Food Packaging and Shelf Life

A Practical Guide

Edited by Gordon L. Robertson



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Contents

	ix
	sxi ns, Acronyms, and Symbols xiii
Chapter 1	Food Packaging and Shelf Life1
	Gordon L. Robertson
Chapter 2	Food Quality and Indices of Failure
	Gordon L. Robertson
Chapter 3	Shelf Life Testing Methodology and Data Analysis
	Michel Guillet and Natalie Rodrigue
Chapter 4	Packaging and the Microbial Shelf Life of Food
	Dong Sun Lee
Chapter 5	Packaging and the Shelf Life of Milk
	Michael G. Kontominas
Chapter 6	Packaging and the Shelf Life of Cheese
	Maria de Fátima Poças and Manuela Pintado
Chapter 7	Packaging and the Shelf Life of Milk Powders
	Elmira Arab Tehrany and Kees Sonneveld
Chapter 8	Packaging and the Shelf Life of Yogurt
	Roger D. MacBean
Chapter 9	Packaging and the Shelf Life of Water and Carbonated Drinks
	Philip R. Ashurst
Chapter 10	Packaging and the Shelf Life of Orange Juice
	Antonio López-Gómez, María Ros-Chumillas, and Yulissa Y. Belisario-Sánchez
Chapter 11	Packaging and the Shelf Life of Coffee
	Maria Cristina Nicoli, Lara Manzocco, and Sonia Calligaris

Chapter 12	Packaging and the Shelf Life of Beer	215
	Charles W. Bamforth and John M. Krochta	
Chapter 13	Packaging and the Shelf Life of Wine	231
	Malcolm J. Reeves	
Chapter 14	Packaging and the Shelf Life of Fresh Red and Poultry Meats	259
	Alex O. Gill and Colin O. Gill	
Chapter 15	Packaging and the Shelf Life of Fish	279
	Steve Slattery	
Chapter 16	Packaging and the Shelf Life of Fruits and Vegetables	297
	Nathalie Gontard and Carole Guillaume	
Chapter 17	Packaging and the Shelf Life of Vegetable Oils	317
	Luciano Piergiovanni and Sara Limbo	
Chapter 18	Packaging and the Shelf Life of Cereals and Snack Foods	339
	Sea C. Min, Young T. Kim, and Jung H. Han	
Chapter 19	Shelf Life of Foods in Biobased Packaging	353
	Vibeke Kistrup Holm	
Chapter 20	Active Packaging and the Shelf Life of Foods	367
	Kay Cooksey	

Preface

Food packaging is an area with which, sooner or later, every practicing food scientist and technologist becomes involved. The importance of packaging hardly needs stressing, as only a handful of foods are sold in an unpackaged state. Furthermore, the fact that, on average, around 25% of the exfactory cost of consumer foods is for their packaging provides the incentive and the challenge for food packaging technologists to design and develop functional packages at minimum cost.

There is an old saying that any fool can do for \$10 what a good engineer can do for \$1. This saying also applies to food packaging technologists. Anyone can overpackage a food, but to provide just enough protection to ensure that the food maintains its acceptability until the end of its shelf life requires detailed knowledge and understanding of both food and packaging and how together they combine to deliver the desired shelf life. Although there are several books on shelf life, they tend to treat packaging in a superficial and unsatisfactory way. It is my hope that this book, by clearly demonstrating the nexus between packaging and shelf life, will provide valuable insights lacking in other texts.

This book introduces for the first time in print the concept of indices of failure (IoFs), first introduced to me when I was an undergraduate student at Massey University, New Zealand, by the late H.A.L. Morris, then a reader in food processing. IoFs are discussed in Chapter 2, and the chapter authors have all adopted this approach in discussing the shelf life of specific foods. I am confident that readers will find it a useful concept. It is hoped that this book will lead to the informed development of food packages that provide just the required amount of protection—no more and no less. With an increasing focus on sustainability, responsible companies no longer want to overpackage their food products and yet many remain unsure just where reductions can effectively be made. This book should help them in their endeavors.

It would obviously not have been possible to complete this book without the active participation of the authors, and I here place on record my appreciation for their willingness to contribute. It is a largely thankless, unpaid task to write a book chapter, and we should all be grateful that busy people are prepared to give of their time in this way. A special mention must also go to Steve Zollo, Senior Editor, Food Science and Technology at CRC Press/Taylor & Francis Group, who first suggested a book on this subject. His encouragement and support have been very much appreciated, as has the efficient attention to administrative details by Kari Budyk, Senior Production Coordinator, Editorial Project Development.

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Editor

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A member of several editorial boards, he is a fellow of the International Academy of Food Science and Technology, a fellow of the U.S. Institute of Food Technologists, a fellow of the Australian Institute of Packaging, and a fellow and former president of the New Zealand Institute of Food Science and Technology. Dr. Robertson received the BTech, MTech, and PhD degrees in food technology from Massey University.

The second edition of his book, *Food Packaging Principles and Practice*, was published by CRC Press in the United States in 2006 and is widely used in universities and by industry around the world. He offers workshops and training courses on food packaging in many countries (see www. gordonlrobertson.com for further details).

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Abbreviations, Acronyms, and Symbols

θ	time
$ heta_{ m s}$	shelf life
°Č	degrees Celsius
Α	area (m ²); frequency factor in Arrhenius equation
A ₄₂₀	absorbance at 420 nm
AA	acrylic acid; arachidonic acid; acetaldehyde
ABS	acrylonitrile-butadiene-styrene
Ac	acrylic
ACTIS	amorphous carbon treatment on internal surface
AITC	allyl isothiocyanate
alufoil	aluminum foil
AM	antimicrobial
AmPA	amorphous polyamide
AN	acrylonitrile
ANMA	acrylonitrile-methyl acrylate
ANOVA	analysis of variance
ANS	acrylonitrile/styrene
AnV	anisidine value
APC	aerobic plate count
APET	amorphous poly(ethylene terephthalate)
Ar	argon
ASLT	accelerated shelf life testing
atm	atmosphere
ATP	adenosine triphosphate
$a_{ m w}$	water activity
BET	Brunauer–Emmett–Teller
BHT	butylated hydroxytoluene
BIB	bag-in-box
BO	biaxially oriented
BON	biaxially oriented nylon
BOPP	biaxially oriented polypropylene
BPA	bisphenol A
BPAA	bis-anthracene-trimethylphenylammonium dichloride
BTW	by the way
С	concentration of permeant in polymer
ca.	approximately
cfu	colony-forming unit
CLCs	calcium lactate crystals
cm Hg	centimeters of mercury
CO	carbon monoxide
CO ₂	carbon dioxide
cP	centipoise (10 ⁻³ Pa sec)
CPET	crystalline poly(ethylene terephthalate)

-	
D	diffusion coefficient (cm ⁻² sec ⁻¹)
Da	dalton = mass of a single hydrogen atom (1.66 x 10^{-24} gram)
DAL	defect action level
DEHA	di-(2-ethylhexyl) adipate
DEHP	di-(2-ethylhexyl) phthalate
DFD	dark, firm, and dry (meat)
DHA	docosahexanoic acid
DLC	diamond-like coating
DO	dissolved oxygen
DMA	dimethylamine
DWI	drawn and wall ironed
E_{a}	activation energy (J mol ⁻¹)
EAA	ethylene-acrylic acid copolymer
ECCS	electrolytically chromium-coated steel
E_{d}	activation energy for diffusion (kJ mol ⁻¹)
ECTA	ethylenediaminetetraacetic acid
EFA	essential fatty acid
EFSA	European Food Safety Authority
$E_{ m h}$	oxidation-reduction potential
EO	essential oil
Ep	activation energy for permeation (kJ mol-1)
ESC	environmental stress cracking
ESE	easy serving expresso
EPS	expanded polystyrene
EU	European Union
EVA	ethylene-vinyl acetate copolymer
EVOH	ethylene-vinyl alcohol copolymer
EVOO	extra-virgin olive oil
FA	formaldehyde
FAST	fluorescence of advanced Maillard products and soluble tryptophan
FCOJ	frozen concentrated orange juice
FDA	Food and Drug Administration
FMP	filled milk powder
FSOJ	freshly squeezed orange juice
GAB	Guggenheim–Anderson–de Boer
GMP	good manufacturing practice
GRAS	generally recognized as safe
H3O+	hydronium ion
HACCP	hazard analysis critical control point
HDL	high density lipoprotein
HDPE	high density polyethylene
HEPA	high-efficiency particulate air
HHRS	highly heat-resistant spore
HIPS	high-impact polystyrene
HPC	hydroxypropyl cellulose
HPMC	hydroxypropyl methylcellulose
HPP	high pressure processing
HQL	high-quality shelf life
HRS	heat-resistant spore
HTST	high-temperature short-time
IBMP	iso-butyl-methoxypyrazine

TE	· · · · · · · · · · · · · · · · · · ·
IoFs	indices of failure
IU	international unit
J	flux of permeant in polymer
LAB	lactic acid bacteria
LBM	Le Bouchage Mecanique
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
LSD	least significant difference
LTLT	low-temperature long-time
k	rate constant
kGy	kiloGray
k ₀	Arrhenius pre-exponential factor
ĸ	Kelvin
KM	Kaplan–Meier
LC-PUFAs	long-chain polyunsaturated fatty acids
LDL	low density lipoprotein
LTLT	low-temperature-long-time
MA	methyl acrylate; also modified atmosphere
MAP	modified atmosphere packaging
Mb	myoglobin
MC	methylcellulose
MCP	methylcyclopropene
Met	Metalized
MetMb	
	metmyoglobin milliorom (1 × 10 ⁻³ orom)
mg MH	milligram $(1 \times 10^{-3} \text{ gram})$
	mercaptohexanol
MHA	mercaptohexyl acetate
MJ	megajoule
mL	milliliter $(1 \times 10^{-3} \text{ liters}) = \text{cc} = \text{cm}^3$
MMT	montmorillonite; million metric tons
MPa	megapascal
mPET	metalized PET
MPFVs	minimally processed fruits and vegetables
MPN	most probable number
MPPO	modified phenylene oxide
MRA	metmyoglobin reducing activity
MXD6	meta-xylylene diamine/adipic acid nylon
NADH	nicotinamide adenine dinucleotide
NDM	nonfat dry milk
NEB	nonenzymic browning
NFCOJ	not-from-concentrate orange juice
nm	nanometer (1 \times 10 ⁻⁹ meter)
NSLAB	nonstarter lactic acid bacteria
OCR	oxygen consumption rate
O ₂ Mb	oxymyoglobin
OPA	oriented polyamide
OPET	oriented polyester
OPP	oriented polypropylene
ORP	oxidation-reduction potential
OS	oxygen scavenger
OTR	oxygen transmission rate

р	partial pressure (cm Hg)
Р	permeability coefficient (mL cm cm ⁻² sec ⁻¹ (cm Hg ⁻¹))
P/X	permeance
PA	polyamide
PAN	polyacrylonitrile
PBT	poly(butylene terephthalate)
PC	polycarbonate
PDLA	poly-D-lactic acid
PDLLA	mixture of poly-D-lactic acid and poly-L-lactic acid
PE	polyethylene
PECVD	plasma-enhanced chemical vapor deposition
PEN	poly(ethylene naphthalate)
PET	poly(ethylene terephthalate) = polyester
PFB	printed fibreboard
PFO	polyfuryloxirane
-	
pg	picogram (1 x 10 ⁻¹² gram)
PGA	propylene-glycol alginate
PHA	polyhydroxyalkanoate
PHB	polyhydroxybutyrate
PLA	polylactic acid or polylactate or polylactide
PLLA	poly-L-lactic acid
PME	pectinmethylesterase
POD	peroxidase
PP	polypropylene
ppb	parts per billion (1×10^{-9})
ppm	parts per million (1×10^{-6})
PPO	polyphenoloxidase
ppt	parts per trillion (1 x 10^{-12})
PS	polystyrene
PUFA	polyunsaturated fatty acid
PV	peroxide value
PVC	poly(vinyl chloride)
PVD	physical vapor deposition
PVdC	poly(vinylidene chloride)
Q	total amount of permeant passing through polymer
Q ₁₀	temperature quotient = ratio of reaction rates for 10°C temperature difference
QIM	quality index method
R	ideal gas constant (= $8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$)
R&G	roasted and ground
RCF	regenerated cellulose film
RFID	radio frequency identification
RH	relative humidity
ROPP	roll-on pilfer-proof
ROTE	roll-on tamper-evident
RTE	ready-to-eat
S	solubility coefficient of permeant in polymer (mL cm ⁻³ (cm Hg ⁻¹))
SiO ₂	silicon dioxide
SiO _x	oxides of silicon
SLO	sulfur-like odor
SLOs	sulfur-like odors
SMP	skim milk powder
	r - · · · · · ·

SO	sunflower oil
SO ₂	sulfur dioxide
SSO	specific spoilage organism
SSSP	Seafood Spoilage and Safety Predictor
STP	standard temperature and pressure
TBA	thiobarbituric acid
TBHQ	tert-butylhydroquinone
TBP	tribromophenol
TCA	trichloroanisole
ТСР	trichlorophenol
TDI	tolerable daily intake
TDN	trimethyldihydronaphthalene
TEBO	tail-end blow-off
TeCA	tetrachloroanisole
Tg	glass transition temperature
TiO2	titanium dioxide
Tm	crystalline melting temperature
TMA	trimethylamine
TMAO	trimethylamine oxide
TNF	thickness normalized flux
TPA	terephthalic acid
TPB	trimethylphenylbutadiene
TPE	thermoplastic elastomer
TQM	total quality management
TR	transmission rate
TTI	time-temperature indicator
UHT	ultra-heat-treated or ultra-high-temperature
ULDPE	ultra-low density polyethylene
UP	ultrapasteurized
UPC	universal product code
UV	ultraviolet
UVA	380–320 nm
UVB	320–280 nm
UVC	280–100 nm
VCM	vinyl chloride monomer
VP	vacuum packaging
VSP	vacuum skin packaging
WMP	whole milk powder
WPNI	whey protein nitrogen index
WVP	water vapor permeability
WVTR	water vapor transmission rate
Х	thickness of polymeric material
μg	microgram (1 × 10^{-6} gram)
μm	micrometer (1 \times 10 ⁻⁶ meter)
μmax	maximum specific growth rate
	I C

1 Food Packaging and Shelf Life

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CONTENTS

Introd	uction	1
1.1.1	Role of Food Packaging	1
	1.1.1.1 Containment	2
	1.1.1.2 Protection	2
	1.1.1.3 Convenience	2
	1.1.1.4 Communication	3
	1.1.1.5 Attributes	
1.1.2	Package Environments	3
	1.1.2.1 Physical Environment	
	1.1.2.2 Ambient Environment	
	1.1.2.3 Human Environment	4
Food	Packaging Materials	4
1.2.1	Polymer Permeability	4
1.2.2	Transmission Rate	7
1.2.3	Surface Area:Volume Ratio	
Shelf	Life	10
1.3.1	Definitions	10
1.3.2	Factors Controlling Shelf Life	11
	1.3.2.1 Product Characteristics	12
	1.3.2.2 Distribution and Storage Environment	12
	1.3.2.3 Package Properties	12
1.3.3	Shelf Life Determination	14
	1.1.1 1.1.2 Food 1 1.2.1 1.2.2 1.2.3 Shelf 1 1.3.1 1.3.2	1.1.1.1 Containment. 1.1.1.2 Protection 1.1.1.3 Convenience 1.1.1.4 Communication 1.1.1.5 Attributes 1.1.2 Package Environments. 1.1.2.1 Physical Environment 1.1.2.2 Ambient Environment 1.1.2.3 Human Environment 1.1.2.3 Human Environment 1.1.2.4 Polymer Permeability 1.2.5 Transmission Rate 1.2.6 Surface Area:Volume Ratio Shelf Life 1.3.2 1.3.2 Factors Controlling Shelf Life 1.3.2.1 Product Characteristics 1.3.2.2 Distribution and Storage Environment 1.3.2.3 Package Properties

1.1 INTRODUCTION

1.1.1 ROLE OF FOOD PACKAGING

Food packaging is essential and pervasive: essential because without packaging the safety and quality of food would be compromised, and pervasive because almost all food is packaged in some way. Food packaging performs a number of disparate tasks: it protects the food from contamination and spoilage; it makes it easier to transport and store foods; and it provides uniform measurement of contents. By allowing brands to be created and standardized, it makes advertising meaningful and large-scale distribution and mass merchandising possible. Food packages with dispensing caps, sprays, reclosable openings, and other features make products more usable and convenient.

A distinction is usually made between the various "levels" of packaging. A primary package is one that is in direct contact with the contained product. It provides the initial, and usually the major,

protective barrier. Examples of primary packages include metal cans, paperboard cartons, glass bottles, and plastic pouches. It is frequently only the primary package that the consumer purchases at retail outlets. This book will confine itself to the primary package.

A secondary package contains a number of primary packages, for example, a corrugated case. It is the physical distribution carrier and is sometimes designed so that it can be used in retail outlets for the display of primary packages. A tertiary package is made up of a number of secondary packages, the most common example being a stretch-wrapped pallet of corrugated cases. In interstate and international trade, a quaternary package is frequently used to facilitate the handling of tertiary packages. This is generally a metal container up to 40 m in length that can hold many pallets and is intermodal in nature.

Four primary and interconnected functions of packaging have been identified: containment, protection, convenience, and communication (Robertson, 2006).

1.1.1.1 Containment

This function of packaging is so obvious as to be overlooked by many, but it is the most basic function of packaging. Food products must be contained before they can be moved from one place to another. The containment function of packaging makes a huge contribution to protecting the environment from the myriad of products that are moved from one place to another on numerous occasions each day.

1.1.1.2 Protection

This is often regarded as the primary function of the package: to protect its contents from the outside environmental effects of water, water vapor, gases, odors, microorganisms, dust, shocks, vibrations, compressive forces, and so on.

For the majority of food products, the protection afforded by the package is an essential part of the preservation process. For example, aseptically packaged milk in paperboard laminate cartons remains aseptic only for as long as the package provides protection; vacuum-packaged meat will not achieve its desired shelf life if the package permits O_2 to enter. In general, once the integrity of the package is breached, the product is no longer preserved.

Freedom from harmful microbial contaminants at the time of consumption can also be influenced by the package. First, if the packaging material does not provide a suitable barrier around the food, microorganisms can contaminate the food and make it unsafe. Microbial contamination can also arise if the packaging material permits the transfer of, for example, moisture or O_2 from the atmosphere into the package. In this situation, microorganisms present in the food but posing no risk because of the initial absence of moisture or O_2 may then be able to grow and present a risk to the consumer.

Effective packaging reduces food waste, and in doing so protects or conserves much of the energy expended during the production and processing of the product. For example, to produce, transport, sell, and store 1 kg of bread requires 15.8 MJ (megajoules) of energy. This energy is required in the form of transport fuel, heat, power, refrigeration in farming and milling the wheat, baking and retailing the bread, and distributing both the raw materials and the finished product. To produce the polyethylene bag to package a 1 kg loaf of bread requires 1.4 MJ of energy. This means that each unit of energy in the packaging protects 11 units of energy in the product. Although eliminating the packaging might save 1.4 MJ of energy, it would also lead to spoilage of the bread and a consequent waste of 15.8 MJ of energy (Robertson, 2006).

1.1.1.3 Convenience

Modern, industrialized societies have seen tremendous changes in lifestyle, and the packaging industry has had to respond to those changes, which have created a demand for greater convenience in household products: foods that are pre-prepared and can be cooked or reheated in a very short time, preferably without removing them from the package; condiments that can be applied simply or by means of pump-action packages; dispensers for sauces or dressings that minimize mess; reclosable openings on drink bottles to permit consumption on the go; and so on. Thus, packaging plays an important role in allowing products to be used conveniently.

Two other aspects of convenience are important in package design. One of these can best be described as the apportionment function of packaging. In this context, the package functions to reduce the output from industrial production to a manageable, desirable "consumer" size. An associated aspect is the shape (relative proportions) of the primary package in relation to convenience of use by consumers (e.g., easy to hold, open, and pour as appropriate) and efficiency in building it into secondary and tertiary packages. Packaging plays a very important role in permitting primary packages to be unitized into secondary packages (e.g., placed inside a corrugated case) and then for these secondary packages to be unitized into a tertiary package (e.g., a stretch-wrapped pallet). As a consequence of this unitizing function, materials handling is optimized, as only a minimal number of discrete packages or loads need to be handled.

1.1.1.4 Communication

There is an old saying that "a package must protect what it sells and sell what it protects"; that is, the package functions as a "silent salesman." The modern methods of consumer marketing would fail were it not for the messages communicated by the package through distinctive branding and labeling, enabling supermarkets to function on a self-service basis. Consumers make purchasing decisions using the numerous clues provided by the graphics and the distinctive shapes of the packaging. Other communication functions of the package include a Universal Product Code (UPC) that can be read accurately and rapidly using modern scanning equipment at retail checkouts, nutritional and ingredient information (including E-numbers for additives), and country of origin.

1.1.1.5 Attributes

There are also several attributes of packaging that are important (Krochta, 2007). One (related to the convenience function) is that it should be efficient from a production or commercial viewpoint, that is, in filling, closing, handling, transportation, and storage. Another is that the package should have, throughout its life cycle from raw material extraction to final disposal after use, minimal adverse environmental impacts. A third attribute is that the package should not impart to the food any undesirable contaminants. Although this last attribute may seem self-evident, there has been a long history of so-called food-contact substances migrating from the packaging material into the food (Grob et al., 2006). Not surprisingly, food packaging materials are highly regulated in many countries to ensure consumer safety.

1.1.2 PACKAGE ENVIRONMENTS

The packaging has to perform its functions in three different environments (Lockhart, 1997). Failure to consider all three environments during package development will result in poorly designed packages, increased costs, consumer complaints, and even avoidance or rejection of the product by the consumer.

1.1.2.1 Physical Environment

This is the environment in which physical damage can be caused to the product, including shocks from drops, falls, and bumps; damage from vibrations arising from transportation modes, including road, rail, sea, and air; and compression and crushing damage arising from stacking during transportation or storage in warehouses, retail outlets, and the home environment.

1.1.2.2 Ambient Environment

This is the environment that surrounds the package. Damage to the product can be caused as a result of exposure to gases (particularly O_2), water and water vapor, light (particularly UV radiation), and

the effects of heat and cold, as well as microorganisms (bacteria, fungi, molds, yeasts, and viruses) and macroorganisms (rodents, insects, mites, and birds), which are ubiquitous in many warehouses and retail outlets. Contaminants in the ambient environment such as exhaust fumes from automobiles and dust and dirt can also find their way into the product unless the package acts as an effective barrier.

1.1.2.3 Human Environment

This is the environment in which the package is handled by people, and designing packages for this environment requires knowledge of the strengths and frailties of human vision, human strength and weakness, dexterity, memory, cognitive behavior, and so on (Yoxall et al., 2007). It also includes results of human activity such as liability, litigation, legislation, and regulation. Since one of the functions of the package is to communicate, it is important that the messages are received clearly by consumers. In addition, the package must contain information required by law, such as nutritional content and net weight. To maximize its convenience or utility functions, the package should be simple to hold, open, use, and (if appropriate) reclose by the consumer.

1.2 FOOD PACKAGING MATERIALS

The materials used to manufacture food packaging comprise a heterogeneous group, including glass, metals, plastics, and paper, with a corresponding range of performance characteristics. The properties of these various materials will not be described here in detail, as they have been well documented elsewhere (Lee et al., 2008; Piringer and Baner, 2008; Robertson, 2006; Yam, 2009). However, some general points will be made.

In the selection of suitable packaging materials for a particular food, the focus is typically on the barrier properties of the packaging material. Foods can be classified according to the degree of protection required, such as the maximum moisture gain or O_2 uptake. Calculations can then be made to determine whether a particular packaging material would provide the necessary barrier required to give the desired product shelf life. Metal cans and glass containers can be regarded as essentially impermeable to the passage of gases, odors, and water vapor, provided that a metal end has been correctly seamed on in the case of cans or a satisfactory closure applied in the case of glass containers. Aluminum foil has excellent barrier properties, provided it is at least 25 μ m thick; below this thickness the likelihood of pinholes increases. It is common to laminate plastic polymers to aluminum foil to provide mechanical support and heat sealability. Paper-based packaging materials can be regarded as permeable and for this reason are normally coated with a plastic polymer to ensure adequate barrier properties for the packaging of foods. This then leaves plastics-based packaging materials, which provide varying degrees of protection, depending largely on the nature of the polymers used in their manufacture.

1.2.1 POLYMER PERMEABILITY

In contrast to packaging materials made from glass or metal, packages made from thermoplastic polymers are permeable to varying degrees to small molecules such as gases, water vapor, organic vapors, and other low molecular weight compounds.

The following expression can be derived from Fick's first law (Robertson, 2006):

$$Q = \frac{DS(p_1 - p_2)At}{X} \tag{1.1}$$

Here Q is the quantity of gas or vapor permeating a polymer of thickness X and surface area A in time t under a pressure gradient of p_1 on one side and p_2 on the other, where $p_1 > p_2$. D is the diffusion coefficient and S the solubility coefficient of the permeant; the product DS is referred to as the

permeability coefficient (or constant) or permeation coefficient, or simply the permeability, and is represented by the symbol *P*. Thus:

$$P = \frac{QX}{At(p_1 - p_2)} \tag{1.2}$$

or

$$\frac{Q}{t} - \frac{P}{X} A\left(\Delta p\right) \tag{1.3}$$

The term P/X is called the permeance. A plastic polymer that is a good barrier to gases and water vapor has a low permeability coefficient.

Four assumptions are made in this simple treatment of permeation: diffusion is at steady state; the concentration–distance relationship through the polymer is linear; diffusion takes place in one direction only (i.e., through the film with no net diffusion along or across it); and both D and S are independent of concentration. However, as with all simplifying assumptions, there are many instances when the assumptions are not valid, and in such cases the predictions made are not subsequently borne out in practice. Although steady state is usually attained in a few hours for small molecules such as O_2 , larger molecules in barrier polymers (especially glassy polymers) can take a long time to reach steady state, this time possibly exceeding the anticipated shelf life. Although D and S are independent of concentration for many gases, such as O_2 , N_2 , and, to a certain extent, CO_2 , this is not the case where considerable interaction between polymer and permeant takes place (e.g., water and hydrophilic films such as polyamides [PA], or many solvent vapors diffusing through polymer films). Typical values for the permeability coefficient of commercial food packaging polymers are presented in Table 1.1.

TABLE 1.1
Permeability to Oxygen, Carbon Dioxide, and Water Vapor of Some Plastic Films

Permeability to	O ₂ ×10 ¹¹ mL cm cm ⁻² s ⁻¹ (cm Hg) ⁻¹ at 23°C, 0% RH	CO ₂ ×10 ¹¹ mL cm cm ⁻² s ⁻¹ (cm Hg) ⁻¹ at 23°C, 0% RH	H ₂ O ×10 ¹¹ g cm cm ⁻² s ⁻¹ at 23°C, 100% RH
LDPE	15-30	60–160	5-10
HDPE	5–17	150	1.8-3.5
EVA (15%VA)	30-40		21-25
Ethylene acid copolymer (ionomer)	20–35	—	5–11
PP	9–16	30–50	4-10
PET	0.14	1.2	4-6ª
PS	18–25	60–90	9–46
PVC plasticized	1.7–100 ^b	6–180	_
PVC rigid	0.3–1.2 ^b	1.2–3	14
PA6	0.09-0.11	0.6–0.8	46ª
PA66	0.2	_	86
PVdC	0.006 ^b	_	0.7ª
EVOH (32% C ₂ H ₄)	0.0015	0.018	17.5ª

Source: Adapted from Massey L. 2003. Permeability Properties of Plastics and Elastomers, 2nd edn. New York: Plastics Design Library.

^a 40°C, 90% RH.

^b 23°C, 50% RH.

The permeability coefficient defined in the preceding text is independent of thickness, as the thickness is already accounted for in the calculation of *P*. However, the total amount of protection afforded per unit area of a barrier material approaches zero only asymptotically. Consequently, as polymer thickness *X* is increased beyond a certain value, it becomes uneconomical to increase it further to obtain lower permeability. For example, to equal the O_2 barrier of a 25-µm film of a high-barrier material such as poly(vinylidene chloride) copolymer (PVdC) would require 62,500 µm of polypropylene (PP), 1250 µm of poly(ethylene terephthalate) (PET), 1250 µm of poly(vinyl chloride) (PVC), or 250 µm of nylon 6.

In general, permeability of a penetrant through a polymer depends on many factors, including the nature of the polymer, thickness of the film, size and shape of the penetrant, pressure, and temperature. The structural attributes that can influence the permeability of polymers include polarity, unsaturation, symmetry, lateral chains, steric hindrance, degree of cross-linking, hydrogen bonding, intermolecular forces, comonomers present, crystallinity, glass transition temperature, and orientation.

Literature data for gas transport coefficients (permeability, diffusion, and solubility coefficients) vary generally with parameters that are intrinsic to the polymer such as degree of crystallinity, nature of the polymer, and the thermal and mechanical histories of samples such as orientation. Sorption and diffusion phenomena take place exclusively in the amorphous phase of a semicrystal-line polymer and not in its crystalline zones.

The effect of crystallinity on the permeability coefficient of high density polyethylene (HDPE) to O₂ was illustrated by Pauly (1999), who showed that $P \times 10^{11}$ decreased from 54.9 mL (STP) cm cm⁻² s⁻¹ (cm Hg)⁻¹ at 60% crystallinity to 20.9 at 69% and 10.6 at 81% crystallinity.

The effect of orientation on the O₂ permeability coefficient was also illustrated by Pauly (1999), who showed that $P \times 10^{11}$ decreased for polystyrene from 25.0 to 17.9 mL (STP) cm cm⁻² s⁻¹ (cm Hg)⁻¹ when oriented 300%; comparable figures for PP were 9.0 to 4.8; for PET, *P* decreased from 0.60 to 0.22 when oriented 500%.

The relative effect of diffusive flow through holes on the atmosphere inside the package can be appreciated by comparing the permeability of gases in air with their permeability in polymers, as shown in Table 1.2. Air is much more permeable than polymeric films, so even a very small hole in a polymeric package can affect the package atmosphere very significantly. This phenomenon is used to advantage with microporous or perforated films. The effect of thin layers and droplets of water on the inside surface of films can also be appreciated by reference to Table 1.2, which shows that the permeability of gases is much higher in water than in polymers. As a result, thin layers and droplets of water (condensation) forming inside polymeric packages do not significantly affect the gas atmosphere in the package (Kader et al., 1998). The permeability ratio β (also referred to as the

TABLE 1.2 Permeability Data of Some Polymeric Films, Air, and Water

	$P \times 10^{11} \mathrm{mL} (\mathrm{STP})$	Permeability Ratio (β)	
	\mathbf{O}_2	CO ₂	CO ₂ :O ₂
Polyethylene (density 0.914)	30.0	131.6	4.39
Polypropylene	17.4	75.5	4.34
Poly(vinyl chloride)	0.47	1.64	3.49
Poly(vinylidene chloride)	0.055	0.31	5.64
Air	2.5×10^{8}	1.9×10^{8}	0.76
Water	9.0×10^{2}	2.1×10^4	23.33

Source: Adapted with permission from Kader A.A., Singh R.P., Mannapperuma J.D. 1998. Technologies to extend the refrigerated shelf life of fresh fruits. In: *Food Storage Stability*. Taub I.A. and Singh R.P. (Eds). Boca Raton, Florida: CRC Press, Chap 16. Copyright CRC Press, Boca Raton, Florida. permselectivity) is the ratio of P for CO₂ to that for O₂ and is particularly useful information when designing modified atmosphere packages.

In the published literature it is rare to find many details about a particular plastic packaging material apart from its name, sometimes the name of the resin supplier, and perhaps whether it has been oriented. This makes it virtually impossible to replicate the experimental conditions described in the literature, as the range of polymers available is vast. For example, the web site www.ides.com contains data sheets on more than 77,000 commercial polymers from 694 resin manufacturers. Of course, many of these polymers are not approved or suitable for use in food packaging.

Consider PP, a polymer used increasingly in food packaging. The properties of PP have improved considerably over the past few decades as a result of a wide range of technical advances ranging from new metallocene catalysts to co-monomers. PP and its copolymers can be classified into three categories (Begley et al., 2008): monophasic homopolymer (h-PP), monophasic random copolymer (r-PP), and heterophasic copolymer (heco-PP). The h-PP can be either isotactic, syndiotactic, or atactic, but the isotactic h-PP is particularly useful due to its stereoregularity and the resulting high crystallinity. Therefore, commercially produced h-PP is up to 95% isotactic. Ides lists data sheets for 19 h-PP food-grade polymers.

The linear polymer chains of r-PP contain copolymers such as ethylene and butene in a random manner, which reduces crystallinity and thus improves the optical clarity, the main commercial advantage of r-PP over h-PP. The heco-PP is a block copolymer made up of h-PP phases and, usually, ethylene-propylene rubber (EPR) phases. This combination leads to superior impact strength at low temperatures. Owing to the variety of PP formulations mentioned here, along with their variety of applications in food packaging, a wide range of diffusion behavior is observed in PP; for example, diffusion coefficients for r-PP are at least one order of magnitude higher than those of h-PP and comparable with those for heco-PP (Begley et al., 2008).

The permeability coefficient of a specific polymer–permeant system may increase or decrease with increases in temperature, depending on the relative effect of temperature on the solubility and diffusion coefficients. Generally, the solubility coefficient increases with increasing temperature for gases and decreases for vapors, and the diffusion coefficient increases with temperature for both gases and vapors. For these reasons, permeability coefficients of different polymers determined at one temperature may not be in the same relative order at other temperatures.

1.2.2 TRANSMISSION RATE

The aforementioned treatment of steady-state diffusion assumes that both D and S are independent of concentration, but, in practice, deviations do occur. Equation 1.3 does not hold when there is interaction such as that which occurs between hydrophilic materials [e.g., EVOH (ethylene vinyl alcohol copolymers) and some of the PAs] and water vapor, or for heterogeneous materials such as coated or laminated films. The property is then defined as the transmission rate (TR) of the material, where:

$$TR = \frac{Q}{At} \tag{1.4}$$

Here Q is the amount of permeant passing through the polymer, A is the surface area, and t is the time. Permeabilities of polymers to water and organic compounds are often presented in this way, and in the case of water and O_2 , the terms water vapor transmission rate (WVTR) and gas transmission rate (GTR), or more specifically oxygen transmission rate (OTR or O_2 TR), are in common usage. It is critical that the thickness of the film or laminate, the temperature, and the partial pressure difference of the gas or water vapor be specified for a particular *TR*.

The specialized instruments commonly used to determine the OTR of plastic packaging materials, such as those manufactured by MoCon, use pure O_2 on one side and measure how much permeates into a carrier gas on the other side (the O_2 gradient is therefore 1 atm). In real life, where there is typically air on one side (O₂ is present at 21% in air) and essentially no O₂ inside the package, the O₂ gradient is 0.21 atm or 16 cm Hg. Thus, to convert OTR values expressed in units of mL m⁻² day⁻¹ atm⁻¹ to "true" OTR units of mL m⁻² day⁻¹, it is necessary to multiply by 0.21; this has been done for the OTR values quoted in this book. An exception to this convention is used in the case of CO₂, where, because of its very low concentration in air (0.03%), CO₂TR units are often given in mL m⁻² day⁻¹ atm⁻¹. In modified atmosphere packaging (MAP), concentrations of CO₂ inside the package are typically 40–60%.

Often the units for WVTR include a thickness term, in which case the WVTR should, strictly speaking, be referred to as the thickness normalized flux, or TNF (Robertson, 2009). To convert a measured WVTR or OTR to *P*, it is necessary to multiply by the thickness of the film and divide by the partial pressure difference used to make the measurement.

Example: Calculate the permeability coefficient of an amorphous polyethylene terephthalate (PET) film to O_2 at 23°C given that the OTR through a 2.54 × 10⁻³-cm-thick film with air on one side and inert gas on the other is 8.8 × 10⁻⁹ mL cm⁻² s⁻¹.

 O_2 partial pressure difference across the film is 0.21 atm = 16 cm Hg.

$$P = \frac{OTR}{\Delta p} \times \text{thickness}$$

= $\frac{8.8 \times 10^{-9} \,\text{mL cm}^{-2} \text{s}^{-1}}{16 (\text{cm Hg})} \times 2.54 \times 10^{-3} \,\text{cm}$
= $1.4 \times 10^{-12} \left[\text{mL} (\text{STP}) \,\text{cm} \,\text{cm}^{-2} \text{s}^{-1} (\text{cm Hg})^{-1} \right]$
= $0.14 \times 10^{-11} \left[\text{mL} (\text{STP}) \,\text{cm} \,\text{cm}^{-2} \text{s}^{-1} (\text{cm Hg})^{-1} \right]$

Therefore

$$P \times 10^{11} = 0.14 \left[\text{mL} (\text{STP}) \text{cm} \text{ cm}^{-2} \text{s}^{-1} (\text{cm} \text{ Hg})^{-1} \right]$$

which is the value given in Table 1.1.

The OTR of packaging materials used for MAP of chilled products varies extensively with temperature, relative humidity (RH), and material thickness after the thermoforming of packages. Gnanaraj et al. (2005) reported OTRs, together with the Arrhenius pre-exponential factor k_0 and activation energy E_a , for a range of films at 10°C, 15°C, 23°C, 30°C, and 35°C and 0% and 50% RH. The OTRs at 10°C were typically half those at 23°C. Jakobsen et al. (2005) studied two different polymer combinations: amorphous PET/low density polyethylene (APET/LDPE) (tray) and PA/LDPE (lid). A temperature reduction of 8°C (in the interval 7–23°C) caused an OTR reduction of 26–48%, depending on material type, degree of thermoforming, and RH. An increased OTR was observed as a result of material thinning; however, the increase was not always directly proportional to the degree of material thinning. The changes in OTR observed emphasize the necessity of evaluating the performance of packaging materials under realistic storage conditions to estimate the real O₂ content of a chosen package solution.

1.2.3 SURFACE AREA: VOLUME RATIO

The dimensions of the package for a given weight of food can have a significant influence on shelf life. Although a spherical shape will minimize the surface area of the package (and thus the quantity of moisture or O_2 that will permeate the package wall), it is not a practical shape for commercial use, and, in practice, most packages tend to be rectangular or cylindrical. Table 1.3 gives the surface areas for a range of different shapes with the same volume (~450 mL). Compared with the surface area of a sphere,

Shape	Dimensions	Surface Area		Increase	Surface Area:
	ст	cm ²	m ²	%	Volume Ratio
Sphere	Diameter 9.52	285	0.0285	0	0.63
Cylinder	Diameter 7.3	331	0.0331	16	0.73
	Height 10.8				
Cube	Sides 7.67	353	0.0353	24	0.78
Tetrahedron	Sides 15.65	424	0.0424	49	0.94
Rectangular pack	Height 3	450	0.0450	58	1.0
	Length 15				
	Width 10				
Thin rectangular pack	Height 1	985	0.0985	246	2.18
	Length 20				
	Width 22.5				

TABLE 1.3 Surface Areas of Different Package Shapes, All with a Volume of ~450 mL

the surface area of a cylinder is 16% greater, a cube 24% greater, a tetrahedron 49% greater, a rectangular shape 58% greater, and a thin rectangular shape 246% greater. Extremely thin packages have a much greater surface area:volume ratio and thus require a plastic with better barrier properties to get the same shelf life than if the same quantity of product were packaged in a thicker format. For different quantities of the same product packaged in different-sized packages using the same plastic material, the smallest package will have the shortest shelf life as it inevitably has a greater surface area per unit volume. Many food companies still seem unaware of this fact as they continue to launch smaller packages without changing the packaging material and then wonder why the shelf life is shorter for the smaller package.

Example: A food powder with a density of 1 is to be packaged in a plastic film that has a WVTR of 2.1 g m⁻² day⁻¹ at 25°C and 75% RH. The initial moisture content of the powder is 3%, and the critical moisture content is 7%. Assuming that each pack will contain 450 g of powder and will be exposed to an external environment at 25°C and 75% RH, calculate the shelf life if the shapes of the packs are the same as those listed in Table 1.3. For simplicity, assume that the driving force for water vapor transmission (WVT) remains constant and that there are no moisture gradients in the powder.

Weight of dry solids = 97% of 450 = 436.5 g Initial weight of water in powder = 3% of 450 = 13.5 g Final weight of water in powder = 436.5/0.93 - 436.5= 469.35 - 436.5= 32.85 gTherefore, weight of water permeating into powder is 32.85 - 13.5 = 19.35 g For a spherical-shaped package: Quantity of water permeating into package per day is $0.0285 \times 2.1 = 0.05985 \text{ g day}^{-1}$ Therefore shelf life $\theta_s = \frac{19.35}{0.05985} = 323$ days For the other package shapes Cylinder: $\theta_s = 278$ days Cube: $\theta_s = 261$ days Tetrahedron: $\theta_s = 217$ days Rectangle 1: $\theta_s = 204$ days Rectangle 2: $\theta_s = 93.5$ days

1.3 SHELF LIFE

The quality of most foods and beverages decreases with storage or holding time. Exceptions include distilled spirits (particularly whiskeys and brandies) that develop desirable flavor components during storage in wooden barrels, some wines that undergo increases in flavor complexity during storage in glass bottles, and many cheese varieties in which enzymic degradation of proteins and carbohydrates, together with hydrolysis of fat and secondary chemical reactions, lead to desirable flavors and textures in aged cheeses.

For the majority of foods and beverages in which quality decreases with time, it follows that there will be a finite length of time before the product becomes unacceptable. This time from production to unacceptability is referred to as *shelf life*. Although the *Wizard of Id* thought that shelf life related to the time until the shelf displaying the food rotted out (see Figure 1.1), shelf life refers to the time on the retailer's shelf as well as the consumer's shelf. Although the shelf lives of foods vary, they are routinely determined for each particular product by the manufacturer or processor. Manufacturers generally attempt to provide the longest practicable shelf life consistent with costs and the pattern of handling and use by distributors, retailers, and consumers. Supermarkets will generally not accept the product into their distribution centers unless at least 75% of the shelf life remains. Inadequate shelf life will often lead to consumer dissatisfaction and complaints. At best, such dissatisfaction will eventually affect the acceptance and sales of brand name products, while, at worst, it can lead to malnutrition or even illness. Therefore, food processors give considerable attention to determining the shelf lives of their products.

1.3.1 DEFINITIONS

Despite its importance, there is no simple, generally accepted definition of shelf life in the food technology literature. The Institute of Food Technologists (IFT) in the United States has defined shelf life as "the period between the manufacture and the retail purchase of a food product, during which time the product is in a state of satisfactory quality in terms of nutritional value, taste, texture and appearance" (Anon., 1974). This definition overlooks the fact that the consumer may store the product at home for some time before consuming it yet will still want the product to be of acceptable quality.

The Institute of Food Science and Technology (IFST) in the United Kingdom has defined shelf life as "the period of time during which the food product will remain safe; be certain to retain desired sensory, chemical, physical, microbiological and functional characteristics; and comply with any label declaration of nutritional data when stored under the recommended conditions" (Anon., 1993).

Another definition is that "shelf life is the duration of that period between the packing of a product and the end of consumer quality as determined by the percentage of consumers who are displeased by the product" (Labuza and Schmidl, 1988). This definition accounts for the variation in consumer

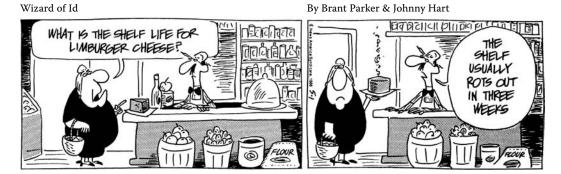


FIGURE 1.1 Shelf life according to the *Wizard of Id.* (Used with permission of John L. Hart FLP and Creators Syndicate, Inc.)

perception of quality (i.e., not all consumers will find a product unacceptable at the same time) and has an economic element, in that, because it is not possible to please all consumers all of the time, a baseline of consumer dissatisfaction must be established. In the branch of statistics known as survival analysis, consumer dissatisfaction can be related to the survival function, defined as "the probability of a consumer accepting a product beyond a certain storage time." Models permitting the application of survival analysis to the sensory shelf life of foods have been published and are discussed further in Chapter 3.

Simply put, shelf life is the time during which all of the primary characteristics of the food remain acceptable for consumption. Thus, shelf life refers to the time for which a food can remain on the retailer's and then the consumer's shelf before it becomes unacceptable.

Until recently, the EU had no definition of shelf life or legislation on how shelf life should be determined; the consolidated EU Directive on food labeling (2000/13/EC) required prepackaged foods to bear a date of "minimum durability" or, in the case of foods that, from a microbiological point of view, are highly perishable, the "use by" date. The date of minimum durability was defined as the "date until which a foodstuff retains its specific properties when properly stored," and any special storage conditions (e.g., temperature not to exceed 7°C) must be specified. This concept allows the processor to set the quality standard of the food, as the product will still be acceptable to many consumers after the "best before" date has passed. More recently, shelf life was defined for the first time in EU legislation, in Commission Regulation (EC) No. 2073/2005 thus: "shelf life means either the period corresponding to the period preceding the 'use by' or the minimum durability date, as defined respectively in Articles 9 and 10 of Directive 2000/13/EC."

According to Cheftel (2005), the date of minimum durability is defined as the date until which the food retains its specific properties when properly stored. It must be indicated by the words "Best before" followed by the date (or a reference to where the date is given on the labeling). Depending on how long the food can keep, the date can be expressed by the day and the month, the month and the year, or the year alone. A list of foods and beverages exempted from date-marking is given in article 9(5) of Directive 2000/13/EC. Foods that are highly perishable microbiologically (and therefore likely to be dangerous for health after a short period) must be labeled with the words "Use by" followed by the date (day and month) or a reference to where the date is given on the labeling. Any distribution after this date is forbidden. The "use by" date must be followed by a description of the storage conditions that should be observed.

In many countries a "best before" date is required on the label. However, if the food is highly perishable from a microbiological point of view and therefore likely, after a short period, to constitute an immediate danger to human health, then the "best before" date must be replaced by a "use by" date. It is illegal to sell food after the "use by" date; food consumed after the "best before" date will still be edible, but its quality will have deteriorated to a level below what the manufacturer considers desirable. Recently, use of the hybrid term "best by" has become popular. A major US brewer now labels bottles of beer with the "born on" date, that is, the date of manufacture, leaving consumers to decide when the beer is no longer acceptable.

1.3.2 FACTORS CONTROLLING SHELF LIFE

The shelf life of a food is controlled by three factors:

- 1. Product characteristics, including formulation and processing parameters (intrinsic factors)
- 2. Environment to which the product is exposed during distribution and storage (extrinsic factors)
- 3. Properties of the package

Intrinsic factors are discussed in Chapter 2 and include pH, water activity, enzymes, microorganisms, and concentration of reactive compounds. Many of these factors can be controlled through the selection of raw materials and ingredients, as well as the choice of processing parameters. Extrinsic factors include temperature, RH, light, total and partial pressures of different gases, and mechanical stresses, including consumer handling. Many of these factors can affect the rates of deteriorative reactions that occur during the shelf life of a product.

The properties of the package can have a significant effect on many of the extrinsic factors and thus indirectly on the rates of the deteriorative reactions. Thus, the shelf life of a food can be altered by changing its composition and formulation, processing parameters, packaging system, or the environment to which it is exposed.

1.3.2.1 Product Characteristics

On the basis of the nature of the changes that can occur during storage, foods can be divided into three categories—perishable, semiperishable, and nonperishable or shelf stable—which translate into very short shelf life products, short to medium shelf life products, and medium to long shelf life products (Robertson, 2006).

Perishable foods are those that must be held at chill or freezer temperatures (i.e., 0° C to 7° C or -12° C to -18° C respectively) if they are to be kept for more than a short period. Examples of such foods are milk; fresh flesh foods such as meat, poultry, and fish; minimally processed foods; and many fresh fruits and vegetables.

Semiperishable foods are those that contain natural inhibitors (e.g., some cheeses, root vegetables and eggs) and those that have undergone some type of mild preservation treatment (e.g., pasteurization of milk, smoking of hams, and pickling of vegetables) that produces greater tolerance to environmental conditions and abuse during distribution and handling.

Shelf stable foods are considered "nonperishable" at room temperatures. Many unprocessed foods fall into this category, and are unaffected by microorganisms because of their low moisture content (e.g., cereal grains, nuts, and some confectionery products). Processed food products can be shelf stable if they are preserved by heat sterilization (e.g., canned foods), contain preservatives (e.g., soft drinks), are formulated as dry mixes (e.g., cake mixes), or are processed to reduce their water content (e.g., raisins or crackers). However, shelf stable foods retain this status only if the integrity of the package that contains them remains intact. Even then, their shelf life is finite due to deteriorative chemical reactions that proceed at room temperature independently of the nature of the package, and the permeation of gases, odors, and water vapor through the package.

1.3.2.2 Distribution and Storage Environment

The deterioration in product quality of packaged foods is often closely related to the transfer of mass and heat through the package. Packaged foods may lose or gain moisture; they will also reflect the temperature of their environment, because very few food packages are good insulators. Thus, the climatic conditions (i.e., temperature and humidity) of the distribution and storage environment have an important influence on the rate of deterioration of packaged foods.

1.3.2.3 Package Properties

Foods can be classified according to the degree of protection required from the package, such as maximum moisture gain or O_2 uptake. This enables calculations to be made to determine whether a particular packaging material would provide the barrier required to give the desired product shelf life. Metal cans and glass containers can be regarded as essentially impermeable to the passage of gases, odors, and water vapor, but paper-based packaging materials can be regarded as permeable. Plastics-based packaging materials provide varying degrees of protection, depending largely on the nature of the polymers used in their manufacture.

In Section 1.2.1 the permeability of thermoplastic polymers was discussed. A discussion of how this information can be used to select the most appropriate polymer for a particular product can be found elsewhere (e.g., see Robertson, 2006).

For a product where the end of shelf life can be directly related to a gain in moisture (e.g., loss of crispness in a snack food), the end of product shelf life is reached when the moisture content m (initially m_i) reaches the critical moisture content m_c , and the following equation applies:

$$\theta_{\rm s} = \frac{X \ W_{\rm s} \ b}{P \ A \ p_{\rm o}} \ln \frac{m_{\rm e} - m_{\rm i}}{m_{\rm e} - m_{\rm c}} \tag{1.5}$$

where m_e is the equilibrium moisture content of the food if exposed to the RH outside the package; W_s is the weight of dry solids enclosed; p_o is the vapor pressure of pure water at the storage temperature (*not* the actual vapor pressure outside the package); and b is the slope of the moisture sorption isotherm when treated as a linear function.

Equation 1.5 and the corresponding equation for moisture loss have been extensively tested for foods and found to give excellent predictions of actual weight gain or loss. These equations are also useful when calculating the effect of changes in the external conditions (e.g., temperature and humidity), the surface area:volume ratio of the package, and variations in the initial moisture content of the product.

The gas of major importance in packaged foods is O_2 , as it plays a crucial role in many reactions that affect the shelf life of foods, for example, microbial growth, color changes in fresh and cured meats, oxidation of lipids and consequent rancidity, and senescence of fruits and vegetables.

The transfer of gases and odors through packaging materials can be analyzed in an analogous manner to that described for water vapor transfer, provided that values are known for the permeance of the packaging material to the appropriate gas and the partial pressure of the gas inside and outside the package. However, the simplifying assumptions made in the derivation of Equation 1.4 can lead to significant errors in the calculated shelf life compared to the actual shelf life. For example, in the case of CO_2 loss from carbonated beverages in PET bottles, the assumption that the gas partitioning between the gas phase and the polymer is described by Henry's law and that mass transfer inside the bottle wall is governed by Fick's law gives rise to the underestimation of the barrier properties of the materials, and, consequently, the predicted shelf life of the carbonated beverage is much shorter than the true one (Masi and Paul, 1982).

Del Nobile et al. (1997) showed the importance of another aspect that is often neglected in predicting the shelf life of carbonated beverages bottled in glassy polymer containers: the influence of the thermal history of the bottle during the period between filling and consumption. In their first example, the shelf life of the beverage was estimated assuming that the storage temperature was constant and equal to room temperature for the entire storage period; the calculated shelf life was 352 days. In the second example, it was assumed that the temperature of the bottle varied during the storage period, but for the sake of simplicity in performing the calculated shelf life was 206 days. In the second example, the actual temperature of storage; the calculated shelf life was 206 days. In the second example, the actual temperature of the bottle of carbonated beverage under conditions comparable to those occurring during distribution led to an estimated shelf life of less than 2 months, significantly less than that predicted by neglecting the temperature rise due to outdoor storage and sunlight exposure. By averaging the temperature and using the corresponding parameters in the calculations, it is implicitly assumed that the diffusion and sorption parameters change linearly with temperature, and this is far from true.

Packaging can control two variables with respect to O_2 , and these can have different effects on the rates of oxidation reactions in foods. One variable is the total amount of O_2 present. This influences the extent of the reaction, and in impermeable packages (e.g., hermetically sealed metal and glass containers), where the total amount of O_2 available to react with the food is finite, the extent of the reaction cannot exceed the amount corresponding to the complete exhaustion of the O_2 present inside the package at the time of sealing. This may or may not be sufficient to result in an unacceptable product quality after a certain period, depending on the rate of the oxidation reaction. This rate will, of course, be temperature dependent. With permeable packages (e.g., plastic packages) into which ingress of O_2 will occur during storage, two factors are important: there may be sufficient O_2 inside the package to cause product unacceptability when it has all reacted with the food, or there may be sufficient transfer of O_2 through the package over time to result in product unacceptability through oxidation. The other variable is the concentration of O_2 in the food. In many cases, relationships between the O_2 partial pressure in the space surrounding the food and the rates of oxidation reactions can be established. If the food itself is very resistant to diffusion of O_2 (e.g., very dense products such as butter), then it will probably be very difficult to establish a relationship between the O_2 partial pressure in the space surrounding the food and the concentration of O_2 in the food.

With certain products packaged with certain materials, the end of shelf life comes when an unacceptable degree of interaction between the package and the product has occurred. Two examples will be given to illustrate the nature of the problem.

The first example is that of a tomato product processed under typical conditions and packaged in a three-piece can with a plain tinplate body and enameled electrolytically chromium-coated steel (ECCS) ends. Over a storage period of 24 months at ambient temperature, several degradative reactions occur. The concentration of tin ions in the product increases rapidly during the first 3 months, from approximately 20 to 160 ppm, reaching 280 ppm after 24 months. Iron also dissolves, increasing slowly from 8 ppm initially to 10 ppm after 18 months, to reach 14 ppm after 24 months. The flavor score declines as a result of the increasing quantities of dissolved tin and iron; the color value shows a decrease owing to an increase in brown pigments, but remains acceptable. The limiting factor for this product is the deterioration in flavor resulting from the dissolution of tin and iron from the package into the product, giving an acceptable shelf life of 24–30 months. If a longer shelf life were required, it would be necessary to use a full enamel-lined can. Alternatively, the product could be stored at chill temperatures to reduce the rate of the degradative reactions.

A second example involves the migration of plasticizers from packaging materials into food such that the legal limit for the migrant in the food is exceeded. For example, gaskets in the lids for glass jars can release epoxidized soy bean oil (ESBO) into meat-containing infant food, and plasticized PVC cling-films have released di-(2-ethylhexyl) adipate (DEHA) into cheese (Grob et al., 2006).

1.3.3 Shelf Life Determination

Methods to determine the shelf life of packaged foods have been published elsewhere (Robertson, 2006) and will not be repeated here. One challenge with shelf life testing is to develop experimental designs that minimize the number of samples required (thus minimizing the cost of the testing) while still providing reliable and statistically valid answers; this is discussed further in Chapter 3. Accelerated shelf life testing (ASLT) applies the principles of chemical kinetics to quantify the effects that extrinsic factors such as temperature, humidity, gas atmosphere, and light have on the rate of deteriorative reactions. By subjecting the food to controlled environments in which one or more of the extrinsic factors is maintained at a higher-than-normal level, the rates of deterioration are speeded up or accelerated, resulting in a shorter-than-normal time to product failure. Because the effects of extrinsic factors on deterioration can be quantified, the magnitude of the acceleration can be calculated and also the "true" shelf life of the product under normal conditions.

The reason behind the need for ASLT of shelf stable food products is simple: as these foods typically have shelf lives of at least one year, evaluating the effect on shelf life of a change in the product (e.g., a new antioxidant or thickener), the process (e.g., a different time/temperature sterilization regime), or the packaging (e.g., a new polymeric film) would require shelf life trials lasting at least as long as the required shelf life of the product. Companies cannot afford to wait for such long periods to know whether the new product, process, or packaging will give an adequate shelf life, and therefore ASLT is used. However, the use of ASLT in the food industry is not as widespread as it might be, due in part to the lack of basic data on the effect of extrinsic factors on the rates of

deteriorative reactions, in part to ignorance of the methodology required, and in part to a skepticism about the advantages to be gained from using ASLT procedures. Of course, in tropical countries, the ambient temperatures and humidities experienced during distribution and in warehouses and homes are in the upper range used for ASLT in temperate climates (45°C and 95% RH); therefore, ASLT is not applicable in such situations, as temperature cannot be accelerated beyond 45°C without the risk of introducing deteriorative reactions that are unrepresentative of what may occur under real circumstances. Although high O_2 pressures can be used to accelerate reactions involving oxidation, this method is not used very often, as oxidation reactions typically become independent of the O_2 concentration above a certain level, which varies with temperature and other conditions. However, Cardelli and Labuza (2001) reported that increasing O_2 concentrations from 0.5 to 21.3 kPa accelerated deterioration of roast and ground coffee 20-fold. If both temperature and O_2 concentration accelerated, then the decreased solubility of O_2 at higher temperatures must be factored into any calculations of shelf life.

In shelf life testing there can be one or more criteria that constitute sample failure. One criterion is an increase or decrease by a specified amount in the mean sensory panel score. Another criterion is microbial deterioration of the sample to an extent that it is rendered unsuitable or unsafe for human consumption. Finally, changes in odor, color, texture, flavor, and so on that render the sample unacceptable to either the panel or the consumer are criteria for product failure. Thus, sample failure can be defined as the condition in which the product exhibits either physical, chemical, microbiological, or sensory characteristics that are unacceptable to the consumer, and the time required for the product to exhibit such conditions is the shelf life of the product.

However, a fundamental requirement in the analysis of data is knowledge of the statistical distribution of the observations, so that the mean time to failure and its standard deviation can be accurately estimated, and the probability of future failures predicted. The shelf life for food products is usually obtained from simple averages of time to failure, on the assumption that the failure distribution is symmetrical. If the distribution is skewed, estimates of the mean time to failure and its standard deviation will be biased. Furthermore, when the experiment is terminated before all the samples have failed, the mean time to failure based on simple averages will be biased because of the inclusion of unfailed data. To improve the methodology for estimating shelf life, knowledge of the statistical distribution of shelf life failures is required, together with an appropriate model for data analysis. This important aspect is discussed further in Chapter 3.

Microbial spoilage of foods is an economically significant problem for food manufacturers, retailers, and consumers. Depending on the product, process, and storage conditions, the microbiological end of shelf life can be determined by either the growth of spoilage or pathogenic microorganisms. Over recent years the development and commercialization of predictive models have become relatively widespread. Predictive models have been used to determine the likely shelf life of perishable foods such as meat, fish, and milk. Despite their increasing sophistication and wide-spread availability, models should not be relied on completely but should rather be used as a tool to assist decision making. Models do not completely negate the need for microbial testing, nor do they replace the judgment of trained and experienced food microbiologists. The use of such models can reduce the need for shelf life trials, challenge tests, product reformulations, and process modifications, thus saving both time and money. The ultimate test for predictive models is whether they can be used to predict outcomes reliably in real situations. For a detailed discussion the reader is referred to Chapter 4.

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2 Food Quality and Indices of Failure

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CONTENTS

2.1	Food (Quality and Safety				
2.2	Deteriorative Reactions in Foods					
	2.2.1	Intrinsic Parameters				
		2.2.1.1 Water Activity			20	
		2.2.1.2	Oxidation-R	eduction Potential		
	2.2.2	Extrinsic Parameters				
		2.2.2.1	Temperature			
				Linear Model		
			2.2.2.1.2 A	Arrhenius Relationship		
			2.2.2.1.3	remperature Quotient		
		2.2.2.2	Relative Hui	nidity	24	
		2.2.2.3	Gas Atmosp	here	24	
		2.2.2.4	Light		24	
	2.2.4	Chemical Reactions				
		2.2.4.1	Lipid Oxida	tion		
				Browning		
		2.2.4.3	Color Chang			
		2.2.4.4	Flavor Chan	ges		
		2.2.4.5	Nutritional C	Changes		
	2.2.5	-				
	2.2.6	Microbiological Changes				
2.3	Rates of Deteriorative Reactions					
2.4	Indices of Failure					

2.1 FOOD QUALITY AND SAFETY

The term "food quality" has a variety of meanings to professionals in the food industry, but the ultimate arbiters of food quality must be the consumers. This notion is embodied in the frequently cited definition of food quality as "the combination of attributes or characteristics of a product that have significance in determining the degree of acceptability of the product to a user." Another definition of food quality is "the acceptance of the perceived characteristics of a product by consumers who are regular users of the product category or those who comprise the market segment." The phrase "perceived characteristics" includes the perception of the food's safety, convenience, cost, value, and so on, and not just its sensory attributes (Cardello, 1998). For the majority of foods and beverages, quality decreases over time. Therefore it follows that there will be a finite length of time before the product becomes unacceptable. This time from production to unacceptability is referred to as shelf life and was discussed in Chapter 1. Quality loss during storage may be regarded as the result of a form of processing at relatively low temperatures that goes on for rather a long time.

Knowledge of the kinds of changes that influence food quality is the first step in developing food packaging that will minimize undesirable changes in quality and maximize the development and maintenance of desirable properties. Once the nature of the reactions is understood, knowledge of the factors that control the rates of these reactions is necessary in order to minimize the changes occurring in foods during storage, that is, while packaged.

The nature of the deteriorative reactions in foods and the factors that control the rates of these reactions will be briefly outlined. Deteriorative reactions can be enzymic, chemical, physical (typically as a result of moisture gain or loss), and biological (both microbiological and macrobiological, that is, due to insect pests and rodents). Biochemical, chemical, physical, and biological changes occur in foods during processing and storage, and these combine to affect food quality. The most important quality-related changes are (van Boekel, 2008) as follows:

- · Chemical reactions, mainly due to either oxidation or nonenzymic browning reactions.
- Microbial reactions: microorganisms can grow in foods. In the case of fermentation this is desired; otherwise, microbial growth will lead to spoilage and, in the case of pathogens, to unsafe food.
- Biochemical reactions: many foods contain endogenous enzymes that can potentially catalyze reactions leading to quality loss (enzymic browning, lipolysis, proteolysis, and more). In the case of fermentation, enzymes can be exploited to improve quality.
- Physical reactions: many foods are heterogeneous and contain particles. These particles are unstable, and phenomena such as coalescence, aggregation, and sedimentation usually lead to quality loss. Also, changes in texture can be considered physical reactions, although the underlying mechanism may be of a chemical nature.

The principal aim of this chapter is to provide a brief overview of the major chemical, biochemical, biological, and physical changes that occur in foods during processing and storage and to show how these combine to affect food quality. Reactions in foods affecting food quality are summarized in Table 2.1. Knowledge of such changes is essential before a sensible choice of packaging materials can be made, as the rate and magnitude of such changes can often be minimized by selection of the correct packaging materials. At the end of the chapter, the concept of indices of failure (IoFs) of food is introduced. IoFs are the quality attributes that will indicate that the food is no longer acceptable to the consumer.

The deterioration of packaged foods (and this includes virtually all foods, because today very few foods are sold without some form of packaging) depends largely on transfers that can occur between the external environment, which is exposed to the hazards of storage and distribution, and the internal environment of the package. For example, there may be transfer of moisture vapor from a humid atmosphere into a dried product, or transfer of an undesirable odor from the external atmosphere into a high-fat product, or development of oxidative rancidity if the package is not an effective oxygen (O_2) barrier. Also, flavor compounds can be absorbed by some types of plastic packaging materials (a phenomenon referred to as scalping), and chemical contaminants can migrate from the packaging material into the food (e.g., plasticizers from plastic film). In addition to the ability of packaging materials to protect and preserve foods by minimizing or preventing the transfers referred to, packaging materials must also protect the product from mechanical damage and prevent or minimize misuse by consumers (including tampering).

Although certain types of deterioration will occur even if there is no transfer of mass (or heat, as some packaging materials can act as efficient insulators against fluctuations in ambient temperatures)

Example	Туре	Consequences				
Nonenzymic browning	Chemical reaction (Maillard reaction)	Color, taste and aroma, nutritive value, formation of toxicologically suspect compounds (acrylamide)				
Fat oxidation	Chemical reaction	Loss of essential fatty acids, rancid flavor, formation of toxicologically suspect compounds				
Fat oxidation	Biochemical reaction (lipoxygenase)	Off-flavors, mainly due to formation of aldehydes and ketones				
Hydrolysis	Chemical reaction	Changes in flavor, vitamin content				
Lipolysis	Biochemical reaction (lipase)	Formation of free fatty acids and peptides, bitter taste				
Proteolysis	Biochemical reaction (proteases)	Formation of amino acids and peptides, bitter taste, flavor compounds, changes in texture				
Enzymic browning	Biochemical reaction of polyphenols	Browning				
Separation	Physical reaction	Sedimentation, creaming				
Gelation	Combination of chemical and physical reaction	Gel formation, texture changes				
Source: Adapted from van Boekel M.A.J.S. 2008. Kinetic modeling of food quality: a critical review. Comprehensive						

TABLE 2.1 Overview of Reactions in Foods Affecting Quality

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between the package and its environment, it is possible in many instances to prolong the shelf life of the food through the use of packaging (Baner and Piringer, 2008).

It is important that food packaging not be considered in isolation from food processing and preservation, or indeed from food marketing and distribution: all interact in a complex way, and concentrating on only one aspect to the detriment of the others is a sure-fire recipe for commercial failure.

The development of an analytical approach to food packaging is strongly recommended, and to achieve this successfully, a good understanding of food safety and quality is required. The more important of these is, without question, food safety, which is the freedom from harmful chemical and microbial contaminants at the time of consumption. Packaging is directly related to food safety in two ways.

First, if the packaging material does not provide a suitable barrier around the food, microorganisms can contaminate the food and make it unsafe. However, microbial contamination can also arise if the packaging material permits the transfer of, for example, moisture or O_2 from the atmosphere into the package. In this situation, microorganisms present in the food but posing no risk because of the initial absence of moisture or O_2 may subsequently be able to grow and present a risk to the consumer.

Second, the migration of potentially toxic compounds from some packaging materials to the food is a possibility in certain situations and gives rise to food safety concerns. In addition, migration of other components from packaging materials, although not harmful to human health, may adversely affect the quality of the product.

The major quality attributes of foods are texture, flavor, color, appearance, and nutritive value, and these attributes can all undergo undesirable changes during processing and storage. With the exception of nutritive value, the changes that can occur in these attributes are readily apparent to the consumer, either before or during consumption. Packaging can affect the rate and magnitude of many of these quality changes. For example, the development of oxidative rancidity can often

be minimized if the package is an effective O_2 barrier; flavor compounds can be absorbed by some plastic polymers but not by others; the particle size of many food powders can increase (i.e., particles can clump) if the package is a poor moisture barrier.

2.2 DETERIORATIVE REACTIONS IN FOODS

Knowledge of the kinds of deteriorative reactions that influence food quality is the first step in developing food packaging that will minimize undesirable changes in quality and maximize the development and maintenance of desirable properties. Once the nature of the reactions is understood, knowledge of the factors that control the rates of these reactions is necessary in order to minimize the changes occurring in foods during storage, that is, while packaged (Robertson, 2006). The nature of the deteriorative reactions in foods is reviewed in this section, and the factors that control the rates of these reactions.

Preservation is a means of protecting a product, usually against microbiological deterioration. It is important to understand the differences between biotic deterioration, which refers to changes in a food product brought about either by a biological function (e.g., ripening of fruit, respiration of vegetables) or attack by microorganisms (e.g., molds, bacteria, and yeasts) and abiotic deterioration, which is brought about by physical or chemical agents (e.g., atmospheric O_2 , moisture, light, odors, and temperature). Both biotic and abiotic deterioration can lead to food spoilage, albeit by different methods. Packaging can be used to provide a barrier to those agents that lead to deterioration.

Deteriorative reactions in foods are influenced by two factors: the nature of the food and its surroundings. These factors are referred to as intrinsic and extrinsic parameters.

2.2.1 INTRINSIC PARAMETERS

Intrinsic parameters are an inherent part of the food and include water activity (a_w), pH, oxidationreduction potential (E_h), O₂ content, and product formulation, including the presence of any preservatives or antioxidants.

2.2.1.1 Water Activity

The parameter a_w is defined as the ratio of the water vapor pressure of a food to the vapor pressure of pure water at the same temperature. Mathematically:

$$a_{\rm w} = p/p_{\rm o} \tag{2.1}$$

where p is the vapor pressure of water exerted by the food and p_o is the saturated vapor pressure of pure water at the same temperature. This concept is related to equilibrium relative humidity (ERH) in that ERH = $100 \times a_w$. However, whereas a_w is an intrinsic property of the food, ERH is a property of the atmosphere in equilibrium with the food. The a_w of most fresh foods is above 0.99. Every microorganism has a limiting a_w value below which it will not grow, form spores, or produce toxic metabolites.

Water can influence chemical reactivity in different ways. It may act as a reactant (e.g., in the case of sucrose hydrolysis), or as a solvent, where it may exert a dilution effect on the substrates, thus decreasing the reaction rate. Water may also change the mobility of the reactants by affecting the viscosity of the food systems and form hydrogen bonds or complexes with the reacting species. Thus, a very important practical aspect of a_w is controlling undesirable chemical and enzymic reactions that reduce the shelf life of foods. It is a well-known generality that rates of changes in food properties can be minimized or accelerated over widely different values of a_w , as shown in Figure 2.1. Small changes in a_w can result in large changes in reaction rates.

When a food is placed in an environment at a constant temperature and relative humidity (RH), it will eventually come to equilibrium with that environment. The corresponding moisture content at steady state is referred to as the equilibrium moisture content. When this moisture content (expressed as mass of water per unit mass of dry matter) is plotted against the corresponding RH or a_w at constant temperature, a moisture sorption isotherm results (see Figure 2.2). Such plots are very useful in assessing the stability of foods and selecting effective packaging. As a_w is temperature dependent, it follows that moisture sorption isotherms must also exhibit temperature dependence. Thus, at constant moisture content (which is the situation existing in a food packaged in an impermeable package), a_w increases with increasing temperature. As rates of deteriorative

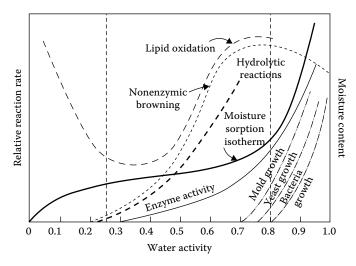


FIGURE 2.1 Rates of reactions as a function of water activity. (Redrawn with permission from Rockland L.B., Beuchat L.R. (Eds). 1987. In: *Water Activity: Theory and Applications to Food*. New York: Marcel Dekker, p. vii. Copyright CRC Press, Boca Raton, Florida.)

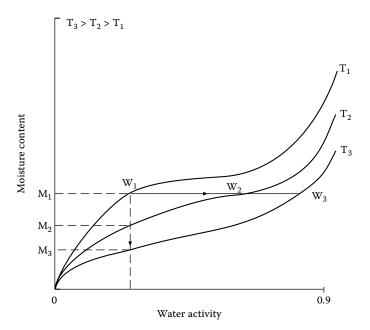


FIGURE 2.2 Schematic of a typical moisture sorption isotherm showing effect of temperature on water activity and moisture content. (From Robertson G.L. 2006. *Food Packaging Principles and Practice*, 2nd edn. Boca Raton, Florida: CRC Press, with permission. Copyright CRC Press, Boca Raton, Florida.)

reactions depend on both a_w and temperature, the increase in rate in such situations will typically be greater than that due solely to an increase in temperature. This has important implications for shelf life.

2.2.1.2 Oxidation-Reduction Potential

The oxidation-reduction potential (also referred to as the redox potential and abbreviated E_h or ORP) is a physicochemical parameter that determines the oxidizing or reducing properties of the medium, and it depends on the composition of the food, pH, temperature, and, to a large extent, the concentration of dissolved O₂ (DO). E_h plays an important role in the cellular physiology of microorganisms, such as growth capacity, enzyme expression, and thermal resistance. Alwazeer et al. (2003) demonstrated that reducing the E_h of orange juice using gas (N₂ and H₂) immediately after heat treatment maximized microbial destruction during pasteurization, prevented the development of microorganisms, and stabilized color and ascorbic acid during storage at 15°C.

The relationship between ORP values and DO levels in milk is not well understood. Several modifications that occur in milk during its processing and storage are driven by different oxidation-reduction reactions. Electrolysis treatments have been applied to milk to produce milk powder with better flavor quality. ORP and DO levels in enriched milk are mainly responsible for the oxidation of unsaturated fatty acids and the loss of viability of probiotic strains such as bifidobacteria. Decreasing the E_h in milk could allow an improvement in the quality of these products. Recent studies on electroreduction of milk by membrane electrolysis have shown that this electrochemical process decreased the E_h of milk without changing the organoleptic and nutritive values (Schreyer et al., 2008).

2.2.2 EXTRINSIC PARAMETERS

Extrinsic factors that control the rates of deteriorative reactions include temperature, RH, gas atmosphere, and light; packaging can, to varying degrees, influence the impact of these factors on the rates of deteriorative reactions, depending on the specific packaging material.

2.2.2.1 Temperature

Temperature is a key factor in determining the rates of deteriorative reactions, and in certain situations the packaging material can affect the temperature of the food. This is particularly so with packaging materials that have insulating properties, and these types of packages are typically used for chilled and frozen foods. For packages that are stored in refrigerated display cabinets, most of the cooling takes place by conduction and convection. Simultaneously, there is a heat input by radiation from the fluorescent lamps used for lighting. Under these conditions, aluminum foil offers real advantages because of its high reflectivity and high conductivity.

Several models have been developed to represent the effect of temperature on the rates of deteriorative reactions.

2.2.2.1.1 Linear Model

This simple expression relating the rate of reactions and temperature has been used for many years:

$$k = k_0 e^{b(T-T_0)} \tag{2.2}$$

where

 $k_{\rm o}$ = rate at temperature $T_{\rm o}$ (°C) k = rate at temperature T (°C) b = a constant characteristic of the reaction e = 2.7183.