Chapter 2 Packaging and Food: A Complex Combination

Abstract The advent of packaging materials in the modern food industry has deeply changed the relationship between people and foods. Food packages have progressively been turned into essential element for the sale and the consumption of food products. On these bases, packaged foods can become communicative media of values and information: the user receives and understands these data by means of suitable tools of physical, cultural and personal nature. Functional and communicative requirements of food packaging are continuously evolving: the careful analysis of these factors should be recommended because of their influence on chemistry of foods, food technology, biochemical interactions between different food phases, and chemistry of food packaging. This section is dedicated to the study and the 'chemical' interpretation of food packaging requirements.

Keywords Food packaging • Communication • Regulatory • Food consumption • Packaging design • Recycling

Abbreviations

BOPP	Biaxially oriented polypropylene
BRC	British retail consortium
Cr_2O_3	Chromium oxide
DOS	Dioctyl sebacate
ECCS	Electrolytic chromium oxide coated steel
ETP	Electrolytic tin plate
EVA	Ethylene vinyl acetate
EVOH	Ethylene vinyl alcohol
EFSA	European food safety authority
EU	European Union
EPS	Expanded polystyrene
FU	Final user
FIFO	First in first out
FP	Food packaging
FM	Food manufacturer
FPM	Food packaging material

FPP	Food packaging producer
FSSC	Food safety system certification
GSFS	Global standard for food safety
BRC/IOP	Global standard for packaging and packaging materials
GMP	Good manufacturing practice
HACCP	Hazard analysis and critical control points
H ₂ S	Hydrogen sulphide
HDPE	High density polyethylene
HIPS	High impact polystyrene
IoP	Institute of Packaging
IFP	Integrated food product
IFS	International Featured Standard
ISO	International Organisation for Standardisation
IUPAC	International Union of Pure and Applied Chemistry
Fe_2O_3	Iron oxide
ITX	Isopropyl thioxanthone
JIT	Just in time
LIFO	Last in first out
LLDPE	Linear low-density polyethylene
LDPE	Low density polyethylene
MAP	Modified atmosphere packaging
MW	Molecular weight
NIAS	Non-intentionally added substance
OBA	Optical brightness agents
OPP	Oriented polypropylene
P&B	Paper and Board
PA	Polyamides
PE	Polyethylene
PET, PETE	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
PVDC	Polyvinylidene chloride
RFID	Radio frequency identification
REACH	Registration, evaluation, authorisation and restriction of chemicals
SBB	Solid bleached board
SBB	Solid unbleached board
TFS	Tin free steel
UV	Ultraviolet
ZnO	Zinc oxide

2.1 Packaging and Food: An Introduction

The historical evolution of commercial products is strictly connected with the concomitant evolution of packaging: container tools and contained goods are components of the same inseparable unit. This link is surely stronger and meaningful in the field of foods and beverages because of the notable symbolic value of food products [1].

The advent of packaging in the modern food industry has caused fundamental transformations with concern to the relationship between people and foods. As a result, food packaging (FP) has progressively been turned into an essential element for the sale and the consumption of the food product [2]. In fact, foods are not exclusively perceived as primary needs by final consumers. The simple eating act is now the expression of strong cultural and ethical values in the current economic context without the risk of sudden famines. Actually, the main problem of the modern world is the overproduction of industrial commodities in several economic cycles and areas.

As a consequence, foods are not different from other consumer goods: this concept is obligatorily correlated to the consumption activity and communication features. Substantially, consumption is not always a mere purchasing activity. Final users (FU) are often used or 'forced' to externalise their personality on purchased goods, even if the unconscious projection of one's own attitudes and feelings is not complete. On these bases, every good or service can become a communication media of values and information: the user receives and understands these data by means of suitable tools of physical, cultural and personal nature [3].

Foods and beverages are often perceived as vehicles of contradictory values and behaviours:

- The hedonistic idea of the maximum pleasure of tastes and the obsessive negation of unpleasant effects on the human being
- The rapidity of individual meals and the pleasure of the conviviality
- The necessity of ready-to-eat products and the increasing attention to healthy foods.

In addition, many urgent topics affect both the regulatory and the social viewpoints: hygiene and safety discussions are essential matters.

FP is the first communicative element of the 'integrated food product' (IFP). The final user is used to expect, see and recognise the exteriority of IPF before other important and meaningful elements, including the real edible content. This mechanism is the most probable behaviour in the modern context of the mass retailing industry: self-service seems the general rule [4]. On these bases, FP should answer to expressed and implicit questions, doubts and needs of FU. As a consequence, FP may become the real intermediary between the food manufacturer (FM), the mass retailer and the FU. Moreover, FP has to comply with peculiar functional features with concern to usability, storage and transportation [5–7].

It is known that functional factors and the communication features are the most important requirements for FP: however, the complex process of packaging design cannot be easily and roughly circumscribed to these aspects. Regulatory requirements concerning FP and food packaging materials (FPM) are more and more urgent and specific: technological roles are constantly examined and reviewed, but other obligations have been recently introduced or suggested. Nutritional labelling measures in the European Union (EU) are certainly good examples. Additionally, packaging designers have to comply with other needs such as the increasing attention to the environmental policy and the sustainable management of resources and wastes.

However, the above-mentioned topics cannot be discussed without the fundamental role of chemistry and technology: the advent of plastic matters in the industry of packaging has completely and irreversibly transformed the concept of FP with unpredictable results [2, 8].

An important aspect is correlated to the geographical availability of certain materials, chemical intermediates and suitable structures for the production of FP. On the other side, packaging can be simply assembled in a few favoured locations fitting together parts, intermediates and chemicals from different geographical areas. This is the natural consequence of the effective (or excessive) industrial specialization in several countries.

The above-mentioned situation should be carefully considered when speaking of food failures and possible contamination events. Several of most recent food scandals may be investigated by this viewpoint [9]: in fact, certain chemical analytes may be (a) absent in food production sites and (b) present near FP plants at the same time. Moreover, the conceptual displacement of FP components can complicate the investigation: every packaging may be seen as a single container with 'n' parts or chemical intermediates/raw materials from 'n' different locations. As a result, every food contamination by FP could have been originated only by one of 'n' different sites.

This consideration should be taken into account when considering chemical contamination and microbiological dangers also. For example, the occurrence of microbial outbreaks with heavy consequences for human safety has been recently correlated with the environmental contamination of packaging machinery into food companies [10]. Once more, the role of FP can be considered of basic importance when speaking of food preservation and food failures.

Anyway, functional and communicative requisites of FP are continuously evolving: the careful analysis of these factors should be recommended because of their influence on the structure and the behaviour of the future IFP. This investigation is mainly based on chemical-physical features of IFP: chemistry of foods, food technology, biochemical interactions between different food phases ... and chemistry of food packaging [10]. In fact, chemistry of FP can influence heavily the future IFP.

Fig. 2.1 The assembled packaging. The subdivision of main requirements for food packaging design



However, the above-mentioned analysis should highlight and clarify existing connections between the chemical features of IPF and complex of PF requirements. This study may appear complicated because of the apparent dissimilarity between two worlds: the materialistic and 'scientifically exact' physicality of chemistry on the one hand, and the creativity of design science on the other side. Apparently, two different and irreconcilable visions of the world are shown here.

First of all, the whole group of food packaging design requirements should be divided into four macro categories, as shown in Fig. 2.1:

- 1. Functional requirements
- 2. Communicative requirements
- 3. Regulatory requirements
- 4. Environmental requirements

However, similar categories are strictly correlated with important juxtapositions during the whole life of the final IPF and FP.

The complete compliance of all requirements is fundamental with relation to the quality of the final FP and the efficacy of design. Different requirements have different importance depending on the final IFP and correlated production processes. Because of the main objective of this book, every requirement with potential influence on foods and related physicochemical features will be discussed and connected with the correspondent design action because of the strict relationship between chemistry and functional performances of IPF and FP.

2.2 Functional Requirements

At present, FP has to comply with different and increasing functional needs: the so-called 'globalisation' of markets and the consequent broadening of the whole 'market arena' have transformed the original packaging into a multifunctional instrument with different responsibilities [11]:

- Preservation of contained foods when assembled to obtain the IFP, and
- Easy shipping of the produced IFP in different and remote markets.

The situation appears complex and FP plays one of the most important roles in the food chain [5]. Perishable foods—fruits, vegetables, and so on—have to be preserved during extended time periods and on long distances. Moreover, the continuous and possibly laborious delivery of food commodities (raw materials, intermediates and final IFP) may be fractionated and carried out by different operators. Frozen products have to be obligatorily stored under—18 °C, while refrigerated IFP should remain constantly stored in accordance to less rigorous conditions (the so-called 'cold chain': $2^{\circ} \pm 2$ °C in several countries). On the other hand, fractionated storage may be carried out with sudden changes in temperature (thermal leaps) and FP have to minimise chemical and microbiological alterations where possible and predictable (mechanical damages should be considered also).

The request and the diffusion of ready-to-eat and pre-cooked foods have also forced packaging producers to create packaging with new features. These FP should be easily opened, possibly usable for sectioning foods and highly resistant to high temperatures when placed into conventional or microwave ovens. With relation to the third feature, FP should not alter contained foods: as a result, every possible chemical reaction at the food/packaging interface should be predicted and possibly avoided. The same thing has to be affirmed when speaking of potential chemical migration of certain analytes, plastic components or possible decomposed matters from FP to foods. Actually, the opposite situation may occur with 'grotesque' results and possible alarming reactions by normal consumers [10].

Another notable question remains to be discussed when considering predictable or unexpected reactions between FP and foods, with reference to predicted performances: the problem of shelf life values. In other words, every packaged food has its own labelled features, including the related durability: this term means the so-called expiration date or 'date of minimum durability' as intended in the EU according to the Council Directive No 2000/13/EC on labelling, presentation and advertising of foodstuffs.

IFP are subject to food degradation because of predictable or unexpected chemical, physical and microbiological degradations, according to the principle of food degradation [5]. Consequently, FP have to preserve packaged foods without the decrease of predictable or calculated shelf life values.

Finally, it should be remembered that different customers can purchase IFP: normal consumers are surely the most important and recognisable target for FM. On the other hand, the 'food and feed chain' is composed of different players, also called 'stakeholders', and some of these subjects is contemporarily producer (of raw materials, intermediated foods or final IFP) and 'user' (of raw materials, or intermediated foods). With exclusive concern to these professional users, the list of requirements for purchased IFP and for every sub-component, including FP, can slightly differ from basic needs of the user. Following requests have to be considered:

2.2 Functional Requirements

- Effective storage systems
- Easier management of the peculiar IFP on shelves near mass retailers
- Increased availability of new and intuitive logistic systems, from the 'First In, First Out' (FIFO) strategy to most recent 'Last In, First Out' (LIFO) and 'Just in Time' (JIT) approaches.

All the earlier discussed points can help to define the whole group of FP requirements: in fact, these factors can be determined by both the main features of the food product (to protect- to transport- to preserve- to store) and the peculiar target (normal consumer, stakeholder and public authorities for food safety).

2.2.1 Preservation and Protection Requirements

Food preservation and food protection are similar concepts. Actually, the first of these definitions is related to the defence of the food product from internal agents and external factors that could enhance food degradation (microbial spreading and degrading chemical reactions such as oxidation or enzymatic browning). Instead, food protection is related to the possible preservation of the whole IFP in every location and during extended temporal periods. Normally, protection requirements concern essentially the defence of the IFP against:

- External physical agents: ultraviolet (UV) rays; powders; compression; crashes; thermal leaps; and
- External chemical agents: environmental moisture; toxic or harmful substances; other chemical contaminants; etc.

One or all of these causes can attack and damage IFP with hygienic problems and/or simple degrading failures: the first and most exposed barrier is naturally the used FP.

On these bases, the initial design of FP and subsequent developments play always a fundamental role with reference to the preservation and the protection of IFP. FP must 'transfer' their peculiar features to the packaged product. Mechanical resistance, flexibility, rigidity, impermeability, gaseous diffusion and less known properties (superficial roughness, porosity, etc.) are surely welcome and desired when the final IFP has to be 'combined' with a sort of chemical and physical impenetrability [12, 13]. Moreover, shapes and sizes are fundamental if packaged products have to be adequately preserved and protected at least from the date of packaging to the end of the minimum durability. Substantially, chemical and technological properties of materials can be enhanced with the 'right' and 'sustainable' choice of the most adaptable shape and/or volumetric capacity [2, 14]. For example, the simple preservation of certain packaged products (FPM: paper and board) against sudden impacts may be notably ameliorated with the correct placement of the food into adequate shapes [15]. It can be assumed that the chemistry of materials is of basic importance for the future performance of FP. The known correlation between the stability of paper and board boxes and certain chemical properties of original FP components (example: dimension, thickness, strength, adhesive power and chemical nature of glues) is a useful example. On the other hand, the chemical nature or FP has to be adaptable to physicochemical features of foods.

Finally, modern closure and opening systems are important elements for the durable protection (impermeability) of IFP against physicochemical agents. In contrast, preservation requirements are mainly related to the protection against microbiological agents: degrading micro organisms (yeasts, moulds, etc.) and pathogenic bacteria [15, 16]. Once more, FP components and original raw materials can play an important role because of the theoretical asepsis of the final container. The same concept has to be repeated when closure systems are created, developed, studied and introduced with the aim of transforming the original food—with its own microbial ecology—into an aseptic, impermeable and 'inviolable' structure.

Actually, the modern FP does not seem to be designed with protective features only: new materials have been recently introduced and developed with innovative features. The most important of these 'enhancements' appears related to the active behaviour of new systems, at present. For example, the so-called 'active packaging' systems are intentionally designed with the aim of enhancing the durability of packaged foods by means of chemical interactions at the food/packaging interface [17, 18].

As a result, it appears that preservation and protection may be obtained at the same time by means of different strategies when speaking of modern packaged foods. However, a useful reflection should be made about unpredictable results of design strategies.

UV rays are known to be active catalysers of microbial spreading and physicochemical reactions (causes: augment of inner temperatures into certain FP; enzymatic reactions; etc.). As a consequence, the above-mentioned design strategies—materials, volumetric capacity, closure systems, and shapes—have to be studied and adapted to every peculiar situation. With reference to this approach, an additional risk is linked to the possible and avoidable damage of the resulting FP by means of packaging strategies. In other words, every design activity is 'forced' to express one or more clear lines of action, while other more or less promising strategies could be judged negatively and preventively eliminated.

Should the 'right' approach be applied to more than one specific situation, normal consumers and official authorities could be obliged to observe predictable failures and consequent hygiene and safety concerns [10, 19, 20]. It may be assumed that every food needs its own active or passive FP [21]: this time, the problem can be originated by the incorrect design and/or incorrect information by FM [5].

2.2.2 Requirements for Transportation and Storage

The most part of packaged foods are the last step of a long 'food chain'. In spite of the increasing sensibility towards ethical and environmental topics and the attention for new concepts—short food chain, aware of consumption in favour of local productions and 'low footprint' impact—the food chain is located everywhere on a macroscopic and worldwide scale. As a logical consequence, this situation implies the careful design of IFP and related components, including FP. In other terms, design should take into account the possibility of long distance-transports and possible intermediate storages near 'temporary' loading platforms between the starting point—FM—and the final destination—mass retailers, other marketplaces, and fairs [22].

Every packaging is (a) stored near the food packaging producer (FPP), (b) delivered to the final user (FU) and finally (c) stored by FM (with peculiar and probably different procedures if compared to FPP's advices).

Subsequently, the subject of storage and transportation steps is not FP, but the final IFP: this item is (d) stored near the food industry, (e) delivered to the final destination and finally (f) stored until the use or the purchase by common users [5, 14]. It should be highlighted that:

- The subject of the above-mentioned steps is completely changed
- The delivery step may be often subdivided in two or more intermediate substeps between steps (f) and (g) with annexed 'intermediate' or 'temporary' storages near different warehouses.

Consequently, the whole chain of transportation can become complex and probably 'long': every step or sub-step can surely increase the probability of damages (mechanical ruptures, microbial spreading, chemical reactions by heat or UV rays-exposure etc.). In addition, the diversification between different ware-houses should be highlighted because of dissimilar storage protocols, distinct managers and so on. From the theoretical viewpoint, it may be assumed that a generic food commodity is subdivided in 'n' different storage warehouses at the final stage just before the purchase. In these conditions, the risk of 'n' or less different behaviours of the same IFP can be predicted with relation to the remaining shelf life (RSL) and correlated original features (colour, aroma, aspect, texture and taste). At present, this discussion is extremely important and 'thorny' [10]. After all, the significance of sampled products for statistical analyses and official examinations may be potentially lowered.

As a result, different exigencies can be discussed when speaking of food transportation and storage; these needs are also correlated to several players of the food chain and different warehousing systems [23]. Anyway, the most influential factors appear to be (a) weight, (b) shape and (c) volumetric capacity: naturally, these features are mainly established in the design step for FP and IFP.

With reference to the primary FP, main challenges appear:

- The definition of the lowest volumetric capacity
- The research of adaptable materials, with some preference for flexible plastics and composite packaging
- The design of protection systems with low encumbrance. Examples: strengthening of lateral ribs; air injection (because of shockproof and insulating properties).

With concern to the secondary packaging, it has to be considered that this container depends strictly on the number and shape of theoretically equal IFP. In fact, every secondary packaging gathers 'n' individual IFP. There is the general opinion that secondary packaging could be more adaptable to different IFP. As a consequence, cardboard (or plastic) boxes are often produced with several standardised sizes only and widely used. On the one hand, the normal placement on single and standardised wooden pallets is surely easier. On the other, available spaces may be irrationally occupied into warehouses, and standardised boxes may be not easily storable onto metallic shelves.

The lack of spaces all around secondary packages can be negatively considered when the so-called 'Hazard Analysis and Critical Control Points' (HACCP) approach is required. In fact, the exposure of IFP to heat, UV rays and other external agents with some degrading importance may be increased if food products are not properly stored: a minimum space around cardboard and plastic boxes should be needed. According to several operators, every 'surrounded' cardboard box should require 20 to 30 cm of free space. This empirical conviction suggests that the heating could be reduced when 30 cm-free spaces are interposed at least between two different secondary packages. The risk of chemical degradations and microbial spreading could be increased if plastic secondary boxes are used because of coefficients of thermal transmission for polymeric materials.

2.2.3 Operational Requirements

The continuous evolution of packaging and FP in particular is influenced by different needs, including 'new' usability requirements. At present, the possibility of using the original food container for heating, cooling or serving packaged foods becomes one of the fundamental and motivational elements for normal consumers. The profound change of current lifestyles has undoubtedly modified the consumeristic behaviour. The IFP should be easily handy and resealable [24]; in addition, it should be dimensionally reduced with possibility of little portions because of the important increase of single (individual) meals, the current 'fast food' tendency to shorter times and the diffusion of intuitive devices [25]. Designers can be extremely creative and produce innovative FP for futuristic IFP, but every new design needs adaptable materials (the role of synthetic chemistry is

the first priority here) and good technologies for production, packaging, superficial treatment and storage.

Another reflection should be made with relation to environmental and sustainable policy statements. New functional requirements have been recently examined in last times: two examples are the need for improving dosing systems and 'durable' FP for repeated uses (the extension of shelf life does not concern the packaged food, but the exterior packaging). Moreover, the possible food contamination by 'Non-intentionally Added Substances' (NIAS) has recently highlighted the role of the recycling of packaging waste in the EU [26]. On the other side, European Institutions and national Agencies do not appear ready to give long-term answers to consumers at present [27, 28]. The most recent of these 'alarms' has concerned the detection of mineral oils in packaged foods and the possible risk on the human health; however, it has to be noted the European Food Safety Authority (EFSA) has clearly advised that safety risks by intake of mineral oils are not known or demonstrated [27].

2.2.4 Requirements for Packaging Disposal

The difficult management of packaging wastes is one of most important critical points in the modern world. With exclusive reference to the European situation, 78.4 million tonnes of packaging wastes are produced every year according to Eurostat [29]. This situation cannot be easily circumscribed to the simple and geographically well-defined portion of 'industrialised countries': other nations must face the menace of waste super-production without reliable disposal opportunities. Moreover, every possible solution should concern the whole life-cycle of FP and IFP instead of the simple last step of disposal. Consequently, a correct strategy should be planned in the design step.

As mentioned earlier, the possibility of toxic effects on human health is one of most important worries today. The problem has been recently correlated with FP when produced by recycled materials also. Additionally, the European regulatory has been enforced with the Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). This Regulation has clearly introduced new rules with reference to chemical substances, their identification and the authorisation or possible restrictions to the use for the production of industrial products in the EU. Naturally, only allowed chemicals can be used to produce FP in Europe. Moreover, the possible or sure recycling of 'long life' FP or other packaging wastes may introduce several of prohibited or 'suspected' substances [27].

Anyway, every disposal requirement for FP involves clearly materials, their chemical composition and the possibility of safe recycling from the functional angle. However, there are different recycling technologies and dissimilar materials; consequently, different recycling performances may be obtained with correlated impacts on the control of gaseous emissions, when measured as 'carbon

footprint', and energy consumption [30, 31]. It should be also noted that recycling performances may be influenced by the peculiar connection between different FP components. For example, recyclable packages may be 'chemically' contaminated because of the use of peculiar glues or adhesive products of different origin [32, 33]. Another important factor is the possibility of reducing the encumbrance of recyclable FP.

On the other side, different components of similar FP may be painstakingly separated and recycled. For this and other reasons, FP designers should create new FP easy to disassemble: so the environmental impact of FP wastes may be reduced with similar strategies. On the other hand, the concept of easy separation between different components can represent a precise environmentally sustainable choice of food and non-food materials in peculiar 'poor' markets: the example of 'fair trade commerce' is notable, at present. Moreover, the lacking of raw material availability and reliable packing machineries in certain sites should be remembered. Substantially, the location of food productions in economically disadvantaged areas (with impetuous and often uncontrolled industrialisation) may impose difficult conditions.

The chronic deficiency of energy and transport infrastructures may also undermine certain food productions and stop economic investments [34]. As a result, the on-site production of basic and primary FP with minimal features becomes absolutely necessary: for example, paper and board packaging might be produced without glues, adhesive additives, printing inks, etc. Naturally, this situation has to be carefully examined when speaking of food packaging.

2.2.5 Communication Requirements

Original FP have been created with functional purposes (preservation and protection). Subsequent evolutions have determined in the '50s the transformation of FP into a communication media. As a result, the communication function of modern FP is considered as important as the functional one.

Actually, communication messages can be:

- Tacitly manipulated for mere commercial purposes with ethical implications, or
- Explicit with the aim of communicating positive ethical elements and environmentally sustainable features of the IFP (food and packaging are on the same ground).

With reference to communication, designers can choose between different requirements depending on the final goal [35].

In fact, FP has to direct the attention of the users to the related IFP despite the presence of different, but similar competitors. This is the 'appellative' function of packaging. In addition, FP must highlight the brand (identifying function) and direct the target to the desired object until the final choice (persuasive function). Finally, the FP should confirm consumers' expectations with adequate information

about food product (informative function) and the effective communication of the main features (prescriptive function).

This theoretical dissertation should be chemically 'translated'. Following sections are dedicated to the detailed discussion of sub-requirements with the aim of demonstrating that:

- A generic FP may comply with different functions, and
- Industrial chemistry may supply (or be forced to give) suitable solutions for dissimilar objectives.

Before starting with this dissertation, it should be remembered that every design activity can bring advantages and disadvantages at the same time. In other words, FP can surely be excellent communication medium, but they can easily and rapidly communicate IFP failures at the same time, with dangerous effects.

2.2.5.1 Appellative Function

Generally, main sales channels are based on the so-called 'self service' system: every consumer buys products without intermediary services. Moreover, department stores can offer many food and non-food products with different brands, weights, volumes and prices. Naturally, FP have an important role: every IFP has to be immediately identified and recognised among other competitors [36, 37].

The concept of 'brand appellation' is not necessarily linked to FP: essential graphic elements may be useful and the use of thin colours can be a distinctive advantage when the attention of consumers has to be appealed without negative influence on persuasive functions. This communication effect can be easily reached in two different ways.

On the one side, FP may be completely transparent or minimally coloured (with a little percentage of covered printed areas). The aim is to show the inner content to interested consumers. For example designers can choose:

- Glass
- Flexible composite materials (closure: thermosealing option). Examples: metallised films for package snacks; flexible bags with a peelable seal covering a dedicated opening, for 1-stop shopping [15]
- 'Hybrid' packaging (the vision of edible content is partially allowed).

With reference to the last situation, it has to be noted the recent proposal of certain paper and board packaging with 'transparent' windows (naturally, every opening is protected with plastic films like polyethylene). Clearly, these choices—glass bottles and jars, composite and hybrid FP—are expressly fit for peculiar IFP categories and usable food packaging machinery. Moreover, the choice of raw materials (glass, paper and board, aluminium, adhesives, inks, flexible plastic films, etc.) can determine the success of IFP in terms of specific advantages (shelf life extension, better appearance, etc.) and opposite disadvantages (packaging

ruptures, strange or grotesque colours, abnormal sensorial properties without clear hygiene concerns, etc.).

On the other side, designers may propose completely coloured and/or printed FP with the aim of projecting most known and inviting attributes of packaged foods. For example, metallic cans show usually external printed images with food representations: these pictures are normally 'better' than original foods because of the intrinsic brightness in contrast with the metallic nature of cans and the plastic composition of coatings and inks on can surfaces, depending also on the type of packaged product [10].

2.2.5.2 Identifying Function

As stated earlier, FP have to be easily correlated with the food category and a specific brand [1]. Generally, the identifying function should immediately comply with these requirements.

With reference to macro food categories, two factors have to be mainly considered:

- The final shape and the immediate appearance of the packaged product
- The composition of exterior FP (materials and components).

For example, the classical glass bottle is normally correlated with wines and other alcoholic beverages because of its own shape and the related composition (transparent glass). However, recent developments in the FP industry have generated new plastic bottles. The correlation between 'synthetic' packaging (the 'synthetic' term is naturally linked to plastic matters, while glass materials are perceived as traditional materials) and wines may appear difficult. In fact, European consumers are well-accustomed at least to associate intuitively traditional wines with traditional glass-made bottles.

On the other hand, the simple concept of plastic bottles is not based on the same and complex system of cultural and historical models if compared with traditional packaging for wines. Several wines are usually fermented in glass bottles instead of the most known barrel or *barrique* fermentation: consequently, glass is synonymous with tradition and wine technology for a notable part of consumers.

This example can be very useful because of strict relationships between original raw materials for FP production and the final use of food contact approved packaging. Basically, the normal consumer cannot be requested to know and/or study chemistry of polymers, glass systems, metals and so on. The food consumer is spontaneously able to classify packaged foods in spite of a certain and unavoidably simplistic approach. For example, the behaviour of modern consumers is easily predictable in front of classic 'tin cans': this FP typology is undoubtedly associated to a relatively short list of processed foods: vegetables, soups, peas, beans, tuna fish and meat products. The normal consequence is the automatic equation 'preserved food' = 'canned food' with the creation of a welldefined food category on the 'apparent' basis of the exterior FP. On the other hand, tin cans are not easily associated with other non-processed foods (vegetable oils are a notable exception). Anyway, it has to be considered that the above-mentioned associations and classifications are mainly operated by consumers without solid knowledge of chemistry, microbiology, food technology and engineering: a very interesting result [36].

The correct identification of brands is strongly linked to the visual appearance of FP: printed logos, peculiar pictures and other graphic information in strict cooperation with the general aspect of the IFP and/or visible sensorial properties [38, 39]. It should be highlighted that this aspect: every known brand name is always connected with (a) pictorial images on FP and (b) physicochemical features of the complete IFP. With reference to the first point, the chromatic performance of certain glass jars is heavily influenced [5] by:

- The chemical composition of used labels
- The chemical composition of used dyes on labels and glass surfaces because of the influence on 'light solidity' of inks (the colorimetric resistance under light exposure)
- The chemical composition of coated supports (glass) because of the connection between chemical elements and brightness performance
- The physical appearance of jars in terms of rough or smooth surfaces (this feature is linked to processing technologies and finishing techniques)

Additionally, chemical features of the whole IFP are function of the exterior FP and the packaged food at the same time. For example, colorimetric performances of certain 'Maghreb' products such as *harissa* sauces in glass jars are dependent on the chemical composition of the edible content in synergy with the exterior container. In addition, the sensorial appearance of these products—*harissa* sauces may appear more or less 'red'—might be easily linked to some peculiar brand by consumers. This phenomenon may not be in connection with printed brands! The example of *harissa* sauces highlights the importance of more or less 'transparent' jars in certain situations.

2.2.5.3 Persuasive Function

Another important element is the so-called 'persuasive stimulus' on users. Once more, different factors have to be considered:

- Visual effects: colours, printed texts and images
- Synesthetic effects: shape, chemistry of materials and odours [5, 36, 37].

With reference to the above-shown features, the mention of chemistry of materials can be surprising. However, the simple introduction of printing inks may be useful to understand the penetration of industrial chemistry in such a case. The different chromatic performance of recent organic dyes and 'traditional' pigments can explain well the observable difference between opposite choices of consumers in front of two distinct, but similar IFP. The general strategy is based on the use of

the most recognisable and bright tint, but other 'minimalist' approaches—simple colours, little chromatic tones—can be successful when the aim is to avoid consumers' disorientation [10].

The above-mentioned 'persuasive power' is mainly based on conceptual elements. Because of the marketing strategy and the peculiar food macro category, best communication strategies should be evocative: IFP have to be rationally perceived as 'good' or 'excellent' articles. Moreover, FP have to be considered and rationally approved—as ergonomic devices. Generally, communication strategies comprehend both conceptual elements in different proportions with the exception of certain IFP categories.

2.2.5.4 Informative Function

Basically, food descriptions are useful after the final choice of IFP; however, the information may have some role when consumers evaluate the peculiar food and ponder negative and positive values.

Anyway, every description has one main goal: to give important and necessary advices about the correct use or interpretation of the purchased product (for example: dietary prescriptions and adaptability for certain recipes).

As a result, FP becomes a sort of information medium. Important descriptions and useful data can be subdivided in different categories:

- 1. Chemical and organoleptic features of packaged foods; shelf life; FP, when the description is mandatory; environmental sustainability; etc.
- 2. Advices for the correct use: opening, closure, dosing systems, peculiar warranties, useful phone numbers, etc.
- 3. Information for correct disposal.

Several advices are mandatory; other data are placed on FP because of their interest for particular consumeristic groups. Anyway, the non-redundant placement of information on the final IFP can determine the success [40].

Texts, images and icons have to be organised with the aim of helping the 'targeted' subject to understand the IFP [41, 42]. In other words, consumers have to be helped when remembering well-defined pictorial hierarchies and visual symbols. This reflection should clarify the role of information: should targets be peculiar people classes with cognitive specificity or physical deficiencies (children, elderlies, etc.), every possible stimulus—touch, sound, etc.—is equally useful and necessary [35].

In addition, several images can give different information with the arrival of new digital technologies and applications for mobile phones, tablets and modern Radio Frequency Identification (RFID) analysers. One of these innovations is currently represented by 'active' and 'intelligent packaging' devices: these instruments can allow the prompt and complete traceability of IFP lots with precious information about the qualitative state of packaged foods [14–43].

With exclusive relation to the chemical viewpoint, some reflection has to be obligatorily made.

First of all, the 'correct' placement of pictures—including related dimensions and reciprocal positions—may represent the concrete expression of a precise design strategy for the creation of the 'best' FP, depending on available productive models and materials. In other words, the availability of particular materials, intermediate chemicals and correlated production technologies can surely influence the dimension and other visible features of texts and images.

The formulation of printing inks and coatings may be very complex. For example, the following list shows a synthetic and non-exhaustive choice of pigments, resins and additives for food and non-food printing inks [44]:

- Inorganic pigments: titanium dioxide (white), carbon black (black), powdered aluminium (aluminated effect), 'Prussian blue' or Fe₄[Fe(CN)₆]₃ · xH2O
- Organic pigments: azo pigments; beta-naphtol pigments; dioxazine pigments; quinophthalone; toluidine red—'International Union of Pure and Applied Chemistry ' (IUPAC) name, (1Z)-1-[(4-methyl-2-nitrophenyl) hydrazinylid-ene] naphthalen-2-one
- Mineral fillers: kaolin types
- Optical brightener agents
- · Photoinitiators like isopropyl thioxanthone, also named ITX
- Plasticisers
- Waxes
- Wetting agents
- Binders: rosin resins, maleic resins and alkyd resins
- Solvents and diluents: mineral oils, fatty acid esters and vegetable oils (soy bean oil, linseed oil, etc.)
- Siccative agents, also known as drying accelerators for oil coatings (alkyd resins) and printing inks: cobalt and cobalt-free carboxylates. For cobalt-free compounds, manganese and iron appear good options.

The choice of best pigments or coatings depends on metallic supports (with relation to the presence of aesthetical failures) and the possible presence of 'strange' colorimetric features of the packaged product. For example, the known 'ghosting effect'—the appearance of 'negative' pictures on inner surfaces of metal cans, while 'positive' images are printed on external surfaces—can be avoided [36] by:

- 1. Augment of polymerisation temperatures into ovens,
- 2. Increase of polymerisation times into ovens,
- 3. Use of different printing inks without affinity for inner coatings.

Secondly, digital technology seems to have displayed new options when speaking of relations between FP users and IFP consumers. At present, FP failures, including future imperfections because of different causes, can be detected and examined easily by means of image analysis software. Similar studies have already been carried out in different fields like chemistry of conservation and restorations. With exclusive reference to food packaging analyses in the EU, the main goal should be to define and develop reliable procedures for rapid FP controls. Should these systems be created and used by FM, the correct and mandatory 'assessment of technological suitability to the intended use' for FP would be easy, economically convenient and demonstrable without complex analytical protocols [10].

2.2.6 Environmental Requirements

At present, environmental sustainability is extremely debated in different fields. One of major concerns is the problem of packaging wastes [26, 45, 46]: this important issue cannot be solved with recycling activities despite notable improvements in recent years from the regulatory and the technological views. In fact, packaging design has been progressively oriented to environmental topics: useful demonstrations are the study of 'green' materials and the concomitant reduction of volumetric capacities and consumed energy in the 'carbon footprint' perspective. However, more efforts are still needed.

The simple quantitative approach to the problem of FP wastes may 'mask' other qualitative critical points: the uneasy separation of joint components and the consequent 'contamination' of mono-material recycled materials; the wide use of composite packages ('hybrid' packaging without a well-defined material classification), the presence of materials difficult to identify etc. As a result, the final performance or 'yield' of industrial recycling—the ratio between the quantity of reusable matter and the initial waste—cannot reach 100 % [34].

For these reasons, the maximisation of material recycling may be obtained if qualitative and quantitative factors are taken into account in the design step. However, environmental requirements have to be satisfied with productive and marketing needs [47], including also the clear separation between food macro-categories and related chemical concerns (different contamination episodes etc.).

It has to be noted that FP environmental requirements do not constitute a single category without other connections: the environmental defence involves different aspects [48, 49], including FPM recycling: on this level all packaging requirements have to be considered.

2.2.7 Regulatory Requirements

Regulatory requests have to be carefully considered when speaking of packaging design. The complete and exhaustive analysis of the regulatory situation in different macroeconomic areas should be highly recommended: however, this discussion is not the basic aim of this book. On the other hand, it may be displayed here a brief and synthetic description of the current EU regulatory concerning FPM.

Existing EU Regulations, norms, voluntary standards and protocols may influence designers' choices: at the same time, chemical features of FP and IFP are dependent on mandatory requirements because of different factors including food safety also. With exclusive reference to FP and features of single materials, the interested reader is invited to consult more specific references.

With relation to EU countries, two regulatory protocols have notable influence on the work of FP designers. By the chemical viewpoint, main requests can be summarised as follows.

First of all, every packaging material for food contact applications has to comply with the Regulation (EC) No 2023/2006 with concern to the obligatory implementation of a system of 'Good Manufacturing Practices' (GMP) by FP producers, distributors and industrial users of FPM and FP. This approach should assure the 'quality' of food contact approved materials and give adequate warranties about the control of the above-defined quality.

In other words, all FP have to be compliant with all applicable norms and defined quality standards with express reference to the intended final use. Anyway, FP is not allowed to cause risks to human health and modify the composition of packaged products with consequent unacceptable failures, including every variation of organoleptic features. It has to be noted that variations are always referred to packaged foods instead of the whole IFP. However, it should be also remembered that all possible damages or modifications of FP can affect the qualitative and quantitative composition of packaged products.

Another important document, the Regulation (EC) No 1935/2004, concerns basic features of food contact approvable materials.

In detail, FP have to be compliant with existing GMP; consequently, they cannot transfer excessive amounts of foreign components to packaged foods in normal and predictable conditions. The final aim is to avoid that contaminated foods may (a) be harmful for the human health and (b) determine unacceptable modifications of food products with reference to composition and sensorial features. Naturally, the chemical composition is inextricably connected to organoleptic features: every little chemical modification may be easily recognised by means of simple sensorial testing methods.

An interesting example concerns processed or analogue cheeses. These products are normally packaged in thermosealable and flexible FP. At first, packaging materials are sold, delivered and stored near FM as simple spools. As a result, the final shape and aspect of packaged cheeses are different from the initial shape of FP before use.

For this reason, the detection of sensorial failures may be easily carried out by operators before use. This obligation is named 'evaluation of technological suitability' in the EU [5]. However, food operators should know or be aware of FP possible failures and complications because of incorrect storage conditions, for example. As a result, it may be assumed that the above-mentioned cheeses may show abnormal colours on surfaces because of the emersion or visible appearance of red spots. Actually, this phenomenon may have distinct causes:

- Food contact transfer of red colorants (printing inks) from the external surface of FP to the inner surface of spools (this situation is known as 'ghosting' effect) and subsequent migration of red inks on food surfaces
- Chemical modification of superficial colours by microbial spreading.

The first cause is clearly dependent on FP. However, the simple storage in incorrect conditions of spools—high temperature and light exposure—can easily worsen observable defects. Similar failures may be easily discovered before use.

The second situation is dependent on microbial spreading. Generally, one of credible causes is the abundant production of red pigments like prodigiosin: molecular formula: $C_{20}H_{25}N_3O$, IUPAC name: (2Z,5Z)-3-methoxy-2-[(5-methyl-4-pentyl-1H-pyrrol-2-yl) methylidene]-5-pyrrol-2-ylidenepyrrole. This pigment is produced by coliform bacteria like *Serratia marcescens* [50].

The occurrence of such a similar contamination can be attributed to simple FP environmental contamination by means of aerosolised dispersions into food production plants. However, the possibility of cheese contamination is initially taken into account [51].

In addition, packaged cheeses show often other interesting and unpleasant features: the augment of moisture is generally concomitant with the weak decrease of fat content values [51, 52] and the notable diminution of proteins. The subsequent production of sulphur amino acids, simple hydrogen sulphide and low molecular weight (MW) molecules by casein decomposition is correlated with (a) excessive cheese softness and (b) negative oxidation-reduction potentials. Basically, these conditions are caused by microbial spreading (coliforms, other lactose-fermenting bacteria and proteolytic micro organisms). However, it should be noted that high environmental humidity can cause the same problem when stored FP are quite able to absorb aqueous vapours on surfaces. This situation highlights the importance of good manufacturing practices in FPP and food production plants also.

Regulation (EC) No 1935/2004 considers all possible FP, including 'active' (also named 'smart') and 'intelligent' objects and materials (Sect. 2.2.1) [14]. Actually, the complete regulatory panorama is extremely complex and in continuous evolution: as a consequence, a single FP or packaging component should be examined on the basis of the above-mentioned Regulations and other national and EU protocols concerning other important aspects of IFP and FP (examples: nutritional labelling, restrictions of use for peculiar materials according to REACH legislation etc.). The interested reader is invited to consult more specific references.

Additionally, there are also specific and 'voluntary' protocols with relation to quality systems, food safety, environmental management, etc. At present, food safety and quality assurance are jointly managed according to most recognised quality standards:

- The ISO 22000:2005 norm by the International Organisation for Standardization (ISO)
- The Global Standard for Food Safety (GSFS) by the British Retail Consortium (BRC)

- The International Featured Standard (IFS) Food, by the IFS
- The 'Food Safety System Certification' (FSSC):22000 by the Foundation for Food Safety Certification.

With reference to FP, other voluntary norms have been recently created: the most known of these protocols is the 'BRC/IOP Global Standard for Packaging and Packaging Materials' by the BRC and the Packaging Society, formerly known as the Institute of Packaging (IoP).

All the above-mentioned standards are completely voluntary. However, FM or FPP cannot supply main mass retailer groups without one or more of related certifications. As a clear consequence, FP designers have to comply with 'voluntary' requirements also, in spite of their unmandatory nature [5].

2.2.8 Food Packaging Materials: Composition, Production, Chemical Features and Correlations with Packaging Design

This Section is dedicated to FP from the viewpoint of chemistry. Actually, the chemical composition of raw materials, intermediates and finished packages can influence and/ or be influenced by designers' choices. In particular, the group of functional requirements is strongly linked to the chemistry and the technology of FP and final IFP. As a result, the careful examination of FP should be recommended and possibly correlated with functional requirements.

First of all, the classification of FP has to be made on the basis of a few parameters. Normally, two approaches may be tried:

- FP can be classified on the basis of the used raw materials and the final appearance [53]
- On the other hand, FP may be classified depending on the final use or food destination [5, 54].

The first approach has been chosen with reference to this book because many of possible advantages and failures for FP are dependent from the chemical nature of non-edible materials. After all, one peculiar food can be packaged with 'n' different packages: as a result, 'n' different behaviours may be expected depending on the peculiar container. Every FP category can be now discussed in relation to:

- · Simplified subcategories of food containers or separated components
- Used raw materials
- The simplified description of FP structures
- Advantages and possible failures of final IFP
- Correlations with functional requisites.

2.2.8.1 Metal Packages

The well known 'tin can' is simply the first and most recognisable subtype of metal container for food applications [5, 36].

Actually, the first mention should be made with exclusive reference to key properties of original raw materials [54]. As a consequence, metal containers have following positive features:

- Notable rigidity and tensile strength
- Excellent 'barrier effect' against light, other external agents and penetrating fluids or solids
- High density for steel-made FP
- · Low density for aluminium-made FP

By contrast, these containers cannot be sealed without adequate plastic or metallic closures. In addition, metallic and plastic raw materials can interact with edible foods [54]. These basic features depend mainly on the composition of basic supports: steel or aluminium.

Steel Supports

Basically, steel materials can be found on the market of metal containers in different forms, depending on the peculiar composition and protection processes against the metallic corrosion. Generally, three materials are fully recognisable at present.

Electrolytic Tin Plate (ETP) is a low-carbon steel with a thin superficial coating. This protection is obtained by the electrolytic deposition of metallic tin on the surface of black carbon steel coils. The structure of ETP is complex enough. With the exclusion of the steel support, following layers may be observed [36]:

- Intermetallic iron-tin complex (FeSn₂), with approximate thickness of 10^{-4} mm
- Metallic tin, approximate thickness: 10^{-3} mm
- Mixed oxides of tin and chromium: SnO₂, SnO, CrO₃; approximate thickness: 10^{-4} mm
- Calcium carbonate (from normal washing treatments), variable thickness
- And finally an organic layer such as dioctyl sebacate (DOS) against the superficial oxidation.

It should be noted that DOS and similar 'protections' cannot prevent chemical interactions between food products and non-coated metal surfaces. For this reason, steel-made packages are usually coated with organic resins and enamels with the aim of avoiding the direct contact between tin surfaces and 'attacking' foods such as white fruits and tomato-based products [54]. Another good support is Tin Free Steel (TFS), also named 'Electrolytic Chromium oxide Coated Steel' (ECCS). With relation to this material, the original low carbon-steel coil is electrolytically

coated with a superficial layer of chrome/chrome oxide [54]. This material needs also an organic protection against the superficial corrosion.

Other possible materials could be 'black plates' or 'coke' tinplates. However, their use has to be carefully considered because black surfaces of uncoated steel plates are easily attacked by environmental oxygen and moisture. With reference to 'coke' materials, these supports correspond to the 'old' version of ETP materials: the deposition of metallic tin is highly irregular. Consequently, adhesion problems may occur when these materials are coated with organic resins or enamels [36].

Aluminium Supports

The first subcategory of metal containers is recognised as 'steel-made' FP because of the use of coated or uncoated steel supports. By contrast, the second subclass of metal cans is identified as 'aluminium-made' FP because of the use of aluminium alloys. It has to be noted that peculiar features of these materials (ductility and low density) determine the final destination of FP.

Chemically, it can be affirmed that aluminium 'alloys' contain also manganese, magnesium and other metals in very low proportions. Normally, mechanical performances can be modified with the addition of non-aluminium metals, magnesium and manganese above all [54]. Another interesting property of aluminium alloys is the impossibility of welding processes differently from ETP; actually, ECCS also cannot be welded. Consequently, aluminium-made containers are generally defined as 'two-piece' FP because of the subdivision of the structure in a basic body and one mechanically-sealed end. On the other hand, steel-made containers can be produced as 'three-piece' metal cans (one body and two ends), 'two-piece' single drawn, multiple drawn, and drawn and wall ironed cans [5, 36, 54].

It should be added that aluminium-made containers are necessarily coated with organic coatings on the inner (food-contact) side for preventing damages to metallic surfaces by foods.

Simplified Description of Metal Containers

It can be also assumed that the description of metal containers is difficult enough: many subtypes of steel-made FP are possible, and the same thing can be affirmed when speaking of aluminium cans. However, a simplified description can be given when speaking of the 'old' three-piece metal can. This steel-made container has the following features [5, 54]:

• The external appearance of the packaging is determined by the presence of a single 'body' with a cylindrical shape. This cylinder is obtained by the welding on two different sides of the same steel sheet. For this reason, ETP materials may be used while TFS/ECCS or aluminium supports cannot be considered

- Two different but similar 'can ends' are applied on the body with the aim of assuring the complete sealability and the protection of contained foods against external agents. The junction is mechanically assisted without welding. For this reason, a thin layer of organic product (polyvinyl chloride gaskets or similar products) is interposed between body and end surfaces because the simple mechanical junction may be insufficient for hermetical closures
- Can ends are normally available as regular or easy-open ends, depending on the specific need and requests of FM. Easy-open ends are also known as 'stay-on tab' systems. The last of these ends is specifically designed for drink (aluminium) cans [54]
- Generally, external and inner sides of body and ends are coated with organic lacquers or enamels. Several exceptions may be tolerated when speaking of non-aggressive foods (examples: weak acid fluids). On the other side, acid or high-pigmented foods such as *harissa* sauces may easily attack metallic surfaces with the consequent corrosion and the dissolution of metallic ions into foods and FP damages. In addition, the external appearance of 'tin cans' is decorated with lithographic systems (Sect. 5.1.2). With the exclusion of two-piece drawn and wall-ironed containers, coating and lithographic operations are made on flat, coil or sheet metal supports. Every coating, enamel and printing ink has to be cured into conventional ovens or under UV lamps: the curing process implies the polymerisation of pre-polymerised resins.

Metal Packages: Advantages and Possible Failures of the Final Product

Many metal containers seem to define a peculiar class of preserved foods. In detail, the description 'canned food' means a diversified but well known miscellany of IFP. The following list is not exhaustive, but several of the most important 'canned' products are mentioned here:

- Canned fish
- Preserved vegetables (peas, maize, beans, ...)
- Vegetable oils

With relation to canned foods, following advantages should be always taken into account:

- Easy preservation, depending on the peculiar preservation during and after the packaging
- Low storage temperatures are not strictly required
- The final IFP is extremely resistant against mechanical damages during transportation and storage steps
- The presence of reduced air into packaged foods is one of main requirements for acceptable closures. As a result, it may be assumed that 'regular' canned foods should not suffer problems by air oxidation

2.2 Functional Requirements

• Finally, thermal treatments (pasteurisation, sterilisation etc.) require that used FP may be resistant enough to sudden temperature leaps. This feature may be a problem when using certain FP, but metal containers should comply with this important requisite. In addition, metal cans may be also used as cooking, self-heating or self-cooling instruments [5].

On the other side, different problems and failures can occur. Actually, defects of the final IFP may be seen as the 'other side' of metal containers because of the insufficient, defective or lacking performance of FP and/or foods. Anyway, it may be assumed that the most part of all known features are related to the chemistry of metal FP, their intermediates and food products.

The following list shows most known defects of canned foods with a chemical origin and the related explanation [5, 36, 54].

Corrosion of Metal Supports and Dissolution of Metallic Ions into Foods

The detection of iron, tin, chromium, copper ions or other foreign metals into certain acid foods (hot sauces etc.) or preserved fruit juices is caused by:

- Insufficient coating of metal surfaces by organic lacquers or enamels, and/or
- · Presence of micro or macro bubbles into organic coatings or enamels, and/or
- Presence of micro scratches on coated surfaces.

Anyway, four results can be observed: (1) the attack of uncoated metal surfaces by organic acids or pigments from foods; (2) the detection of metallic ions into foods; (3) the dissolution of inorganic elements from demolished white enamels when used (many metallic FP are white-coated on the inner side; white enamels contain usually titanium oxide) and finally (4) the partial demolition of organic networks (lacquers, enamels) with the possible detection of suspect intermediates.

The fundamental role of tin as a sacrificial anode in the corrosion process should be highlighted. However, this process is not rapid because of the superficial presence of hydrogen. In addition, superficial iron would be demolished by food products without tin protection with chromatic alterations, off-flavours and can swelling [54]. Anyway, critical factors for the dissolution of tin are generally: storage temperatures, the extension of uncovered areas, insufficient coating thickness, excessive amount of residual oxygen, passivation, high acidity and notable quantities of organic pigments in certain products. The possible presence of 'catalysing' ions such as nitrate should be also remembered [54].

Other contaminants may cause notable worries [5, 54]. The dissolution of iron may cause colorimetric modifications in peculiar foods. Aluminium could cause cloudiness or haze in sensitive beverages (beers). Sulphur staining (blue-black or brown marks on the inner side of coated ETP- or TFS- cans) is well known. The critical factor is the presence of foods with notable protein amounts (peas and fish). In fact, the attack of hydrogen sulphide (H₂S) to coated tin surfaces causes the formation of iron sulphides, oxides and hydroxides (black or brown substances). Normally, the solution is offered by 'zinc oxide' (ZnO) paste: this fluid material is

produced with epoxyphenolic resins and added to organic coatings for food-contact side. The reaction between H_2S and metallic surfaces produces white zinc sulphide instead of black substances. However, the defect may be important depending on the quantity of added ZnO paste. Moreover, the occurrence of white or black colours is important because of the demonstration of the chemical permeability of epoxyphenolic coatings with relation to acid attacks.

Corrosion of Metal Supports and Other Failures

The corrosion of metal supports can be cause of different failures. One of most discussed dangers in recent years has been the detection of bisphenol A and other chemicals (intermediates in the production of selected organic resins) such as bisphenol A diglycidyl ether in foods [5, 54]. In fact, organic lacquers are generally produced and used as dispersions of selected pre-polymerised matters: epoxyphenolic, epoxidic, polyester, vinyl resins etc. These coatings are usually deposed on metallic surfaces and cured at different temperatures into dedicated ovens. For example, a general epoxyphenolic coating may be completely polymerised on metal surfaces after 15 min at 200 °C, with the exclusion of UV lacquers [55]. Superficial organic layers are very thin (up to 15 μ m), but several differences might be observed. Anyway, every can coating, enamel or similar product should assure [5]:

- Good resistance to thermal treatments (sterilisation, pasteurisation etc.)
- · Good mechanical resistance to impacts, drawing and stretching
- Excellent chemical inertness
- Absence or reduction of food adhesiveness (packaged foods may adhere to organic surfaces such as canned salmon in polyester-coated cans).

Anyway, the detection of organic intermediates in foods may have following causes [5]:

- Superficial fractures, presence of damaged micro bubbles (also named 'blistering' effect)
- Incomplete reticulation (polymerisation) of pre-polymerised resins on metal surfaces
- Rheological instability of liquid coatings, including storage failures
- Partially active fractions of organic resins and/or inks. Ink residues may be transferred from the external to the inner side of cans because of the simple contact between unassembled sheets. This defect is named 'ghosting'
- Insufficient adhesion of coatings to metallic surfaces (low chromium amounts mean low chelating effects).

Other can failures without direct food safety consequences concern the external side: once more, origins are related to chemistry and process controls [5]:

- Chemical incompatibility between enamels and printing inks
- Chemical incompatibility between inks and the finishing or transparent coating

2.2 Functional Requirements

- Superposition of different inks on the same zone
- Excessive water quantity (printing inks are hydrophobic)
- Presence of micro water bubbles in the printed area after sterilisation (also named 'meshing' effect).

2.2.8.2 Glass Packages

Glass bottles, jars and similar containers have a long historical tradition [56].

From a general viewpoint, glass is a versatile material for food and non-food applications. Normally, following properties are well known and recognisable when speaking of similar containers [53, 56]:

- Chemical inertness
- Impermeability
- Transparency
- Rigidity
- Breakability
- Virtual endless reusability
- Superficial properties (smooth appearance, roughened ice-like effect etc.)
- Different shapes
- Perceived hygiene

By contrast, glass packages are surely fragile and are not usually closed with glass systems because of the insufficient hermeticity. Mentioned features depend strongly on the peculiar chemical composition and possible differences on the market. Moreover, the importance of recycled materials cannot be excluded: 50 % and more of the total amount of raw materials for glass containers are recycled at present.

Chemical Composition of Glass Materials

It may be affirmed that glass corresponds to a melted mixture of silica, lime and soda materials [56]. The result of the fusion may be defined as a metastable system: the ordered glass network is continually 'blocked' in one of the possible high-energy viscous structures, from the thermodynamic viewpoint. By contrast, the most preferred structure should be highly chaotic and fluid.

Five main typologies of glass materials may be recognised at present [56]:

- White flint (or clear) glass
- Dark green glass
- Pale green glass
- Blue glass
- Amber glass

White Flint Glass

Basically, 'clear' glass corresponds [56] to the 'pure' melted mixture of silica (72%), lime or calcium oxide (12%) and soda or sodium oxide (12%). Other minerals may be present depending on the composition of original raw materials: alumina, magnesium oxide and potassium oxide. The 'neutral' appearance is function of the absence of chromatically recognisable mineral elements with distinct colours. In other words, the 'white' and completely transparent glass corresponds to a tri-dimensional matrix based on silicon, oxygen, sodium and calcium. This network contains many intra-molecular empty spaces, also named 'vacancies', with the possible addition of different metallic ions. Should vacancies be filled with a metallic cation, the macroscopic network should appear as a coloured and possibly transparent matter to an external observer. The absence of recognisable colours is function of silicon, sodium and calcium.

Dark Green Glass

This material is obtained [56] by means of the addition of chromium oxide (Cr_2O_3) and iron oxide (Fe_2O_3) to glass mixtures. Chemically, empty spaces are filled with chromium and iron: the result is the 'dark green' appearance of the network. Actually, the intensity of blue-green colours is mainly caused by the prevailing amount of trivalent chromium if compared with iron.

Pale Green Glass

This material, also named 'half white' glass, is obtained by means of the addition of Fe_2O_3 and Cr_2O_3 with the abundance of iron (green colour) if compared to trivalent chromium [56].

Blue Glass

Normal 'blue glass' can be obtained by means of the addition of cobalt ions to glass mixtures with low abundance of iron [56]. It should be considered that 'blue' types are very expensive in certain productions: as a clear result, blue bottles for carbonated soft drinks or mineral bottles may be expensive. The same thing can be told for the final IFP. For this reason, the chromaticity of certain beverages may be discussed with the aim of obtaining the desired colour of bottled products with transparent containers (Sect. 4.3.1).

Amber Glass

The last type of glass material is widely used in the market of light-sensitive beverages because of the 'filtering' function against UV rays (Sect. 4.3.1). The brown aspect of related bottles can be obtained by means of the addition of ferric ions to glass mixtures: ferrous ions should be much reduced [56]. In addition,

carbon atoms are inserted in the tri-dimensional matrix, while chromium should be virtually absent [57].

Simplified Description of Glass Containers

Glass containers for food applications are generally subdivided in two categories [5]: bottles (for wines, beers, mineral waters etc.) and jars. Actually, different types and subtypes of glass FP can be designed. However, the most part of similar containers are often found in these two groups.

Anyway, the basic concept is not strictly related to the chemical composition of mineral mixtures. On the contrary, the shape of final containers is often determined after the evaluation of different factors [56]:

- Type of food product
- Volumetric capacity
- Type of closure (metallic or plastic system)
- Dimension of necks
- Typology of the filling process. Beverages and fluid foods may be hot-filled with possibility of pasteurisation, sterilisation, mixes systems, etc.
- · Mechanic resistance of filled containers when piled up into pallets
- Necessity of UV protection for packaged foods.

With reference to bottles and jars, the description of forming procedures ('press and blow', 'blow and blow', and 'narrow neck press and blow' processes) may be not interesting when speaking of pure design and relations with chemical features of FP and IFP. On the contrary, surface treatments can be discussed.

In detail, the 'hot-end treatment' is designed [56] to prevent superficial damages on hot bottles (at the end of forming procedures). As a result, the strength of containers should be improved. Generally, tin oxide is used as coating; lubricant additives should be also used because of friction risks.

Alternatively, the 'cold-end treatment' may be used on annealed containers (residual strain has been removed). In detail, glass surfaces are lubricated with the addition of polyethylene, waxes etc. [56]. The discussion of this system can be important because several adhesive labels may not adhere properly to treated surfaces in spite of the presence of adequate dextrine products as adhesives.

Another important discussion should be made with concern to closures. At present, plastic or metallic caps are used for the most part of bottles despite the presence of common cork closures for wines [56]. Normally, following solutions are available:

- Tight fitting plugs
- Screw threaded caps
- Metal caps.

Other closures are possible with excellent results with relation to hermeticity [56]. Anyway, available closures are defined 'normal', 'vacuum' or 'pressure' seals depending on the peculiar system and the type of packaged product.

Glass Packages: Advantages and Possible Failures of the Final IFP

With relation to recognised advantages, glass materials have been already discussed. Generally, following properties are considered with positive results in the food sector [56]:

- Chemical inertness
- Impermeability
- Transparency
- Rigidity
- Breakability
- Virtual endless reusability
- Superficial properties
- Different shapes
- Perceived hygiene
- Retention to carbonated drinks.

In addition, the possibility of different printing techniques and labelling choices should be highlighted. On the other hand, possible failures of glass FP should be discussed with relation to the safety and integrity of the final IFP [5]. In detail, the following situations should be considered [5, 56, 57]:

- Superficial defects, including foreign bodies. Examples: micro 'stones'. Detection by means of scanning electron microscopy and X-ray microanalysis
- Micro bubbling. Detection by means of optical microscopy
- Micro fractures
- Scratches (forming and glass annealing procedures)
- · Colorimetric variations. Detection by means of optical microscopy
- Insufficient UV protection (for light-sensitive foods)
- Mechanical damages (insufficient strength)
- Insufficient adhesion (when self-adhesive labels are used), including also the presence of condensate on glass surfaces
- Closure failures
- Defects by washing treatments
- Gradient failures
- Sharp edges, scraps and shivers
- Weathering of the inner surface (during storage, usually for white flint glass)
- Insufficient cleanliness, when speaking of reusable FP.

In particular:

- For micro bubbling, the total elimination of air bubbles in glass matrices should be obtained with the 'gradient' prolongation of melting procedures. Otherwise, micro air bubbles may 'force' glass structures to exhibit crystalline-like behaviours and thermodynamically-favoured amorphous structures. After all, containers can suffer possible fractures where micro bubbles are present

2.2 Functional Requirements

- With relation to colorimetric variations, this failure can be important for two reasons. First of all, many preserved foods are requested to exhibit uniform colours. This requirement should imply that transparent (coloured or 'white') glass jars show a defined and constant colorimetric tint, where expected [5]. However, the presence of different atoms with small amounts (iron, chromium etc.) has to be evaluated when speaking of normal jars by recycled glass materials. Because of the abundance of recycled matters, chromatic modifications of glass containers should be expected and possibly minimised, similarly to 'stones' and micro bubbles. These defects are virtually detectable in all possible glass containers. For these reasons, the use of optical microscopy and digital imaging techniques for the analysis of colours [10] can be very useful. In addition, colorimetric variations may damage several light-sensitive foods (insufficient UV protection) with clear worries for food packagers and producers
- The so-called 'weathering' of glass FP may be very important in the food sector because of the necessity of avoiding food contacts with abnormal surfaces. In detail, weathered surfaces of soda-lime silicate glasses show irregular white deposits of sodium and calcium carbonates [58]. The defect may be avoided or limited if environmental conditions are monitored with reference to the relative humidity. Generally, the best strategy for the examination of incorrectly stored glass materials is the visual evaluation, while other most sensitive procedures (electron microscopy, adsorption of generated alkali) appear useful for research purposes [59]
- The problem of the insufficient adhesion (with self-adhesive labels) is mainly caused by the presence of condensate on glass surfaces. Normally, glass has to be conditioned thermally to prevent this situation. However, 'cold end' containers show lubricated glass surfaces with the use of water-based polyethylene emulsions, derivatives of polyester waxes, etc. [56]. Actually, other substances might be used: soaps, stearates, silicones, glycerides, oleic acid, etc. However, their use is very limited or rejected by FM. For example, breweries should not accept oleic acid as lubricant for glassware in spite of the easy removability and low lubricant properties during storage periods, because of the possible flavour alteration of beers [60]. As a result, several adhesive labels may not adhere properly to treated surfaces. For this reason, new types of self adhesive labels may be designed for specific purposes: the formulation of adhesive products should contrast lubricating effects. Normally, casein adhesives are used extensively [61], but other solutions may be applied when high water resistance is required to labels for high speed processes [62]. Anyway, the problem can be also linked to the correct cold-end treatment: for instance, the use of water-base polyethylene emulsions requires the additional use of normal or distilled water. With the exception of nonionic polyethylene coating materials, the presence of calcium salts may affect the process and alter subsequent steps, including the choice and the adhesion of dedicated labels.

Glass Packages: Correlations with Functional Requisites

The good preservation and protection of foods in glass packages are strictly linked to the chemical inertness, the full or modified transparency and other variables: possible UV protection, impermeability to gases and vapours, rigidity and reusability [56].

Naturally, the inertness should be always assured: on the other side, several contaminations by alkali production (during the storage) and/or lubricant additives should be considered. However, the lubrication is absolutely needed for preventing superficial damages.

The transparency of glass containers is clearly expected by normal consumers: as a result, this requirement should be 'obvious'. Once more, superficial damages or weathering may cause important worries. In addition, the absence of peculiar colours (and the consequent UV protection of bottled beverages) may be seen as a distinctive advantage by the marketing viewpoint (Sect. 4.3.1) despite the number of available examples of glass FP with blue, amber and other colours [56].

Transportation and storage requirements are extremely important in the sector of glass containers and bottled beverages. For instance, beers and wines may require low storage temperatures. As a result, the final IFP must resist at least to the inner dilatation, the pressure of carbonated products and sudden bumps. In addition, the superficial appearance and the resistance to scratches have to be always assured.

With concern to operational requirements, glass containers may be used for 'ageing' packaged foods. This is not specifically true for preserved vegetables, sauces, seafood products and so on. On the other hand, red and some white wines can be initially aged in oak wood barrels and subsequently continue the ageing period in bottles for one or 2 years [63]. As a consequence, glass bottles can have a precise technological function with relation to the evolution of anthocyanins and non-anthocyanin phenolic compounds [64]. Naturally, the hermetic closure of bottles and the well known inertness of glass surfaces are important. In addition, glass packages are well recognised as resealable containers.

Finally, glass packages are reusable—the 'old' British example of fresh milk in reused bottles is well known—and easily recyclable with excellent results [56].

2.2.8.3 Plastic Packages

Plastic materials are used for the manufacturing of different food and non-food packages. With reference to food and beverage products, there are many possible solutions including also 'hybrid' packages: after all, the whole group of metal containers can be defined as the classic example of plastic/metallic container because of the synergic coexistence of metal supports and plastic coatings, enamels, gaskets and other organic components, including printing inks [54].

Probably, the classification of plastic packages may be very difficult because of two reasons:

2.2 Functional Requirements

- Every food or beverage may be associated with different packages, and
- The same plastic package may be designed and redeveloped with the aim of obtaining similar performances with different food products.

As a consequence, the best strategy could be the subdivision of the whole range of plastic FP in four macro categories without a direct food correlation. According to this approach [5], plastic packages for food applications may be classified and described as follows:

- · Rigid and semirigid containers
- Flexible FP
- Polycoupled FP (these containers are different from flexible containers and plastic components)
- Plastic components for plastic and hybrid packages.

Rigid and Semirigid Plastic Containers

This macro category contains many typologies of plastic FP with peculiar features and different destinations. Generally, rigid plastic containers are produced [65] as:

- Bottles and jars (main competitor for this type of FP: glass packages)
- · Trays and boxes
- Drums, intermediate bulk containers, crates, etc.
- Expanded or foamed plastic containers.

The rigidity of these containers may be strengthened or diminished depending on the composition of plastic mixtures. Normally, semirigid containers contain different polymeric materials and several additives with the aim of enlarging the possible range of plastic containers: economic reasons are certainly important, but other factors can be part of the final decision, including packaging disposal requirements.

Flexible Plastic Packages

This heterogeneous subgroup of plastic FP comprehends [5, 65]:

- Flexible heat-sealed bags, pouches and sachets
- · Flexible films with possibility of heat sealability near FP
- Plastic films for wrapping and similar uses. Example: regenerated cellulose films.

This nonexhaustive list contains different types of plastic matters. Once more, plastic components and polymers may be mixed or coupled (example: coextruded plastic films) with the aim of obtaining enhanced strength, impermeability to vapours or gases, etc.

Polycoupled Food Packages

The class of polycoupled FP is continually evolving: in fact, the most part of new designs and redevelopments may be found in this subsector of the plastic industry. Generally, following types are found in this category [5, 65]:

- Polycoupled packages (plastic films and paperboard foils are joint)
- 'Tetrahedral' package systems (plastic films, aluminium and/or paperboard foils are joint).

This classification is very simplified: however, the aim of this book is to give evidence of correlations between the design of FP and physicochemical features of containers and final IFP. The interested reader is invited to consult more specific references.

Plastic Components for Plastic and Hybrid Packages

Finally, the group of plastic components for a whole range of plastic and 'hybrid' applications is mentioned. Actually, the below shown classification should also take into account the notable class of intermediate plastic films for coupling purposes. Following components may be mentioned [5, 36, 64]:

- · Plastic lacquers, enamels, gaskets and printing inks for metal containers
- Plastic lids and caps (for closures)
- Plastic seals
- Dispensing systems
- Adhesive films, labels, etc.

Once more, the composition of these accessories can be diversified. In addition, there are not reasonable connections between the shape or other visible features of separated components and the chemical composition, with some exception. In fact, many factors—economic convenience, logistics, environmental policies, commercial requirements, etc.—should be considered; anyway, the final destination of FP has to be considered first.

On these bases, the discussion should now consider main plastic materials for food packaging applications. It can be anticipated that chemical features of polymers and plastic additives may heavily influence the design of a specified food packaging, although a whole range of intermediate possibilities and 'compromises' between different requests may be obtained.

Main Plastic Polymers

At present, the use of polymers for FP applications is mainly oriented to following chemicals [5, 36, 64]:

2.2 Functional Requirements

- Polyethylene (PE), also defined as 'low density polyethylene (LDPE), 'high density polyethylene' (HDPE). Other types are available
- Polypropylene (PP). Different varieties are available, including oriented polypropylene (OPP)
- Polystyrene (PS), including also expanded polystyrene (EPS)
- Polyvinyl chloride (PVC)
- Polyesters: polyethylene terephthalate (PET or PETE) and other varieties
- Polyvinylidene chloride (PVDC)
- Polyamides (PA)
- Ethylene vinyl acetate (EVA)
- Various ionomeric materials
- Ethylene vinyl alcohol (EVOH)
- Fluoropolymers
- Derivatives of cellulose.

This list cannot be exhaustive because of the complexity of the market of plastic matters [5]. After all, the most part of polymers for FP production are PE, PP, PVC, PET and PS, while other raw materials are destined to peculiar applications. Anyway, the most used matters are thermoplastic polymers: they can be produced and subsequently reworked with the aim of obtaining different shapes and chemical mixtures without chemical degradations.

This simple consideration highlights the role and the importance of the preventive design and end-use properties [64]. The following features can determine the initial choice of the most useful polymers:

- · Resistance to tension and compression forces mechanical strength
- Heat sealability
- Optical properties (light reflection, transparency, etc.)
- Scratch resistance
- Permeability to gases and aqueous vapours.

On these bases, designers and FM may propose different containers for a single food product: the higher the number of available prototypes is, the larger will be the range of different IFP.

Moreover, the method of production can influence final properties of FP. Three different methods are recognised at present [5, 64]:

- Melting of polymers or polymer mixtures (with addition of stabilisers, colours, catalysers, etc.), extrusion and moulding (production of rigid and semirigid containers)
- Melting of polymers or polymer mixtures and realisation of thin layers by means of the passage through narrow slots or dies.

With reference to the second method, two different subprocesses may be applied [5, 64]:

- Melted mixtures are forced to pass through a narrow slot or die by means of two opposed cylinders. This 'cast' procedure is specifically used to obtain thin films and sheets for coupling or coating applications
- Melted mixtures are forced to pass through a die; subsequently, they are extruded with air pressure. This 'blow' procedure is specifically used to obtain tubular materials with specified diameters.

In addition, obtained films may be stretched in one direction (mono-oriented plastic film) or in two directions (biaxially-oriented plastic material). The aim is to strengthen mechanical resistances of films [5, 64] along one or two preferential directions: for example, the elongation may be reduced from 600 to 60 % [64]. An example of mono-oriented polymer is the linear low-density polyethylene (LLDPE); on the other side, biaxially-oriented polypropylene (BOPP) is very much appreciated for improved resistances. With reference to most used polymers, a synthetic description may be shown.

Polyethylene

PE is available in different typologies, depending on the polymeric density of produced materials. This plastic is obtained by the simple polymerisation of ethylene under high temperatures and pressures (Fig. 2.2). The density of materials is decided in the polymerisation stage [64], depending on temperatures, pressure and catalysers: in other words, polymerisation degrees may vary with the consequent decrease of 'empty spaces' in the tri-dimensional matrix of PE.

LDPE is usually considered for the production of films, sheets and other similar layered materials. It can be easily coloured (before extrusion), laminated and coupled with PP, EVA and other materials such as paperboard. LLDPE, a variety of LDPE, shows superior tensile and impact strength and puncture resistances [64].

On the opposite hand, HDPE represents the densest material. It is generally used for closures, pallets, crates, drums, rigid or semirigid containers because of the improved 'barrier effect' (impermeability to gases and water vapours) and the mechanical resistance if compared to LDPE [64]. An intermediate medium density polyethylene may be also used when HDPE properties are not strictly requested.

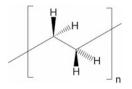


Fig. 2.2 A simplified chemical structure of polyethylene chains. BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure

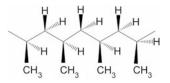


Fig. 2.3 The chemical structure of isotactic polypropylene. BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure

Polypropylene

This polymer can be seen as the main competitor for PE in the plastic industry because of the enhanced hardness, density and transparency.

Chemically, it can be produced by propylene with a dedicated addition process by means of Ziegler-Natta type catalysers [64, 66]. The resulting chain is polymerised under pressure and heat; the structure is always ramified because of the presence of external methyl groups (Fig. 2.3). It should be considered that PP is the best available thermoplastic polymer with reference to low density, high melting point and acceptable costs if compared with other thermoplastic resins. On these bases, PP may be worked to obtain rigid and flexible FP. Moreover, this polymer may be easily coupled (extruded and laminated at the same time) with other materials, including PET, PE, EVOH and PS. The final aim is to produce high resistant temperature films for thermosealed packages: thermosealing should be carried out between 115 and 130 °C. In addition, laminated materials should at least be fit for sterilising purposes [64, 67].

Other interesting features of common PP are:

- Excellent inertness against chemical agents
- Good or acceptable barrier properties
- · Low permeability to lipids
- Good resistance against plastic ageing (environmental stress cracking tests are normally very good for this material).

On the other hand, the resistance of PP to aromatic and aliphatic solvents is not good and should be ameliorated in spite of the known similarity between the above-mentioned solvents and propylene. Generally, PP can be produced also in the mono-oriented version, OPP or in the bi-dimensional type, BOPP. These materials can be easily laminated with acrylic resins with a general enhancement of all positive properties of the common PP. In addition, the problem of solvents and other impurities may be partially solved in this way [64, 68]. For these reasons, laminated acrylic/OPP and BOPP materials can substitute regenerated cellulose films.

Polystyrene

This polymer is widely known because of the versatility. In fact, the peculiarity of PS is the possible use for following products [64, 69]:

- · Packed jams
- Fruit products
- Fresh meats
- Pasta
- Salads
- · Cream yoghurts
- Yoghurt-based desserts
- Thermally treated milks
- Cheeses
- Margarines.

By the chemical viewpoint, PS may be seen as a different form of PP because of the substitution of methyl groups along the polymeric chain with a benzene ring (Fig. 2.4). It can be obtained by catalytic addition of styrene: the isotactic PS chain should be composed of approximately 1,000 styrene units [64, 69]. Generally, isotactic PS is known because of the adaptability to different uses; the atactic version is not good for food applications. Isotactic PS may be laminated for the production of monolayer plastic films. In addition, it can be thermoformed, moulded by injection and foamed. On these bases, isotactic PS can be used to obtain a wide range of FP.

Normal PS shows following positive features [5, 64, 69]:

- Good transparency
- High rigidity
- High chemical resistance at low temperatures;
- · Good compatibility with pigments in mixtures
- Good printability
- Good thermal resistance (up to 70 °C).

On the other hand, PS films have not good barrier effects to water vapour and atmospheric gases. On these bases, PS may be suitable for the packaging of 'respiring' vegetable products. Moreover, PS is strongly attacked by aromatic solvents [69].

Another defect of common PS is the well-known fragileness. For these reasons, the biorientation and the copolymerisation with other plastic monomers—styrene

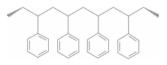


Fig. 2.4 The chemical structure of isotactic, semicrystalline polystyrene. BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure

butadiene (SB) and acrylonitrile butadiene styrene (ABS) copolymers are well known– is recommended. The final product is known as high impact polystyrene (HIPS). Interestingly, new products can be ameliorated with the coupling with PE, PP, PET, and chemically similar polymers. Anyway, the most known form of PS is surely EPS. Fundamental properties of EPS packs are the exceptional low density and the good thermal insulation [64, 69].

Actually, nine different types at least are available at present [5]; however, only pure PS and HIPS seem to be interesting in the food sector.

Polyvinyl Chloride

By the chemical viewpoint, PVC may be seen as a different form of PP because of the substitution of methyl groups along the polymeric chain with a chloride atom (Fig. 2.5). It can be obtained by the catalytic addition of vinyl chloride. However, the normal PVC is too hard and fragile. Consequently, the addition of plasticisers is necessary; on the other hand, the original material may show interesting properties [64]. Substantially, plasticisers are needed for obtaining more workable materials: preferably, PVC without additions is used for the production of rigid trays [64]. The addition of pigments is possible and preferable [64, 69]. On the other side, PVC is cheap enough [5].

Generally, PVC is prepared in suspension and in emulsion: mass or solution procedures can be also used. Anyway, radical initiators—peroxides and azo compounds—may be needed [5]. This aspect should be carefully evaluated with relation to the migration of packaging components into foods [5, 64].

It should be also noted that PVC obtained in emulsion may absorb water; the possible aqueous absorption has to be taken into account with concern to the packaging of perishable products: moisture vapour transmission rates are notable [5, 64].

On the other hand, PVC products show low adhesiveness, good compatibility with pigments, good weldability and sticking [5]. Actually, PVC is not always used for heat- sealable packages. In fact, other PVC applications concern extruded and oriented films for wrapping [64].

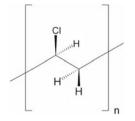


Fig. 2.5 The chemical structure of polyvinyl chloride chains. BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure

By the chemical viewpoint, PVC is recommended for fat foods and fluids, including fruit drinks, because of the remarkable resistance to lipids. In addition, good transparency and elongation properties should be signalled, while other mechanical features—tensile strength, etc.—have to be ameliorated with plasticisers. Another big concern is the low resistance to high temperatures: the production of hydrochloric acid has to be considered; moreover, the tendency of PVC to soften when temperatures exceed 80–95 °C is well known.

Another interesting property of PVC is related to barrier effects. Actually, the permeability to aqueous vapours and other gases depends mainly on the possible addition of plasticisers: normal PVC is very good when used as a barrier for these gases; however, the higher the presence of plasticisers is, the lower will be the barrier effect [64]. For these reasons, certain PVC films for wrapping applications may be recommended for 'respiring' vegetables and 'modified atmosphere packaging' (MAP) products—red-coloured meats above all—because of the notable permeability to oxygen [64].

Finally, PCV can be produced as copolymer: polyvinylidene chloride (PVDC) is well known for the production of flexible and thermoretractable films. Chemically, vinylidene chloride and vinyl chloride monomers correspond to 80 and 20 part, respectively of the definitive copolymer. The use of PVC for heat-sealed packages is not always recommended [5, 64].

Polyesters: Polyethylene Terephthalate

Normally, food technologists and other professionals with some involvement in the food industry are accustomed to speak of 'polyesters' instead on the main polymer of this category: PET or PETE. The chemical structure of this condensation polymer is shown in Fig. 2.6.

Chemically, PET is a thermosetting polymer with melting point of $260^{\circ}-265 \,^{\circ}$ C. It is obtained by the condensation of terephthalic acid and ethylene glycol ester monomers. When speaking of general polyester, the condensation involves a carboxylic acid and an alcohol [5, 64]. Because of the main importance of PET in the industry of food packages, this Section is dedicated to this polymer.

PET is well known and highly recommended because of the following features [5, 64]:

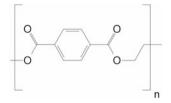


Fig. 2.6 The chemical structure of polyethylene terephthalate. BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure

2.2 Functional Requirements

- Excellent chemical resistance to different acids
- Excellent and ameliorable resistance to vegetable oils. The copolymerisation with phenolic resins is highly recommended on condition that production costs may be affordable
- Higher heat resistance
- Remarkable mechanical strength (oriented polymers)
- Absence of shrinking below 180 °C
- Absence of processing additives for the polymerisation
- Possibility of different applications. PET can be blow- or injection-moulded, foamed, used as a coating for paperboard packages, extruded for thermo-formable and heat-sealable sheets, oriented in two directions.

For these reasons, PET is recommended for high-temperature applications, including sterilisation, 'boil in the bag', cooking or reheating packages. When used for film coating, it can be coupled with HDPE, PP, PVDC, aluminium and EVA in extruded films: obtained results are the enhancement of the initial barrier effect (discrete values for oxygen) with relation to UV light. Moreover, PET can be metallised with aluminium [5, 64]: it is a medium oxygen barrier on its own, but becomes a high barrier when coated. Another possibility for the amelioration of impermeability is the coating of PET with silica [64].

On the other hand, it should be remembered that polyesters are thermosetting polymers: they cannot be remoulded after the final hardening. In addition, the modification of mechanic resistances may be made with the variation of functional groups, while subsequent additions of peculiar chemicals may be not useful in certain situations [5].

The copolymerisation is a deal for polyesters. Thermoretractable and biodegradable co-polyesters may be obtained by means of the polycondensation with substituted amines or synthetic starch [5].

Polyamides

PA are mainly known for the important presence of the original 'nylon' brand by DuPont [64]. Chemically, PA are obtained by the condensation reaction between a diacid and a diamine. On the other hand, various possible PA can be obtained with other monomers. With reference to industrial applications for food packaging, nylon 6 and nylon 6,6 can be used as valid competitors for PET: many of excellent features of polyesters are also shown by these PA. In addition, biaxially oriented PA films demonstrate good flavour and odour barriers. Anyway, the lamination with PVDC or PE can be used to ameliorate the above-mentioned features.

On the other side, one of main problems with PA may be the excessive aqueous adsorption. This aspect is correlated with the remarkable number of peptide groups on PA chains and the increased possibility of hydrogen bonds on three molecular levels [70].

Should this adsorption exceed 2 %, mechanic resistances might be enhanced with the concomitant augment of rigidity: this phenomenon can be very

important—and dangerous—when PA are moulded [5]. When speaking of MAP foods and 'respiring' vegetables, other problems may be observed [5]:

- The superficial oxidation of wetted PA films and the consequent yellow-to brown tint instead of the desired transparency
- The volumetric augment of certain packages because of the known permeability to carbon dioxide
- The strong adhesiveness, also named 'para-adhesion', between PA films and packaged foods because of the similarity between polymeric films and proteins.

Plastic Packages: Advantages and Possible Failures of the Final IFP

With relation to recognised advantages, it can be affirmed that:

- Plastic materials may be subjected to different productive processes such as moulding, extrusion, etc.
- These matters can be chemically inert and/or impermeable to different agents and food components
- Plastic polymers can be cheap enough if compared with other raw materials for similar packages
- These matters can show low density, good transparency, excellent attitudes to heat sealing and thermal processes, good or acceptable printability, etc.

These properties have been shown when discussing of PE, PP, PVC, PET and PA: in fact, the five classes of polymers can represent the whole group of plastic materials despite the presence of other extremely interesting polymers [5, 64, 69].

On the other side, possible failures of plastic FP should be discussed with relation to the safety and the integrity of the final IFP [5]. In detail, following situations should at least be considered [5]:

- Bubbling
- Undesired polymeric agglomerations—crystallites and separated accumulations—with consequent fragility and delayed fractures
- Micro fractures caused by (a) the incorrect thermal control during the orientation process and (b) heating and/or cooling steps
- Amorphous polymeric agglomerations in different zones. Causes: incorrect temperature and viscosity values during the orientation process
- Coupling failures. Examples: presence of inner creases, insufficient adhesion with air incorporation and bubbling
- Co-extrusion failures in multilayered packages. Examples: micro scratches; different flexibility of separated materials and consequent wrinkles
- Superficial opacity. Cause: reduction of extrusion-blow times with delayed and semi-amorphous polymerisation
- Moisture incorporation

- Superficial dripping, also named 'warping' or 'twisting', during the injection process
- Superficial blistering
- · Other defects: flash contamination and colorimetric variations
- Partial polymerisation. When speaking of coatings for metal cans, the phenomenon is named 'partial reticulation'
- Possible transfer of chemicals from printed images
- Plastic ageing under UV exposure and excessive storage temperatures.

The discussion of the above-mentioned failures has been partially made with relation to coatings for metal can packages and glasses. Other defects have been discussed when speaking of some peculiar property of PET and PA. The interested reader is invited to consult more specific references with relation to the chemistry and the technology of packaging-related failures of food products.

2.2.8.4 Paper and Board Packages

Paper and Board (P&B) packages have a long and historical tradition in the field of food and non-food containers. The use of waxed paperboard cartons has been extensively reported in the early twentieth century and the same thing can be affirmed for the old 'paper bottle'. This coupled container, the Pure-Pack, was composed of different joint layers: paper sheets, glues, wax coatings were used as containers for cream [53, 69]. After these packages, other containers have been proposed with interesting properties. Anyway, the main feature was always the coating of paper surfaces with synthetic polymers.

From a general viewpoint, P&B packages show the following positive features [5, 53]:

- Low density
- Good stiffness
- Absence of fragileness
- Excellent printability.

In addition, P&B can be easily folded, creased and coated with adhesive products (dextrines, etc.) for the subsequent assembling.

On the other side, the following negative properties should be considered [53]:

- (1) P&B materials cannot exhibit good barrier effects against water and chemical agents, including food and beverage mixtures. Paper adsorbs easily moisture, liquids and aqueous solutions
- (2) At the same time, P&B packages cannot be considered good insulating containers. Actually, coating or lamination treatments may modify this property with good results
- (3) Finally, paper materials do not show good tensile strength values if compared with metal supports.

On these bases, it can be affirmed that P&B packages can be used in a number of food and beverage applications. Moreover, three additional factors should be remembered [5]:

- (a) Related costs are quite low if compared with other containers. P&B packages do not seem to be influenced by recurrent economic crises in the same way of other containers for non-food applications
- (b) P&B packages may be reusable, recyclable, destined to the production of energy by combustion, etc.
- (c) Finally, there is a virtually unlimited availability of dimensions, shapes and destinations.

At present, 50 % at least of the yearly production of P&B packages are destined to food products [5]. The following list shows several applications [71]:

- Confectionery products, including also sugar, chocolate, etc.
- Dry foods. Examples: especially bakery products, coffee, tea, etc.
- Fluid foods and other beverages
- Chilled foods
- · Frozen products
- Meat, fruits and vegetables for fast consumption, with the exclusion of MAP products.

With reference to the common opinion of consumers, the main problem seems related to the identification between the so-called 'carton' and the real structure of modern P&B packages. In summary, it may be supposed that the main part of consumers consider folding cartons, paper bags and all possible P&B containers as simple accessories for foods. The superposition of different materials onto the main and structural paper support is not easily recognised.

By contrast, papers are obtained by the mixing of different raw materials [2, 5, 32, 71]:

- Vegetable fibres: cellulose, hemicellulose and lignin
- Adhesive products and glues. Examples: carboxymethylcellulose, modified resins, dextrines, etc.
- Paper colorant substances. Usually, these chemicals are inorganic pigments or optical brightness agents (OBA), also named fluorescent whitening agents
- Different additives for dry papers of synthetic origin, including PA and ureaformaldehyde resins, softeners, antistatic and antifoam chemicals
- Mineral fillers such as talc, kaolin, titanium dioxide, calcium carbonate, etc.

The use of similar formulations is strictly required for several applications. For instance, paper FP should not be formulated with the concomitant addition of glues and printing additives on the one side and mineral fillers on the other. In fact, talc or kaolin may easily reduce the superficial roughness of cellulosic plain packages with difficult printing. Moreover, the superficial hygroscopicity can be reduced.

With relation to the main support, the tripartite composition of cellulosic fibres might be questionable. However, cellulose and hemicellulose are the normal basis

for cellulosic packages. On the other hand, lignin—a non-carbohydrate polymer present in wooden fibres—may be seen as a natural strengthener of wooden plants. For this and other reasons, lignin appears to be an undesired presence between cellulosic fibres [5]: excessive amounts could compromise the desired homogeneity of produced sheets.

By a general viewpoint, the difference between 'paper' and 'paperboard' packages should be also considered. Paperboard is generally thicker than paper: in addition, the last material has lower weights per square meter. In fact, ISO defines paper materials over 200 g/m² as 'paperboard' or 'board' sheets.

The description of the technology of production of paper materials is not the basic aim of this book. Consequently, the interested reader is invited to consult more specific literature with concern to this matter. However, the process influences basic features of P&B containers: strength, colours, thicknesses, etc. As a result, it may be synthetically explained here that paper materials can be produced by the preliminary separation between original cellulosic and non-cellulosic fibres. Actually, used raw materials can be 'virgin'—or primary—and recycled, recovered or 'secondary' sources (40–60 % of the total quantity). The chemical pulp has to be obtained by means of the effective elimination of non-cellulosic components with 'sulphate' (also known Kraft) or 'sulphite' processes [71]. Actually, recovered papers have to be de-inked; the elimination of bleaching agents in recycled papers, mineral oils, etc. has to be also carried out. After pulping, cellulosic mixtures can be sent to sheet forming procedures, but the addition of selected chemicals—water repellents such as synthetic resins, OBA, etc.—is required before this stage.

General Classification of Paper and Paperboard Types

At present, the market of commercially available P&B shows an interesting variety. Basically, the difference is related to the average length of fibres: the higher this value is, the stronger will be the resulting material. By contrast, short fibres may mean an enhanced surface smoothness [71]. This is a preliminary classification.

The origin of fibres is also important: cellulosic materials can be available as bleached, unbleached, virgin or recycled types at the same time. In addition, parameters such as grams per m^2 values and thicknesses may notably vary; the same thing may be affirmed with concern to the superficial appearance of papers and the quali-quantitative addition of chemicals [5, 71].

The following list may show many of currently appreciated solutions for the industry of P&B containers, excluding corrugated boards, boxboards, chipboards and packaging containers for secondary purposes [5, 71–74]:

• Wet strength paper. This material is resistant to water absorption. The chemical modification is obtained by the insertion of cross-linked urea formaldehyde and melamine formaldehyde. Dry polymers should correspond to a sort of paper

coating. This material may be seen as a direct evolution of sack Kraft, the normal unbleached paper by sulphate treated-pulps. Grammages can vary from 70 to 100 g/m^2

- Micro creping paper. This material can be more stretched than usual
- Greaseproof, glassine and vegetable parchment types. The first material is hydrated with the aim of preventing greasy exudations (application: food products with emission of oil exudates). It can be also laminated. Glassine is a development of greaseproof papers with improved density and high glossiness. The third material is obtained by conventional chemical pulp after immersion in sulphuric acid. It shows enhanced grease resistance and wet strength
- Laminating papers (grammages: 40–80 g/m²). These materials are both coated and uncoated papers. The composition involves pulps based on both Kraft and sulphite pulps. Subsequently, sheets can be laminated to aluminium foils and extrusion-laminated with PE
- Aluminium laminated tissues for bags, wrappings and infusible paper packages. These lightweight tissues, obtained with low chloride and sulphate traces, show notable permeability and grammages from 12 to 30 g/m²
- Paper labels. These coated materials show grammages from 70 to 90 g/m^2
- Bag papers. These materials can be coated or uncoated, bleached or unbleached papers with 90–100 g/m²
- Wax-coated papers. These materials are treated with fluorocarbon dispersion treatments for improving grease resistances
- Solid bleached board (SBB). This material can be easily printed, embossed, creased, cut, folded and glued. For these reasons, the design of innovative packages can easily consider the use of SBB for the preservation of aromatic foods. Chemically, the primary support is virgin paperboard obtained by bleached chemical pulp. Surfaces are coated with mineral pigments on the external side or on both sides. It is different from solid unbleached board (SUB) type because of the origin: the last paper is made from unbleached chemical pulp and colours are brown, although the coating with mineral pigments may be required. SUB may be useful when high strength and/or good wet resistances are required for liquid foods.

This list is not exhaustive, but most important types of paper materials for FP are included here. With reference to coating materials, normal solutions are LDPE, PP, LDPE/EVA, PET, PA, EVOH, and polymethylpentene and ionomer resins.

Paper and Board Containers: Advantages and Possible Failures of the Final IFP

Possible failures of P&B packages should be discussed with relation to the safety and the integrity of the final IFP [5]. In detail, many situations may be observed. Following defects should be considered at least [5], although the list could be longer:

2.2 Functional Requirements

- Increased rigidity. Substantially, the incorrect mixture of glues in the second step may generate damages and possible lacerations of obtained sheets or spools before cutting. The same failure may be also seen if excessive amounts of mineral fillers are added for whitening paper sheets. In addition, cellulosic fibres can be partially incompatible with mineral fillers. Finally, organic pigments and natural substances such as albumins may interact with fibres because of the chemical similarity
- Bleeding, also named 'ink shifting'. Main probable cause: transfer of printing inks on hydrophilic and unprinted areas in the offset printing technique
- Flexographic defects. Examples: incorrect drying, residual absorption of water or organic molecules with the consequent softening of printed materials
- Chromatic variations. Causes: presence of natural substances such as albumins with the consequent yellow tint under light exposure; excessive amount of OBA
- Wrinkling. Cause: initial pulp mixtures do not appear homogeneous. Cellulosic fibres are not amalgamated as expected because of the incorrect viscosity
- Other failures: defective adhesion, pulverisation of supports. Cause: excessive moisturisation of paper supports and raw materials during the storage in humid warehouses
- Mildewing by moulds (microbial spreading). Cause: storage in contaminated and humid warehouses.

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