h) in MW promotes degradation of antioxidant in food simulants compared to conventional heating using oil bath. The processing temperature was maintained at 80 °C for both MW and conventional heating. However, this 1 h of MW heating in contact with food is impractical for industrial or domestic applications. High temperature caused more swelling of PP in isooctane during MW heating and increased the diffusion coefficient by factors of 100 to 1000 (Alin and Hakkarainen 2010). They also reported that aqueous soluble antioxidants migrate into aqueous food simulants.

Gao and others (2011) measured the migration of 8 antioxidants: BHA, BHT, Cyanox 2246, Irganox 1035, Irganox 1010, Irganox 1330, Irganox 1076, Irgafos 168, and its degradation product DBP at 40 °C in a 10-d storage study (Table 7). BHA, DBP, BHT, Cyanox 2246, Irganox 1035 migrated into aqueous simulants; Irganox 1010, Irganox 1330, and BHT were detected in oil. Beldi and others (2012) studied the effect of fat content and storage temperature on the migration of Irganox 1076 from LDPE to several foods (cheese sauce, chicken, chocolate, margarine, mayonnaise, milk, orange juice, soft cheese, pork, salmon, and wheat flour) and food simulants (distilled water, 3% acetic acid, ethanol 10%, rectified olive oil, isooctane, and 95% ethanol). They found that migration increased as the fat content of the food and storage temperature increased, with the highest level of migration (1413 $\mu\text{g}/\text{dm}^2$) for chocolate (32.1% fat) at 40 °C after 30 d of storage. Linssen and others (1998) found that migration of antioxidants (Irganox 1076 and Irgafos 168) increased with increasing concentration (40% to 100%) of ethanol in food simulants, with the highest percentage of migration in 100% ethanolic simulants. Reinas and others (2012) compared migration kinetics of antioxidants (Irganox 1076 and Irgafos 168) into precooked white rice and Tenax[®] at 23, 40, and 70 °C, and found that migration into rice is slower than into Tenax due to the lower porosity and adsorption capacity of rice (Reinas and others 2012).

Monomers and oligomers. There is growing interest in studying the effect of monomers on human health (Tawfik and Huyghebaert 1998) and the sensory properties of food (Ehret-Henry and others 1994), since residual monomers can migrate from the food–contact layer into food. The residual monomer, styrene, that is always present in PS, raises the greatest concern. Important applications of PS include cups, packaging trays for yogurt and cheese, and so on. Several studies report the migration of styrene into food (Lickly and others 1995; Nerin and others 1998; Tawfik and Huyghebaert 1998; Jin and others 2005; Khaksar and Ghazi-Khansari 2009) 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 (Arvanitoyannis and Bosnea 2004). Lickly and others (1995) studied 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 70 °F (21 °C) for 10 d, 120 (49 °C), and 150 °F (65.5 °C) for 1, 4, and 10 d. Migration increased from 1 to 10 d 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, following Fickian diffusion models where equilibrium partitioning was not a controlling factor.

Styrene migration from GPPS and HIPS to hot drinks (tea, milk, and cocoa in milk) was highly dependent upon temperature of drinks and fat content, with the highest level of migration in

Table 6—Migration of chemical substances at different microwave and oven heating conditions.

Packaging material	Migrants/ Migration studied	Food/Food stimulant (FS)	Heating conditions			Observations/ Comments	Reference
			Method	Temp (°C)	MW power (W)		
PET susceptor	Markers (volatile and nonvolatile)	Food	MW	NA	650	2, 7.5, 4, 2.75 min	Tenax can be considered as one of the food simulants. For pizza susceptor, the migration result at 180 °C is comparable with the value obtained from MW. However, amount of marker migrated in food was substantially lower than that of Tenax. Olive oil is not suitable for susceptor because a considerable amount of oil penetrated into susceptor film. The amount of benzene migrated after oven study was always higher than other volatiles (toluene, Et-benzene, <i>p</i> -xylene, and <i>o</i> -xylene). In case of microwave heating, benzene concentration was <0.01 mg/kg for almost all of the food samples that is due to short cooking time in MW and relatively low-temperatures experience than olive oil study.
		Olive oil	Oven	180, 200	—	10 min	
		Semi-solid simulant	MW	NA	650	2, 7.5, 4, 2.75 min	
		Tenax	MW	NA	650	1.5 min	
Polyester Polyester	Nonvolatile markers	Tenax	Oven	180, 200	—	10 min	
		Olive oil	Oven	175	—	1 h	
		Cakes	MW	NA	600	2 min	
		Omelette	MW	NA	600	4 min	
		Chicken breast	MW	NA	600	3.5 min	
		Mushroom	MW	NA	600	5 min	
		Mashed potatoes	MW	NA	600	1 min	
		Pie	MW	NA	600	7 min	
		Fish	MW	NA	600	5 min	
		PET tray	Oligomers	Pizza, bacon	MW	NA	600
Chicken casserole	Oven			150	—	90 min	
Fish in sauce	Oven			160	—	50 min	
Lasagne	MW/Oven			NA/204	600	3/80 min	
Sausages	Oven			204	—	60 min	
French fries	Oven			204	—	40 min	
Baked beans	Oven			204	—	30 min	
Stewed apple	Oven			204	—	40 min	
Stewed cherries	Oven			204	—	40 min	
Chicken curry	MW			NA	600	3 min	
Peanut brittle	MW			NA	600	15 min	
French fries	MW			NA	600	3 min	
Susceptor cartoon bag	Oligomers	Popcorn	MW	NA	600	5 min	
		Roast beef	Oven	204	—	90 min	
		Roast pork	Oven	204	—	90 min	
		Olive oil	MW/Oven	145/150	—	1080 s/2 h	
CPET	OM	Olive oil	MW/Oven	148/150	—	1200 s/2 h	
		Olive oil	MW/Oven	142/150	—	820 s/2 h	
CPET PET gf	OM	Olive oil	MW/Oven	143/150	—	900 s/2 h	
		Olive oil	MW/Oven	123/120	—	525 s/0.5 h	
PET Susceptor PET/steel PPO/EPS	OM	Olive oil	MW/NA	117/NA	—	780 s NA	
		Olive oil	MW/Oven	198/NA	—	600 s/NA	
		Olive oil	MW/Oven	123/120	—	1120 s/0.5 h	
		Olive oil	MW/Oven	91/90	—	780 s/1 h	

(Continued)

Table 6—Continued

Packaging material	Migrants/ Migration studied	Food/Food stimulant (FS)	Heating conditions		Time	Observations/ Comments	Reference
			Temp (°C)	MW power (W)			
PPO/EP PPO/HIPS	OM	Olive oil	92/90		898 s/1 h		
HIPS	OM	Olive oil	123/110		738 s/2 h		
PP/EVOH/PP	OM	Olive oil	92/90		738 s/1 h		
PP/PVDC/PP	OM	Olive oil	130/150		1080 s/2 h		
PA 66	OM	Olive oil	122, 125/150		1080 s/2 h		
PVDC	OM	Olive oil	130/130		1080 s/2 h		
GPPS, HIPS cups	OM	Olive oil	132/150		680 s/2 h		
	Styrene monomer	Tea, milk, cocoa milk	136/150		1200 s/2 h		
			20, 60, 100		10, 30, 60 min		Khaksar and Ghazi-Khansari (2009). Begley and others (1995) Jickells and others (1992)
Nylon baking bag	Caprolactam, Nylon 6/66 oligomers	Oil	176		30 min		
CPET	Total oligomers	Olive oil, isooctane	NA	220	—		
PVDC/PVC	ATBC		NA	220	—		
TPX	DLDTP		NA	220	—		
Polyester	Toluene, ethylbenzene		NA	220	—		
PP	Irganox 1076		NA	220	—		
PP-C, PP-R	2,4-DTB, 2,6-DTBQ, OM	FS	80		1 h		Alin and Hakkarainen (2011)
PA, PE/PA	OM	Olive oil	100/121		30/2 min		
PA, PE/PA	OM	Ethanol 95%	60		3.5, 4.5 h		
PA, PE/PA	OM	n-Heptane	50, 60		15 min		
PA, PE/PA	OM	Iso-propanol	60		1.5, 2.5 h		
PP	OM	Olive oil, n-heptane	—	800	1, 3 min		Galotto and Guardia (2004)
PP, PVC	OM	Ethanol, iso-propanol	—	800	1.5 min		
PVC	OM	Olive oil, n-heptane	—	800	1, 7 min		
PVC, PVDC	DOA, ATBC	Distilled water, olive oil	—	700, 400	2, 4, 6, 8, 10, 15, 20		Badeka and Kontominas (1996)
PA/adh/PA/ adh/Suriyn	OM	F5-A, B, C	NA/80, 121		3/30 min		Galotto and Guardia (1999)
PE/adh/PA/ adh/PET-PE	OM	F5-A, B, C	NA/80, 121		3/30 min		
BOPP/PA/adh/ PA/adh/PE	OM	F5-A, B, C	NA/80, 121		3/30 min		
PE/adh/PA/adh/PE	OM	F5-A, B, C	NA/80, 121		3/30 min		
PVC, PP	OM	F5-A, B, C	NA/80, 121		3/30 min		

Table 7—Migration of chemical substances at different storage conditions.

Packaging material	Migrants/ Migration studied	Food/Food stimulant (FS)	Storage conditions		Observations/ Comments	Reference
			Temp (°C)	Contact time		
PS cups	Styrene	Distilled water	100	1, 2 h	Fat content and storage temperature of food have strong influence on styrene migration, showing higher migration in hot beverages. The styrene concentration in the 3.6% fat milk or soup and 1.5% ethanol at 40 °C after 24 h can be comparable. The migration of styrene into hot beverages was more than into the cold ones.	Tawfik and Huyghebaert (1998)
		Distilled water	60, 40, 20, 4	3 d		
		Milk	100, 60, 40, 20	2 h		
		Milk	40, 20, 4	24 h		
		Milk	4	3 d		
		Juice	20	16 h		
		Cola, beer	20	16 h		
PVC	DHA, HOA, HDA	Drinking chocolate	20	16 h	HDA showed higher migration in ham after 45 min, migration was proportional to fat content of material and contact time.	Lau and Wong (1996)
		Drinking yogurt	4	3, 7, 14 d		
		Jelly, pudding	4	1, 3, 7 d		
		Ice-cream	-10	30, 60 d		
		Hot beverage	100	1 h		
		Cheese	Room	5 min		
			Room			
PVC	DHA, HOA, HDA OM, DEHA	Sliced ham	Room	0, 1, 3, 5, 10, 30, 45 min	Iso-octane can be used as alternative FS considering OM, DEHA must be determined for each of FS in order to get proper amount migrated during study.	Petersen and others (1997)
		Olive oil	40	10 d		
PS	OM, DEHA Styrene	Iso-octane	40	2 h	Migration of styrene was always higher than ethylbenzene, longer contact time and higher fat content results in higher migration.	Ehret-henry and others (1994)
		Yoghurt, dessert	Room	8 to 28 d		
PVC	Ethylbenzene DEHA	Yoghurt, dessert	Room	8 to 28 d	Kefalotyri (fat: 30%) has shown highest level of migration followed by Edam (fat: 23%) and Feta (fat: 19%).	Goulas and others (2000)
		Kefalotyri, Edam and Feta cheese	5	1 to 240 h		
PVC	DEHA	Cheese	40	2 h, 1 d	DEHA migration was highest at 21 °C after 5 d, whereas lowest migration was observed at 5 °C after 2 h.	Petersen and others (1995)
			21	2 h, 1, 5 d		
			5	2 h, 1, 5, 10 d		

(Continued)

Table 7–Continued

Packaging material	Migrants/ Migration studied	Food/Food stimulant (FS)	Storage conditions		Observations/ Comments	Reference
			Temp (°C)	Contact time		
Retail packaging material	BHA, DBP, BHT, Cyanox 2246, Chinoxorb 81, Irganox 1035, 1010, 1330, 1076, Irgafos 168, Tinuvin 326, 328	FS-A, B, C, D	40	10 d	Low-molecular weight compound (BHA, DBP, BHT, Cyanox 2246, Tinuvin 326 and Tinuvin 328) were detected in aqueous simulants. Irganox 1010 and 1330 were detected in oil simulants	Gao and others (2011)
Cup, plate-container, meat tray	Styrene	Oil	70	10 d	Cup has shown higher migration level at 150 °C (1.39 µg/cm ²) after 10 d of exposure than other materials	Lickly and others (1995)
PVC gasket	ESBO, DEHP, DINP, DIDP, DEHA, DEHS, ATBC	Oily food (Olive, mussels in oil, tuna in oil, and so on)	120, 150 40	1, 4, 10 d 10 d	Migration of phthalates (average transfer rate exceeded 100%), DEHA, ATBC, and DEHS was substantially higher than ESBO (average transfer rate 46%).	Fankhauser-Noti and Grob (2006)
LDPE	BHA, DBP, BHT, Irganox 1010, 1076, Irgafos 168, Ethanox 330	Distilled water	60 40 ± 1	20 d 10 d	Only Irgafos 168 and Ethanox 330 were detected in food simulants.	Dopcio-Garcia and others (2003)
PA, PE/PA, PP, OM	OM	Olive oil, ethanol 95%	40	10 d	For PA/PE, 95% ethanol can be considered as best alternative fatty food simulant. For PP, isopropanol and n-heptane yield almost same amount of OM.	Galotto and Guardia (2004)
LDPE, PVC	Oleamide	n-Heptane/ Iso-propanol FS-A, B, C, D	20 40	30 min/2 d 10 d	Polyolefin has shown highest amount of migration with higher amount of erucamide. Up to 100% of slip compounds was migrated from 65 µm LDPE film whereas PVC or PS has shown very little migration (< 1% of total).	Cooper and Tice (1995)
LDPE, PP LDPE, PS LDPE	Erucamide Stearamide Stearyl erucamide Oleyl palmitamide DPBD	FS-A, B, C, D FS-A, B, C, D				
LDPE		Chicken, pork	5, 25	10 d	Migration increased with increase in storage time and temperature. However, no significant difference was observed between migration at 5 and 25 °C	Silva and others (2007)
PVC	DEHA, ATBC	Sesame paste	25	0.5 to 240 h	Amount of ATBC at equilibrium was found to be approximately 2.5 times lower than the amount of DEHA that is due to lower initial concentration of ATBC (1.8 mg/dm ²) in film as compared with DEHA (3.2 mg/dm ²).	Goulas and others (2006)
Plastic container	Phthalates	Cooking oil and mineral water	20, 40, 60	60 d	Cooking oil was found to be more suitable medium for phthalate migration than mineral water. Migrations were more significant at higher temperature, longer contact time.	Xu and others (2010)

hot cocoa with milk (Khaksar and Ghazi-Khansari 2009). Others have reported increasing styrene migration with increasing fat content (Ramshaw 1984; Tawfik and Huyghebaert 1998). Paraskevopoulou and others (2011) noticed higher styrene migration in ethanolic solutions compared to isooctane, with no styrene found in aqueous food simulants. Less styrene migration was observed in aqueous foods compared to oily foods, since styrene is hydrophobic (Flanjak and Sharrad 1984).

Bisphenol A has received much attention by toxicologists and food scientists, since this compound migrates from can linings and PC bottles into food, and may act as an endocrine disruptor, which can cause developmental and neurological impacts. Several studies have investigated BPA release from can linings and PC bottles (Biles and others 1997; Goodson and others 2002, 2004; Kubwabo and others 2009; Nam and others 2010).

A study was conducted to examine the influence of storage conditions and can-denting on BPA migration into 4 different foods: minced beef in gravy (20% fat), evaporated milk (8% fat), carrots in brine (0% fat), spring vegetable soup (0.3% fat), and a food simulant (10% ethanol) (Goodson and others 2004). Filled cans were processed at 121 °C for 90 min prior to storage. The cans were stored at 20 and 5 °C to represent ambient storage and chilled conditions for up to 9 mo. Additionally, an accelerated test was carried out to simulate 3 y of storage by storing cans at 40 °C for 10 d to 3 mo. 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). However, no further migration of BPA was observed for these 4 model foods and food simulants after up to 9 mo of storage, indicating that high processing temperatures promote migration. BPA migration into 10% ethanol ($68.3 \pm 9.0 \mu\text{g}/\text{kg}$) was significantly higher than in the other foods (minced beef: $53.8 \pm 7.6 \mu\text{g}/\text{kg}$; milk: $49.8 \pm 10.9 \mu\text{g}/\text{kg}$; carrots: $47.2 \pm 5.1 \mu\text{g}/\text{kg}$; soup: $45.7 \pm 5.0 \mu\text{g}/\text{kg}$) (Goodson and others 2004). This may be attributed to solubilization of ethanol with the can coating during processing. In addition, results showed that can damage had a negligible effect on BPA migration.

Studies showed that BPA migration into water increases after repeated use. In one study on PC baby bottles, extraction at 40 to 100 °C up to 100 times (Nam and others 2010) showed that concentrations of BPA migrating from brand-new PC baby bottles were 0.03 ppb and 0.13 ppb at 40 °C and 95 °C, respectively. A sharp increase in migration was observed at 80 °C. Three regions of BPA migration were defined: lag effect, steady, and aging. Aging of PC bottles was found after being used 60 times (corresponding to the 3 mo of use), resulting in increased BPA migration. The BPA level was 1.1 ppb after 10 times of repeated use and remained constant up to 60 uses, increasing to 3.8 ppb at the 100th uses. Repeated use of bottles affects PC structure, with increased *d*-spacing from 0.499 nm in brand-new bottles to 0.511 nm for the bottles used for 6 mo. Therefore, the release of BPA from the PC bottles increased with repeated use.

Kubwabo and others (2009) studied the migration of BPA into water, and 10% and 50% ethanol using a polycarbonate and other plastic containers (PC baby bottles, non-PC baby bottles, baby bottle liners, and reusable PC drinking bottles). They reported that higher temperatures and longer treatment periods resulted in higher BPA migration from PC bottles. The average concentration of residual BPA in 50% ethanol was higher ($2.39 \mu\text{g}/\text{L}$) compared to water ($1.88 \mu\text{g}/\text{L}$) at 40 °C after 240 h. However, a trace amount of BPA was found due to migration from non-PC baby bottles and baby bottle liners compared with PC bottles.

Munguía-López and Soto-Valdez (2001) determined the migration of BPA and BADGE from 2 types of cans made for tuna fish and jalapeño peppers into distilled water. Tuna cans and jalapeño pepper cans were heated up to 121 °C for 90 min and 100 °C for 9 min, respectively, followed by storage at 25 °C up to 70 d. BPA migration from tuna cans was not influenced by storage time, whereas an increase in BPA migration from jalapeño pepper cans was observed during the storage period. Some part of the BPA residual remains in the coating of the jalapeño pepper cans due to low processing temperatures and shorter processing time compared with tuna cans (Munguía-López and Soto-Valdez 2001). BADGE migration during the storage was found to decrease over time due to its instability and the fact that it hydrolyzes in the aqueous medium. The level of migration for BPA and BADGE were within 0.6 to 83.4 and <0.25 to 4.3 $\mu\text{g}/\text{kg}$, respectively, which is below the level set by EU 10/2011. Effect of heat processing and storage time from can coating to jalapeño peppers and acid food simulant (Munguía-López and others 2002), fatty food and tuna fish (Munguía-López and others 2005) were also investigated.

According to the the amendment of commission implementing regulation (EU) 321/2011, bisphenol A is restricted for the manufacture of polycarbonate infant feeding bottles. The SML of BPA is set as 0.6 mg/kg in foods (EU 10/2011). However, the FDA allows BPA migration at very low level that is recommended as safe (bisphenol A: use in FDA 2012, updated April 2013). In a recent study by FDA and CFSAN, the estimated new daily BPA exposures to infants and adults are 0.2 to 0.4 $\mu\text{g}/\text{kg}$ bodyweight/d and 0.1 to 0.2 $\mu\text{g}/\text{kg}$ bodyweight/d, respectively.

Barkby and Lawson (1993) quantified caprolactam and its oligomer during migration from nylon 6 film into boiling water. Films of different thickness (15 and 80 μm) were analyzed after successive 1-h periods up to 6 h. The migration decreased as the subsequent extraction time increased. Films with a higher thickness showed higher migration. When the extraction time was longer (4 h) for 80 μm film, almost complete removal of residual oligomers was possible. However, this extraction time was also much longer than the normal cooking period.

Begley and others (1995) determined the migration of caprolactam (residual monomer) and oligomers from nylon 6 and nylon 6/66 polymer into oil following a 30 min treatment at 176 °C (usually represents oven cooking condition). The total amount of nylon 6/66 oligomers migrating after oven heating (176 °C or 350 °F for 30 min) was 15.5 $\mu\text{g}/\text{g}$ (ppm). This was equivalent to almost 43% of the total oligomers present in the packaging polymers. Bomfim and others (2011) studied the migration of ϵ -caprolactam from nylon 6 packaging to 95% ethanol. Packages were held at 72 to 100 °C for 1 to 4 h until the center of the food reached 72 °C. A total of 40 samples were analyzed, including 2 for poultry breast, 1 for ham, 3 for pâté, 3 for turkey blanquettes, and 23 for bologna sausages. Results showed that migration of ϵ -caprolactam exceeded the SML(T) value of 15 mg/kg (10/2011/EU) for 35% of the bologna sausage packaging, 33% of the turkey blanquettes packaging, 100% of the pâté packaging, and 100% of the poultry breast packaging.

PET is known to contain small amounts of low-molecular-weight oligomers of cyclic compounds ranging from dimer to pentamer. PET oligomers showed less migration (29% of the available unreacted/unpolymerized oligomer in PET) compared to nylon (43% of total oligomers) (Begley and others 1995). Although heating has an effect, few studies have explored the effect of MW on the migration of oligomers in PET (Castle and others 1989;

Jickells and others 1992; Mountfort and others 1996) that is an important packaging in MW-heating applications.

Mountfort and others (1996) studied the migration of PET cyclic trimers from impregnated susceptors used for pizza, pasty, popcorn, and chips (French fries) after conventional oven and MW heating (see Table 6 for study conditions). Standard methods (ASTM method 1349 and ASTM method F-1308) were followed, with olive oil and a semisolid simulant. In addition, the migration of marker substances was analyzed from susceptors to 4 different food materials: pasty, pizza, popcorn, and chips. Trimers were detected only in pizza, and migration was higher (7.4%) than other marker substances. This indicates that oil may not be a good choice as a food simulant for MW-treated foods, since absorption into packaging material may be too high to provide reliable results.

Castle and others (1989) studied migration of PET oligomers from plastics to various foods and beverages under different MW and oven treatments. As anticipated, temperature and exposure times influenced migration. MW exposure showed lower migration compared to oven heating due to shorter exposure time under MW heating (maximum 15 min) than oven heating (exposure time was 80 min) (Table 6). For example, a 10-fold higher level of PET oligomer migration was observed after conventional cooking of lasagna as opposed to MW cooking. Migration in aqueous beverages was either not detectable or barely above detection limits, whereas slightly higher levels of migration were detected in alcoholic beverages.

According to Commission Regulation (EU) No 10/2011, cyclic oligomers of butylenes terephthalate can only be used in PET, PBT, PC, PS, and rigid PVC plastics with the maximum concentration of 1% (w/w) in contact with aqueous, alcoholic, and acidic foods for long-term storage at room temperature.

Slip additives. Fatty acid amides such as oleamides, stearamide, erucamide, stearyl erucamide, and oleyl palmitamide are the most commonly used slip additives in plastics, where they gradually bloom to the surface to act as a lubricant, thus preventing films from sticking together (Lau and Wong 2000). In one study, migration of 5 fatty acid amides: oleamide, erucamide, stearamide, stearyl amide, and oleyl palmitamide from 4 polymer materials (LDPE, PP, PS, and PVC) were determined (Cooper and Tice 1995) at 40 °C after 10 d of storage. The food simulants A, B, C, and D (according to EU Council Directive 82/711/EC) were used in this study. The highest migration of fatty acid amides occurred from polyolefins (LDPE) to olive oil. Additive migrations from LDPE were as follows: 88%, 98%, and 95% for oleamide, erucamide, and stearamide, respectively. Slip additive migration was highest from 65 μm LDPE film, compared to PVC or PS films (<1% of the total compounds). The difference in migration levels can be attributed to the low solubility of fatty acid amides in LDPE and the high penetration rates into LDPE polymer, which increases diffusion rates (Cooper and Tice 1995).

Light stabilizers. Light stabilizers protect plastics from degradation due to sun and weather exposure. Polyolefins are susceptible to ultraviolet light, oxygen, moisture, and heat, resulting in polymer brittleness, surface crazing, and color change and product failure. Polyolefins usually contain hindered amine light stabilizers (HALS) such as Tinuvin 622, Chimasorb 944 (Lau and Wong 2000). Monteiro and others (1999) investigated migration of Tinuvin P from PET bottles into fatty-food simulants (olive oil, soybean oil, *n*-heptane, and isooctane) at 40 °C for 2 to 10 d. The stability performance of different UV stabilizers (Cyasorb UV 5411, Tinuvin P, Tinuvin 326, and Tinuvin 327) in *n*-heptane and isooctane was also evaluated. Migration was sinusoidal and showed a rapid

increase up to 10 d of storage. The migration of Tinuvin P was much higher in olive and soybean oils compared to *n*-heptane. Iso-octane was found to be more suitable fatty-food simulant than *n*-heptane, because it showed similar migration as olive and soybean oil (Monteiro and others 1999). Begley and others (2004) determined the migration of Tinuvin 234 (T234) from PET into Miglyol, water-ethanol solutions, and isooctane. They reported that the migration of Tinuvin 234 from PET is very slow. The obtained migration data (2 μg/dm²) at 40 °C in 95% ethanol were almost comparable to the amount of migration (3 μg/dm²) in olive oil and soybean oil found by Monteiro and others (1999). They also reported that migration can occur faster in polymer and foods with a similar nature (for example, polar solvents in contact with polar polymer), which is evident from the obtained value of diffusion coefficients. The diffusion coefficient of T234 from PET with isooctane ($D = 3 \times 10^{-16}$ cm²/s) was found to be less than the values obtained with ethanol at 60 °C ($D = 1 \times 10^{-14}$ cm²/s). Ethanol and PET both are considered as polar substances in this case (Begley and others 2004), and isooctane can be a substitute to the fatty food simulant Miglyol.

Overall migration. The concept of the OM 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 SM experiments (Arvanitoyannis and Bosnea 2004). One study examined different polymers under MW and oven heating for OM in olive oil (Rijk and Kruijf 1993). Materials included CPET, PPO/EPS, PPO/HIPS, HIPS, PP/EVOH/PP, PP/PVDC/PP, PA 66, PVDC, PET-coated board, PET/steel, PP/aluminum, and PP. The proper test conditions for migration analysis with olive oil in a MW oven (Table 6; Rijk and Kruijf 1993) were derived from temperature measurements using macaroni with cheese, pizza, and chips. The OM values obtained using MW heating were within the OM limit of 10 mg/dm² or 60 mg/kg, as specified in Commission Regulation (EU) No 10/2011. Results showed that MW heating causes less migration than conventional heating, with the exception of PET-coated boards.

Galotto and Guarda (2004) studied the influence of MW and thermal heating on OM. Thermal and MW heating was carried out on PE/PA (thickness is 200 μm), nylon 6 (thickness is 40 μm), and PVC (thickness is 10 μm), PP films with fatty food simulants (olive oil, 95% ethanol, isopropanol, and *n*-heptane). An increase in intensity of thermal treatment did not significantly influence OM (see Table 6 for heating conditions; Galotto and Guarda 2004). For PA/PE, ethanol 95% may be the best alternative for a fatty food simulant to reproduce the OM observed with olive oil. This can be attributed to the high polarity of ethanol, which is more attractive to the polar migrant. PVC showed higher migration, with higher levels of MW heating increasing the OM up to 45 mg/dm². Very low migration was observed with MW heating indicating that polyolefins are relatively inert. For PVC, isopropanol provided similar migration results to olive oil. Galotto and Guarda (1999) found that the migration level in food simulants was higher after MW heating, only when in contact with PVC.

Chromatographic Methods for Detection of Migrants from Packaging Polymers

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. Several hundred SML's can be found in Commission Regulation (EU) 10/2011 and Directive 2002/72/EC amendments that cover

plastic monomers and compounds. However, no specific analytical methods have been mandated for some restricted substances. It is always necessary to validate and verify the analytical test methods in order to ensure the precision and accuracy of experimental results. Four approaches are used for experimental method validation (Bratinova and others 2009): “full” single laboratory validation protocol, “standard level” of single laboratory validation, “basic level” of single laboratory validation, and “method verification.” The first three approaches are applicable to the food-contact materials and articles. Full validation is usually carried out for a newly developed method by thorough analysis and characterization of the experimental parameters and system performance. The “standard level” shows the minimum requirement to establish the criteria for noncompliance of an analysis of a material in food-contact applications. The basic level, as the name indicates, is the starting point from which the update and improvement of the test procedures must be done to show that the method can be validated under a set of standard conditions. The “method verification” refers to the analysis in accordance with the method parameters those are already specified in the validation method (Bratinova and others 2009).

Mathematical models have been developed and are used frequently to predict the migration of the low-molecular-weight components from plastic packaging (Silva and others 2006) and may be suitable for materials with migration data. However, these models do not adjust to different polymeric properties and behavior, especially in terms of migration from new polymeric materials without well-characterized properties (Helmroth and others 2002). Therefore, experimental determination of migrating compounds must be conducted to verify the accuracy of the migration results predicted by the developed mathematical models.

The following section will focus on chromatographic techniques for determination of the migration in food and food simulants and predictive models for migrant behavior. Table 8 shows different chromatographic conditions followed for detection and quantification of chemical substances in food and food simulants.

Plasticizers

A number of gas chromatographic techniques for different plasticizers have been developed (Goulas and others 2000; Cano and others 2002; Biedermann-Brem and others 2005; Fankhauser-Noti and Grob 2006; Goulas and others 2007; Ežerskis and others 2007; Wei and others 2009; Guo and others 2010). Cano and others (2002) used a capillary (15 m × 0.53 mm i.d., SPB-5 stationary phase) gas chromatography (GC) method for adipates extracted from PVC film with hydrogen as carrier gas (50 kPa inlet pressure) equipped with flame ionization detector (FID). A similar GC technique was used to analyze ESBO and DEHA in PVC gaskets of lids for glass jars (Biedermann-Brem and others 2005) and ESBO, DEHP, DINP, DIDP, DEHA, DEHS, and ATBC level in a wide range of oily foods (Fankhauser-Noti and Grob 2006). Hirayama and others (2001) analyzed migration of plasticizers extracted from cap-sealing resins of bottled foods under certain conditions using an HP-5 column in split mode, using a temperature gradient from 150 to 250 °C. Quadrupole GC–mass spectrometry (MS) was also used to analyze compounds and plasticizers in food samples (Ežerskis and others 2007).

Lau and Wong (1996) determined migration of DHA, HOA, and HAD from cling film to fatty food by using GC with a low-background DB-5 capillary column and helium gas as carrier media and an ion trap detector. Prior to the analysis, a gel permeation chromatography column (Bio beads SX3) was used to

clean up the food extract. Badeka and Kontominas (1996) analyzed DOA and ATBC in olive oil and water using GC/FID with an alumina column packed with 10% SE-30. A similar method was used by Goulas and others (2000) to determine DEHA migration from PVC to cheese.

Other researchers have used high-performance liquid chromatography (HPLC), ultra-performance liquid chromatography–mass spectrometry (UPLC–MS), and liquid chromatography/tandem mass spectrometry (LC/MS/MS) methods for detection of phthalates (Sørensen 2006; Xu and others 2010; Simoneau and others 2011). Xu and others (2010) determined phthalate levels in cooking oil and mineral water using a reversed phase C18 column with acetonitrile/water as the mobile phase and UV (230 nm). Simoneau and others (2011) used UPLC–MS coupled to an electrospray interface in multiple reaction–monitoring mode (MRM) and C18 column with an eluent of aqueous ammonium acetate 1 mM/methanol for diethyl phthalate, diisobutyl phthalate, DBP, and diethylhexyl phthalate.

Ultra-performance quadrupole time-of-flight mass spectrometry (UPLC–Q–TOF–MS) is a useful technique for analysis of non-volatile components such as phthalates (Aznar and others 2012). The TOF mass analyzer provides high sensitivity for identifying non-volatile migrants from packaging material. A BEH C18 column (particle size 1.7 μm) was used. The chromatographic analysis was performed in an Acquity system equipped with an ESCI probe coupled to Xevo G2 QTOF. Water with 0.1% formic acid and methanol with 0.1% formic acid was used as phase A and phase B, respectively.

Antioxidants

The first step in analysis of antioxidant migration is to determine the level of primary and secondary antioxidants in the plastics. ASTM standard D6953–11 and D6042–09 are available to determine the antioxidant concentration in PE and PP homopolymer, respectively. In the method D6953–11, the PE sample is ground to 1 or 0.5 mm particle size to extract the antioxidants in isopropanol (PE resin density < 0.94 g/cm³) or cyclohexane (PE resin density > 0.94 g/cm³) followed by C-8 or C-18 reverse phase LC and UV detection technique. Concentration is determined with an external calibration curve using reverse chromatography equipped with a C-8 or C-18 column and a UV detector. The initial and final mobile phase conditions are 60% acetonitrile plus 40% water, and 100% acetonitrile plus 0% water, respectively. Beldi and others (2012) analyzed Irganox 1076 extracted from food samples using GC–MS and a DB-17HT column (30 m × 0.25 mm i.d., 0.15 μm thickness). Garde and others (2001) characterized antioxidants extracted from fatty food simulants using GC/FID and a SPB5 column.

The use of electrospray ionization mass spectrometry (ESI–MS) has been evaluated in conjunction with GC–MS to follow SM and also to correlate the migration of higher molecular-weight compounds to the OM values. Alin and Hakkarainen (2011) used solid-phase microextraction (SPME) technique to extract antioxidants from food simulants prior to GC–MS analysis using a wall-coated open tubular (WCOT) CP–SIL 8 CB low-bleed/MS with helium as a carrier gas. The mass scan range was set to 35 to 400 (*m/z*). For an ESI–MS study, nitrogen was used as the nebulizing gas and helium was used as the damping and collision gas. Reinas and others (2012) used GC–MS technique equipped with Quad mass spectrometer in SIM mode to quantify the antioxidants (Irganox 1076 and Irgafos 168).

Table 8—Chromatographic conditions used for determination of chemical substances.

Technique	Compounds analyzed	Analytical column	Mobile phase/oven program	Detector conditions	Type of sample	Reference
HPLC-UV	Caprolactam, oligomers	Spherisob C ₈	Water–acetonitrile	λ = 210 nm	Cooking oil	Begley and others (1995)
HPLC	Caprolactam, nylon oligomers	Spherisob 5 ODS reversed phase C18	Methanol–water	λ = 210 nm	Chicken	Gramshaw and Soto-Valdez (1998)
HPLC-UV-DAD	Antioxidants	Hypersil ODS	Methanol–water	λ = 276 nm	Food simulants	Dopico-García and others (2003)
HPLC-UV	Chimmasorb		Tetrahydrofuran–acetic acid/water	λ = 285 nm	Olive oil	Quinto-Fernández and others (2003)
HPLC-diode array UV	DPBD	Kromasil 100 C18	Acetonitrile–water	–	Meat products	Silva and others (2007)
HPLC-DAD	Antioxidants, UV absorbers	Zorbax eclipse XDB C18	Acetonitrile	λ = 276 nm	Food simulants	Gao and others (2011)
HPLC-UV	Styrene	Zorbax ODS1	Water–acetonitrile	λ = 245 nm	Hot drinks	Khaksar and Ghazi-Khansari (2009)
HPLC-UV	Phthalates	Reversed phase C18	Acetonitrile–water	λ = 230 nm	Cooking oil and mineral water	Xu and others (2010)
HPLC-UV	Irgafos 168, Irganox 1010	Supelcosil C18, Hypersil ODS C18	Acetonitrile–tetrahydrofuran	λ = 280 nm	Food simulants	Alin and Hakkarainen (2011)
Headspace GC-MS	Styrene	DB to 624	From 80 to 250 °C	–	Cooking oil	Lickly and others (1995)
GC-FID	DOA, ATBC	SE-30	165 °C	–	Olive oil, distilled water	Badeka and Kontominas (1996)
GC-MS	Tinuvin P	DB1701	From 100 to 280 °C	–	Fatty food simulants	Monteiro and others (1999)
GC-FID	Overall migration	RTX 2330	160 °C	–	Fatty food simulants	Galotto and Guardia (2004)
GC-FID	DEHA, ATBC	BPX-5	From 100 to 360 °C	–	Sesame paste	Goulas and others (2007)
GC-MS	Plasticizers	DB-17HT	From 60 to 300 °C	–	Fatty food simulants	Ezerskis and others (2007)
GC-MS	Adipates	DB-5MS	From 90 to 270 °C	Mass scan: 50 to 400 (m/z)	Ham sausages	Wei and others (2009)
GC-MS	Phthalates	DB-5MS	From 70 to 280 °C	Mass scan: 50 to 400 (m/z)	Ham sausages	Guo and others (2010)
GC-MS	Irgafos 168, Irganox 1010	CP-SIL 8 CB	From 40 to 270 °C	Mass scan: 35 to 400 (m/z)	Iso-octane, ethanol, water	Alin and Hakkarainen (2011)
GC-MS	Irganox 1076	DB-17HT	From 70 to 350 °C	–	Food and food simulants	Beldi and others (2012)
UPLC-MS-ESI	BPA	BEH C18	Water–ammonium acetate	Mass scan: 133 and 212 (m/z)	Food simulants	Simoneau and others (2011)
UPLC-QTOF-MS	nonvolatile	BEH C18	Water–formic acid and methanol–formic acid	–	Food simulants	Aznar and others (2012)
UPLC-ESI-MS/MS	ESBO	BEH C18	Ammonium formate–methanol	–	Foodstuffs	Suman and others (2010)

UV, ultra violet; FID, flame ionization detector; DAD, diode array detector.

HPLC with a photodiode array detector (HPLC-DAD) has been used to analyze antioxidants (Dopcio-García and others 2003; Gao and others 2011). Gao and others (2011) followed a solid-phase extraction (SPE) technique with a silica C18 cartridge prior to analysis using a XDB C18 column (150 × 4.6 mm; 5 μm particle size) and UV detection (276 nm).

Analysis of Monomers and Oligomers

Determinations of styrene monomer in food and food simulants using GC techniques are common (Ehret-Henry and others 1994; Lickly and others 1995; Nerín and others 1998; Choi and others 2005; Paraskevopoulou and others 2011) including GC/FID (Choi and others 2005; Paraskevopoulou and others 2011). For example, one study used a HP-FFAP column for styrene (Paraskevopoulou and others 2011) and Rtx-5 column for oligomers. In another study with GC-FID, Gramshaw and Vandenburg (1995) used a BP-1 column (oven temperature 200 °C) and injecting in a cold on-column mode, while a HP-5 column was used with a lower oven temperature program (from 50 to 150 °C), followed by SPME extraction (Silva and others 2000). Dynamic headspace chromatography equipped with purge-and-trap injector, and a FID detector was used to determine styrene in yogurt (Ehret-Henry and others 1994), employing separation on a DB-5 column (30 m × 0.32 mm).

Tawfik and Huyghebaert (1998) analyzed styrene migration using HPLC plus UV detector (245 nm) with a Lichrosorb RP-18 column, while Khaksar and Ghazi-Khansari (2009) employed a different column packed with 6 μm Zorbax. PET oligomers in olive oil and iso-octane have been determined using GC-MS with selective ion monitoring (SIM) and HPLC-UV (5 μm ODS2 column, 241 nm) (Jickells and others 1992; Mountfort and others 1996). Begley and others (1995) used HPLC (210 nm) with a Spherisorb C8 column to analyze caprolactam and oligomers in nylon food packaging.

Light Stabilizers

Chimassorb 81, a UV stabilizer, was analyzed with GC-MS (Monteiro and others 1998). Quinto-Fernandez and others (2003) used a HPLC-UV technique with Hypersil ODS column (280 nm). Use of other techniques such as UPLC-UV-visible (UV/Vis) (Noguerol-Cal and others 2010) and HPLC-DAD (Gao and others 2011) have also been reported. To analyze Chimassorb 944 and Tinuvin 770, UPLC, equipped with a gradient pump and automatic injector was used (Noguerol-Cal and others 2010). Others have used a stainless steel column packed with bridge ethylene hybrid (BEH)-based particle C18 with 2 different detector wave lengths: 220 and 230 nm for Tinuvin 770, and Chimassorb 944, respectively.

Heat Stabilizers

Epoxidized soybean oil (ESBO) is a common plasticizer and stabilizer used in production of lid-gaskets for glass jars and food-packaging plastics. ESBO in food products can be determined by reversed phase LC-ESI-MS/MS (Suman and others 2005, 2010). Biedermann-Brem and others (2006) used GC-FID and GC-MS to determine ESBO in oily foods. For most foods in which components do not interact, GC-FID can be adopted; otherwise GC-MS technique is more suitable (Biederman-Brem and others 2006).

Slip Additives

Cooper and Tice (1995) utilized GC-FID for the analysis of oleamide, stearamide, and erucamide in food simulants. A differ-

ent oven program is needed for the analysis of migrants of different weights and polarities. Splitless and cold on-column injection systems have also been employed.

Legislation

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 plastics/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. This section is briefly focused on the general framework and legislative aspects from different countries.

European legislation

Framework Directive 89/109/EEC (CEC 1989) provides 2 basic principles on which the legislation is based. These include “inertness” of the food-contact materials and articles, and “safety.” The principle of inertness is that any material, article, or its components should be inert enough not to pose any health hazards, unacceptable changes in food composition or deterioration of food qualities. However, Directive 89/109/EEC was repealed by 1935/2004/EC, and addressed general rules for some new topics related to active food-contact materials, safety provisions. Directive 2002/72/EC establishes basic rules and guidelines related to food-contact plastics. This directive is related to the materials only made of plastics and plastic gasket in lids (10/2011/EU), and does not consider plastics with other multimaterial multilayers. 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 (CEC 2011a) and 1282/2011/EU (CEC 2011b) amendments have been implemented to the Commission Regulation (EU) No 10/2011 (CEC 2011c) for the restriction of use of BPA in plastic infant bottles, and the correction of regulations for plastic materials, respectively.

FDA legislation

The U.S. Food and Drug Administration considers substances that are not added internationally, 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. With the help of the Center for Food Safety and Applied Nutrition (CFSAN), the FDA provides the guidance and regulatory aspects for food, cosmetics, drugs, and so on. 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). General provisions for the indirect food compounds and threshold of regulation for substances in FCM is documented in 2 subparts: 174.5 and 174.6, respectively under title 21. 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). CFR 170.30 provides the classification criteria for GRAS. GRAS materials can be found in the part 182 (GRAS material for human consumption like nutrients, chemical preservatives, and so on), 184 (direct food substances), and 186 (indirect food substances).

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 (AS 2070–1999). FSANZ (2000) surveyed approximately 65 foods and beverages packaged in different materials such as plastic packaging, glass, and paper for a wide range of chemical substances.

Canada

The safety issues regarding food packaging in Canada are managed by 2 agencies: the Canadian Food Inspection Agency (CFIA) and Health Canada. The CFIA is responsible for enforcing the policies and food inspection standards, whereas the Health Products and Food Branch (HPFB) under Health Canada establishes and implements the standards and policies. The federal government amended the existing documents related to the acts and regulation and provided a consolidated or updated version that is “Consolidated Regulations.” This is maintained by the Department of Justice of the Government of Canada. Food and Drug Regulations (C.R.C., c. 870, 2013) Division 23 deals with food-packaging materials and has recently been amended on March 21, 2013. The section B. 23.001 clearly states that “No person shall sell any food in a package that may yield to its contents any substance that may be injurious to the health of a consumer of the food.” The HPFB provides a “no objection letter” (NOL) to ensure the suitability of the use of food-contact materials. A list of polymers has been developed by the Chemical Health Hazard Assessment Division (Food Directorate), and NOLs have already been issued for the enlisted polymers (list of acceptable polymers use in food-packaging application, Health Canada). However, section B.23.003 indicates that except for milk, beverages can be sold in a PVC package that does not contain total octyltin more than 3% of the resin polymer, and food in contact with packaging must contain less than 1 ppm of total octyltin (Food and Drug Regulations).

Japan

Food safety legislation in Japan is based on 2 national laws: the “Food Safety Basic Law (enacted in 2003) and the Food Sanitation Law (1947).” The Food Safety Commission (FSC) was established under food safety basic law for risk assessment, and the food sanitation law is basically for risk management. General requirements for packaging and containers are set in chapter 3 (Article 16, 17, and 18) under this law (Food Sanitation Law 1947, amended in 2006). Specifications and standards for foods and food compounds are also provided under the Food Sanitation Law (Act no 233, 1947; last amendment 2006) (JETRO 2006). Under chapter 3 of this law, a different section provides the information on (A) general specifications and restrictions for apparatus and packages/containers and their materials, (B) general test methods for packages/containers or apparatus such as migration testing and conditions, (C) reagents, test solutions (D) specification containers, packages, and their materials such as glass, plastics, metal cans, rubber, (E) specification for packages and containers for particular food type, and (F) standards for manufacturing the apparatus and packages/container.

Final Remarks

This article reviewed the migration of chemical compounds as influenced by MW and conventional heating, as well as during storage. Treatment protocols and analytical methods were briefly presented to set the stage for migrant determination. Although this article reviewed studies to identify and quantify the migration of additives, monomers, and oligomers in food materials, different approaches must be followed to determine overall and SM of substances, due to the complexity of foodstuffs and migration processes. However, measurement of OM is relatively straightforward compared to SM analysis.

For migration analysis, the most commonly studied packaging materials are made of PVC, PP, PET, PE, PA/nylon, and PS. The chemical compounds of greatest interest include DEHA, ATBC for PVC, antioxidants for PP and PE, oligomers for PET, caprolactam monomer for PA, and styrene monomer for PS, since these show higher levels of migration into food. Studies show that BPA is prone to migrate into food from epoxy resins for internal can linings used for foods and PC baby bottles. Migration from PP is much faster than from PET.

However, the study of migration should not be confined to these chemicals only, since migration of other chemicals may also occur, depending on study conditions, the nature of the chemicals, and the complexity of foods. Nevertheless, it is not possible to conclude unequivocally whether SM for a particular substance has a higher migration level, since the amount of substances migrating into food depends upon the initial concentration of substances in polymer packaging. In addition, the nature of food, food-additive interaction (lipophilic or hydrophilic), and time-temperature conditions significantly influence additive migration. It is important to quantify the migration of a compound of particular interest, depending on the toxicity level and packaging material type. Foods with a higher fat content usually have shown a higher level of migration.

Migration of compounds is higher if foods remain in contact with polymer packaging for extended periods. MW heating has been found to be a reliable technique in food processing, it also causes less OM than conventional heating under similar processing conditions. However, more systematic studies are needed to evaluate the influence of MW heating on the level of migration from different polymeric packaging using time-temperature profiles used in industrial MW processes. PVC is not suitable for MW treatment, since it has shown more OM than other polymeric packaging materials. In some cases, prolonged heating in MW degrades the antioxidants in food-contact plastics than conventional heating. Swelling of polymers is an important factor that accelerates additive migration under high temperature and durations.

Different analytical techniques have been adopted for the determination of chemical substances. Among the several analytical methods, HPLC or LC-MS, ESI-MS for semivolatiles, and GC-MS for volatile substances are the most commonly used techniques for the detection/identification of migrants from polymers. For example, static or dynamic headspace GC-FID technique is excellent for the determination of styrene. Recently, UPLC is being adopted due to its improved sensitivity, resolution, and overall performance compared to HPLC. In the literature, most of the MW studies have involved OM, with only very few on antioxidant degradation. Further systematic study and experimental work of conventional heating is necessary, since this type of heating requires more time than MW processing/heating for sterilization or pasteurization. Further research is also needed on storage under

anticipated and moderate abuse conditions, for better understanding of overall and SM of chemical substances. Such systematic study can elucidate migration behavior during sterilization or pasteurization processes from conventional retort and MW heating.

Abbreviations

APET—Amorphous polyethylene terephthalate
 ATBC—Acetyl tributyl citrate
 BADGE—Bisphenol A diglyceride ether
 BBP—benzyl butyl phthalate
 BHA—Butylated hydroxyanisole
 BHT—Butylated hydroxytoluene
 BOPA—Biaxially oriented polyamide
 BPA—Bisphenol A
 CPET—Crystalline polyethylene terephthalate
 DAD—Diode array detection
 DBP—Di-n-butyl phthalate
 DCHP—Dicyclohexyl phthalate
 DEHA—Di(2-ethylhexyl) adipate
 DEHP—Di-2-ethylhexyl phthalate
 DEHS—Diethylhexyl succinate
 DEP—Diethyl phthalate
 DHA—Diheptyl adipate
 DIBP—Diisobutyl phthalate
 DIDP—Diisodecyl phthalate
 DINP—Diisononyl phthalate
 DMP—Dimethyl phthalate
 DOA—Dioctyl adipate
 DOP—Dioctyl phthalate
 DPP—Di-n-propyl phthalate
 EA—Ethyl acetate
 EAA—Ethylene acrylic acid
 ESBO—Epoxidized soybean oil
 ESI—Electrospray ionization
 EVA—Ethyl vinyl acetate
 EVOH—Ethylene-vinyl alcohol
 FCM—Food-contact material
 FID—Flame ionization detector
 GC—Gas chromatography
 GPPS—General purpose polystyrene
 HAD—Heptyl adipate
 HDPE—High-density polyethylene
 HIPS—High-impact polystyrene
 HOA—Heptyl octyl adipate
 HPLC—High-performance liquid chromatography
 LC—Liquid chromatography
 LDPE—Low-density polyethylene
 LLDPE—Linear low-density polyethylene
 MPPO—Modified polyphenylene oxide
 MS—Mass spectrometry
 MW—Microwave
 OM—Overall migration
 OPP—Oriented polypropylene
 PA—Polyamide (nylon)
 PC—Polycarbonate
 PP—Polypropylene
 PS—Polystyrene
 PVC—Poly vinyl chloride
 PVDC—Polyvinylidene chloride
 SIM—Selected ion monitoring
 SM—Specific migration

SML—Specific migration limit
 SPME—Solid-phase micro-extraction
 TDI—Total daily intake
 TNPP—Tris-nonyphenyl phosphate
 TPA—Terephthalic acid
 UPLC—Ultra-performance liquid chromatography
 VA—Vinyl acetate
 VDC—Vinylidene chloride
 VOH—Vinyl alcohol
 WVTR—Water vapor transmission rate

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