

Susan E.M. Selke
John D. Culter
Ruben J. Hernandez

Plastics Packaging

Properties, Processing, Applications,
and Regulations



2nd Edition

HANSER

Susan E.M. Selke
John D. Culter
Ruben J. Hernandez

Plastics Packaging

Properties, Processing, Applications,
and Regulations

2nd Edition

Hanser Publishers, Munich

•

HANSER
Hanser Publications, Cincinnati

The Authors:

Professor Dr. Susan E.M. Selke, Michigan State University, School of Packaging, East Lansing, MI 48824-1223, USA
John D. Culter, President Advanced Materials Engineering Inc., Naples, FL 34114-9232, Silver Lake Blvd. 1231, USA
Professor Ruben J. Hernandez (†)

Distributed in the USA and in Canada by
Hanser Publications
6915 Valley Avenue, Cincinnati, Ohio 45244-3029, USA
Phone: (513) 527-8996 or 1-800-950-8977
www.hanserpublications.com

Distributed in all other countries by
Carl Hanser Verlag
Postfach 86 04 20, 81631 München, Germany
Fax: +49 (89) 98 48 09
www.hanser.de

The use of general descriptive names, trademarks, etc., in this publication, even if the former are not especially identified, is not to be taken as a sign that such names, as understood by the Trade Marks and Merchandise Marks Act, may accordingly be used freely by anyone.

While the advice and information in this book are believed to be true and accurate at the date of going to press, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Library of Congress Cataloging-in-Publication Data

Selke, Susan E. M.

Plastics packaging: properties, processing, application and regulations /
Susan E.M. Selke, John D. Culter, Ruben J. Hernandez.-- 2nd ed.
p. cm.

Ruben J. Hernandez appears first on the previous edition.

Includes bibliographical references and index.

ISBN 1-56990-372-7 (hardcover)

1. Plastics in packaging. 2. Polymers. I. Culter, John D., 1937- II.
Hernandez, Ruben J., 1945- III. Hernandez, Ruben J., 1945- Plastics
packaging. IV. Title.

TS198.3.P5H47 2004

688.8--dc22

2004020052

Bibliografische Information Der Deutschen Bibliothek

Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie;
detaillierte bibliografische Daten sind im Internet über <<http://dnb.ddb.de>> abrufbar.

ISBN 3-446-22908-6

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying or by any information storage and retrieval system, without permission in writing from the publisher.

© Carl Hanser Verlag, Munich 2004

Production Management: Oswald Immel

Typeset by Susan E.M. Selke, USA

Coverconcept: Marc Müller-Bremer, Rebranding, München, Germany

Coverdesign: MCP • Susanne Kraus GbR, Holzkirchen, Germany

Printed and bound by Druckhaus "Thomas Müntzer" GmbH, Bad Langensalza, Germany

In memory of

Ruben J. Hernandez
1945-2002

Professor
School of Packaging
Michigan State University

Preface

This book is intended to provide a basic understanding of plastic packaging materials. It covers the properties of common packaging plastics, and relates these properties to the chemical structure of the polymers. Common processing methods for transforming plastic resins into packages are covered.

In this book we discuss the uses of plastics in packaging. Although this is not a course in chemistry nor in material science, we attempt to stress the relationship between chemical structure and packaging material properties. We expect the reader to have some knowledge of chemistry and physics. The major purpose of this book is to provide the students in the School of Packaging with reading material on plastics for packaging; however, we hope that it can also be useful to packaging professionals responsible for writing specifications, designing, fabricating, testing, and controlling the quality of plastic materials. We also hope to trigger the reader's curiosity to pursue further studies in the exciting world of packaging materials.

This second edition fixes some of the errors that, despite our best efforts, found their way into the first edition. Unfortunately, we're sure that we have not yet found them all! We have also expanded and updated the discussion of PET bottle production, retort pouches, polylactides, plastics recycling, and a variety of other topics.

We have deliberately included some information that goes well beyond what would normally be included in an introductory level packaging course, in order that it will be available for the more advanced student and for the practitioner. In the first edition, we attempted to identify this material by putting it inside grey boxes. We have abandoned that convention in this edition for a variety of reasons, the most compelling being that instructors vary in what they choose to incorporate in an introductory course. We decided that it is better to leave it up to individual instructors to tell students what sections, or portions of sections, to omit in their study of this text.

Contents

Preface	v
Chapter 1 Introduction	1
1.1 Historic Note	1
1.2 Role of Plastics in Packaging	2
1.3 Book Structure	6
Chapter 2 Basic Concepts and Definitions	7
2.1 Terminology	7
2.1.1 Macromolecule	7
2.1.2 Polymer	8
2.1.3 Plastic	8
2.1.4 Monomer	10
2.1.5 Constitutional Unit	11
2.1.6 Homopolymer	11
2.1.7 Copolymer	11
2.2 Polymer Nomenclature	12
2.3 Interatomic and Intermolecular Forces in Polymers	13
2.3.1 Interatomic Forces	13
2.3.1.1 Covalent Bonds	14
2.3.1.2 Ionic Bonds	15
2.3.2 Intermolecular and Intramolecular Forces	15
2.3.2.1 Dispersion Forces	16
2.3.2.2 Induction Forces	17
2.3.2.3 Dipole Forces	17
2.3.2.4 Hydrogen Bonds	17
2.4 Properties Determined by Chemical Composition	18
2.5 Categorization of Plastics	19
Study Questions	19

Chapter 3	Polymer Structure and Properties	21
3.1	Introduction	21
3.2	Molecular Architecture	21
3.2.1	Linear Polymers	22
3.2.2	Branched Polymers	22
3.2.3	Cross-Linked Polymers	24
3.3	Copolymer Structure	25
3.3.1	Random Copolymers	25
3.3.2	Alternating Copolymers	26
3.3.3	Block Copolymers	26
3.3.4	Graft Copolymers	28
3.3.5	Combinations of Copolymer Types	29
3.4	Chain Polymerization, Addition Polymers	29
3.4.1	Addition or Chain Polymerization	30
3.4.2	Vinyl Polymers	31
3.4.3	Free-Radical Polymerization	33
3.4.3.1	Initiation	33
3.4.3.2	Propagation	33
3.4.3.3	Termination	34
3.4.4	Polyethylene Polymerization Processes	34
3.4.5	Other Addition Polymerization Mechanisms	38
3.5	Molecular Configuration and Conformation	38
3.6	Head-to-Head and Head-to-Tail Configurations of Vinyl Polymers	38
3.7	Stereochemistry	40
3.8	Step Polymerization, Condensation Polymers	42
3.9	Molecular Weight and Molecular Weight Distribution	46
3.9.1	Degree of Polymerization	46
3.9.2	Molecular Mass (Weight) and Molecular Weight Distribution	46
3.9.3	Number Average Molecular Weight	48
3.9.4	Weight Average Molecular Weight	49
3.9.5	Other Molecular Weight Averages	52
3.9.6	Determination of MWD	52
3.9.7	Effect of Molecular Weight and Molecular Weight Distribution on Flow and Mechanical Properties	53
3.10	Polymer Morphology	56
3.10.1	Crystallinity	57
3.10.2	Polymer Orientation	62
3.10.3	Degree of Crystallinity	64
3.11	Thermal Properties	65
3.11.1	Melting Temperature	65
3.11.2	Glass Transition Temperature	66
3.11.2.1	Measuring T_g	69
3.11.2.2	Variables Affecting T_g	70
3.11.3	Other Thermal Transitions	72
3.11.4	Heat Capacity	72
3.11.5	Heat of Fusion	73
3.11.6	Thermal Conductivity	73

3.11.7	Thermal Expansion Coefficient	74
3.11.8	Other Dimensional Changes	74
3.11.9	Dimensional Stability	75
3.12	Mechanical Properties	75
3.12.1	Tensile Properties	76
3.12.2	Tear Strength	78
3.12.3	Impact and Bursting Strength	78
3.12.4	Other Mechanical Properties	79
3.13	Barrier Properties	80
3.13.1	Diffusion Coefficient	80
3.13.2	Solubility Coefficient	81
3.13.3	Permeability Coefficient	81
3.14	Surfaces and Adhesion	81
3.14.1	Surface Tension	81
3.14.2	Wettability	82
3.14.3	Adhesive Bond Strength	82
3.14.4	Cohesive Bond Strength	83
3.14.5	Blocking	83
3.14.6	Friction	83
3.14.7	Heat Sealing	84
3.15	Optical Characteristics	84
3.15.1	Gloss	85
3.15.2	Haze	85
3.15.3	Transparency and Opacity	86
3.16	Electrical Properties	86
3.17	Plastics Identification Using IR Spectrophotometry	87
	References	89
	Study Questions	89
Chapter 4	Major Plastics in Packaging	91
4.1	Branched Polyethylenes	91
4.1.1	Low Density Polyethylene	93
4.1.2	Ethylene Vinyl Acetate (EVA)	94
4.1.3	Ethylene Acrylic Acid (EAA)	95
4.1.4	Ionomers	96
4.2	Linear Polyethylenes	97
4.2.1	High Density Polyethylene (HDPE)	98
4.2.2	Linear Low Density Polyethylene (LLDPE)	100
4.2.3	Metallocene Polymers	101
4.2.4	Property Trends in the Polyethylene Family	105
4.3	Polypropylene (PP)	105
4.3.1	PP Homopolymer	107
4.3.2	Random Copolymer Polypropylene	107
4.4	Polyvinyl Chloride (PVC)	109
4.5	Vinylidene Chloride Copolymers (PVDC)	111
4.6	Polystyrene (PS)	112
4.7	Polyvinyl Alcohol (PVOH) and Ethylene Vinyl Alcohol (EVOH)	114

4.7.1	Polyvinyl Alcohol	114
4.7.2	Ethylene Vinyl Alcohol	115
4.8	Nylon	117
4.9	Polyester	120
4.9.1	Polyethylene Terephthalate (PET)	120
4.9.2	Glycol Modified PET, Other PET Copolymers, and PET Blends	122
4.9.3	Polyethylene Naphthalate (PEN)	122
4.10	Polycarbonate (PC)	124
4.11	Fluoropolymers	125
4.12	Styrene-Butadiene Copolymers	126
4.13	Acrylonitrile Copolymers	127
4.14	Cyclic Olefin Copolymers	128
4.15	Liquid Crystal Polymers	128
4.16	Conductive Polymers	129
4.17	Thermoplastic Elastomers	130
4.18	Thermosets	131
4.19	Cellophane and Cellulosic Plastics	133
4.19.1	Cellophane	133
4.19.2	Cellulosic Plastics	134
4.20	Polymer Blends	135
	References	138
	Study Questions	138
Chapter 5 Additives and Compounding		141
5.1	Introduction	141
5.2	Compounding	142
5.3	Antioxidants	144
5.4	Heat Stabilizers	147
5.5	UV Stabilizers	148
5.6	Additives to Modify Surface Attractions	149
5.6.1	Antiblocking Agents	150
5.6.2	Slip Agents	150
5.6.3	Antislip Agents	151
5.6.4	Lubricants	151
5.6.5	Mold Release Agents	152
5.7	Colorants	152
5.7.1	Dyes	152
5.7.2	Organic Pigments	152
5.7.3	Inorganic Pigments	152
5.7.4	Specialty Pigments	152
5.7.5	Colorants and the FDA	155
5.8	Antifogging Agents	155
5.9	Nucleating Agents	156
5.10	Antistatic Agents	157
5.11	Plasticizers	158
5.12	Oxygen Scavengers, Desiccants and Fragrance Enhancers	159
5.13	Fillers and Reinforcers	161

5.14	Antimicrobials or Biocides	162
5.15	Other Additives	163
	Study Questions	163
Chapter 6	Adhesion, Adhesives and Heat Sealing	165
6.1	Adhesion	165
6.2	Adhesives	166
6.3	Adhesive and Cohesive Bond Strength	167
6.3.1	Adhesive Bond Strength	168
6.3.1.1	Surface Tension	168
6.3.1.2	Solubility Parameter	169
6.3.1.3	Viscosity	171
6.3.1.4	Estimation of Adhesive Bond Strength	172
6.3.2	Cohesive Bond Strength	172
6.4	Types of Adhesives	173
6.4.1	Reactive Adhesives	173
6.4.2	Hot Melt Adhesives	174
6.4.3	Solvent-Borne Adhesives	174
6.4.4	Water-Borne Adhesives	175
6.4.5	Pressure Sensitive and Remoistenable Adhesives	176
6.4.6	Cold-Seal Adhesives	177
6.5	Application of Adhesives	177
6.6	Adhesive Terminology	179
6.7	Adhesive Additives	179
6.8	Heat Sealing	180
6.8.1	Sealing Methods	181
6.8.1.1	Bar or Thermal Sealing	182
6.8.1.2	Impulse Sealing	182
6.8.1.3	Band Sealing	183
6.8.1.4	Hot Wire or Hot Knife Sealing	183
6.8.1.5	Ultrasonic Sealing	184
6.8.1.6	Friction Sealing	184
6.8.1.7	Hot Gas Sealing and Contact Sealing	185
6.8.1.8	Radiant Sealing	185
6.8.1.9	Dielectric Sealing	185
6.8.1.10	Magnetic Sealing	185
6.8.1.11	Induction Sealing	185
6.8.1.12	Solvent Sealing	186
6.8.2	Heat Conduction in Multilayer Flexible Materials	187
6.8.3	Hot Tack	188
6.8.4	Heat Seal Jaws	188
6.8.5	Heat Seal Failure Modes	189
6.8.6	Evaluation of Seals in Flexible Packaging Materials	190
	References	191
	Study Questions	191

Chapter 7 Extrusion, Film and Sheet	193
7.1 Extrusion and Extruders	193
7.1.1 Hopper and Feed Port	194
7.1.2 Feed Section	195
7.1.3 Compression Section	196
7.1.4 Metering Section	197
7.1.5 Mixing Devices	197
7.1.6 Extruder and Screw Design and Size	198
7.1.7 Dies	199
7.1.8 Melt Filters	199
7.1.9 Drive Mechanisms and Screw Speeds	199
7.1.10 Special Designs	200
7.1.11 Extrusion Temperatures	200
7.1.12 Extrusion Pressures	201
7.2 Cast Film and Sheet	202
7.2.1 Cold Cast or Chill Roll Cast Process	202
7.2.2 Roll Stack and Calendering Processes	202
7.2.3 Quench Tank or Water Bath Process	203
7.2.4 Nip Rolls and Winding	204
7.2.5 Gauge Control	204
7.2.6 Orientation	204
7.2.7 Cast Film Dies	206
7.3 Blown Film	207
7.3.1 Blown Film Extrusion	208
7.3.2 Blown Film Dies	209
7.3.3 Air Rings and Internal Bubble Cooling (IBC)	211
7.3.4 Collapsing Frames	213
7.3.5 Nips	214
7.3.6 Slitting and Winding	215
7.3.7 Double-Bubble Process	216
7.4 Stretch and Shrink Wrap	216
7.4.1 Stretch Wrap	216
7.4.2 Shrink Wrap	217
7.5 Film and Sheet Coextrusion	218
7.6 Surface Treatment	220
7.7 Yield of Film	221
7.8 Testing and Evaluation of Films	222
References	223
Study Questions	223
Chapter 8 Converting, Lamination and Coating	225
8.1 Extrusion Coating and Laminating	225
8.2 Hot Melt Lamination or Coating	228
8.3 Adhesive Lamination	229
8.4 Thermal Laminating	231
8.5 Metallized Film	231

8.6	Silicon Oxide Films	233
8.7	Other Inorganic Barrier Coatings	233
8.8	Building Multilayer Structures	234
	References	235
	Study Questions	235
Chapter 9 Flexible Packaging		237
9.1	Characteristics of Flexible Packaging	237
9.2	Pouch Styles	238
	9.2.1 Pillow Pouches	238
	9.2.2 Three-side Seal Pouches	239
	9.2.3 Four-side Seal Pouches	239
	9.2.4 Stand-up Pouches	240
9.3	Forming Pouches	241
9.4	Bulk and Heavy-Duty Bags	243
9.5	Retort Pouches	244
9.6	Bag-in-Box	245
	References	245
	Study Questions	245
Chapter 10 Thermoforming		247
10.1	Introduction	247
10.2	Heating the Sheet	248
	10.2.1 Temperature Selection	248
	10.2.2 Radiative Heating	248
10.3	Forming the Sheet	250
	10.3.1 Basic Methods	250
	10.3.1.1 Drape Forming	250
	10.3.1.2 Vacuum Forming	251
	10.3.1.3 Pressure Forming	251
	10.3.2 Sheet Deformation	252
	10.3.3 Thermoforming Variations	253
	10.3.3.1 Plug-Assist Thermoforming	254
	10.3.3.2 Solid Phase Pressure Forming	254
	10.3.3.3 Bubble or Billow Forming	254
	10.3.3.4 Vacuum Snap-Back Thermoforming	255
	10.3.3.5 Matched Mold Forming	255
	10.3.3.6 Scrapless Thermoforming	255
	10.3.3.7 In-Line Thermoforming and Melt-to-Mold Thermoforming	257
	10.3.3.8 Twin-Sheet Thermoforming	258
	10.3.3.9 Skin Packaging	258
	10.3.4 Selection of Thermoforming Method	259
10.4	Trimming the Sheet	259
10.5	Part and Mold Design	259
	10.5.1 Prototype Molds	260
	10.5.2 Production Molds	263

10.6	Thermoform-Fill-Seal Systems	264
	References	264
	Study Questions	264
Chapter 11 Injection Molding, Closures, Rotational Molding, Compression Molding, and Tubes		267
11.1	Injection Molding	267
11.1.1	Injection Molding Machines	267
11.1.2	Injection Mold Units	268
11.1.3	Polymer Flow	269
11.1.4	Removal of Molded Parts	272
11.1.5	Hot Runner Molds	273
11.1.6	Venting	273
11.1.7	Applications of Injection Molding	274
11.2	Closures	274
11.2.1	Friction Closures	275
11.2.2	Snap-fit Closures	275
11.2.3	Threaded Closures	276
11.2.4	Specialty Closures	278
11.2.5	Fitments and Overcaps	279
11.3	Rotational Molding	279
11.4	Compression Molding	279
11.5	Plastic Tubes	280
	References	282
	Study Questions	282
Chapter 12 Blow Molding and Bottles		283
12.1	Blow Molding	283
12.2	Extrusion Blow Molding	284
12.2.1	Basic Extrusion Blow Molding Process	284
12.2.2	Parison Dimensions	286
12.2.3	Extrusion Blow Molding Variations	287
12.2.4	Container Designs	287
12.2.5	Die Shaping	288
12.2.6	Programmed Parison	289
12.2.7	Coextruded Bottles	290
12.3	Injection Blow Molding	292
12.3.1	IBM Process	292
12.3.2	Preform Design Process	294
12.3.3	Comparison of Injection and Extrusion Blow Molding	297
12.4	Stretch Blow Molding	297
12.4.1	Plastic Soft Drink Bottles	297
12.4.2	Overview of Stretch Blow Molding	298
12.4.3	Manufacture of PET Preforms	300
12.4.4	Bottle Blowing	303
12.4.4.1	Preform Heating	304

12.4.4.2	Blowing the Bottles	305
12.5	Hot Fill Bottles	306
12.6	Coinjection Blow Molded Bottles	309
12.7	Foam Blow Molding	310
12.8	Blow Molds	311
12.9	In-Mold Labeling	312
12.10	Aseptic Blow Molding	313
12.11	Surface Treatment	313
12.11.1	Flame Treatment	313
12.11.2	Coatings	313
12.11.3	Fluorination	314
12.11.4	Sulfonation	315
12.12	Dimensions and Tolerances for Plastic Bottles	315
	References	316
	Study Questions	316
Chapter 13	Foams, Cushioning and Distribution Packaging	319
13.1	Foams	319
13.1.1	Polystyrene Foam	320
13.1.1.1	Expanded Polystyrene Foam (EPS)	320
13.1.1.2	Extruded Polystyrene Foam	321
13.1.1.3	Styrene Copolymer Foams	322
13.1.2	Polyolefin Foams	322
13.1.3	Polyurethane Foams and Foam-in-Place Systems	323
13.1.4	Starch-Based Foams	324
13.2	Non-Foam Plastic Cushioning Systems	324
13.3	Cushioning	325
13.4	Thermal Insulation of Foams	327
13.5	Plastic Pallets	328
13.6	Plastic Drums and Other Shipping Containers	329
13.7	Packaging for Electrostatic Discharge Protection	330
	References	331
	Study Questions	331
Chapter 14	Mass Transfer in Polymeric Packaging Systems: Sorption, Diffusion, Permeation and Shelf Life	333
14.1	Introduction	333
14.2	Physical and Chemical Basis for Interactions	334
14.3	Types of Interactions	335
14.3.1	Permeation	335
14.3.2	Migration	336
14.3.3	Sorption	337
14.4	Thermodynamic Equilibrium	338
14.4.1	Gas Phase Chemical Activity	339
14.4.2	Solubility	339
14.4.3	Partition Coefficient	341

14.5	Diffusion	342
14.6	Steady State Diffusion Across a Single Sheet: Permeability	343
14.7	Variables Affecting Permeability	348
14.7.1	Chemical Structure of the Polymer	348
14.7.2	Chemical Structure of the Permeant Molecule	348
14.7.3	Effect of Temperature	351
14.7.4	Effect of Humidity	354
14.7.5	Physical Structure of the Polymer	354
14.7.6	Effect of Permeant Concentration	357
14.8	Experimental Determination of Permeability	358
14.9	Multilayer Structures	360
14.10	Applications of the Permeability Equation	363
14.11	Shelf Life Estimation	364
	References	370
	Study Questions	371
Chapter 15 U.S. Regulations and Plastic Packaging		375
15.1	Introduction	375
15.2	The U.S. Federal Food, Drug and Cosmetic Act	376
15.3	Medical Packaging Regulations	376
15.3.1	Drug Packaging	376
15.3.2	Medical Device Packaging	377
15.4	Food Packaging Regulations	378
15.4.1	What is a Food Additive?	378
15.4.1.1	Example 1: Information on Nylon Available in the CFR	380
15.4.1.2	Example 2: Identification of Relevant Regulations for Fabrication of an Adhesive-laminated Plastic Bag	380
15.4.2	Acceptable Amounts of Migration	381
15.4.3	Threshold of Regulation	382
15.4.4	Food Processing Equipment and the Housewares Exclusion	383
15.4.5	Determining the Conditions of Use	383
15.4.6	Multilayer Food Packages	384
15.4.7	GRAS and Prior-Sanctioned Additives	385
15.4.8	Use of Recycled Plastics for Food Packaging	385
15.4.9	Role of Manufacturers and Users in Determining FDA Compliance	388
15.5	Cosmetic Packaging Regulations	388
15.6	State Laws and Regulations	388
15.6.1	Degradable Beverage Carriers	389
15.6.2	“Model Toxics” Legislation	389
15.6.3	Resin Coding on Plastic Bottles	391
15.6.4	Recycling Rate/Recycled Content Requirements	393
15.6.4.1	Oregon	393
15.6.4.2	California	393
15.6.4.3	Wisconsin	394
15.7	Potential Future Issues	394
	References	395
	Study Questions	395

Chapter 16 Environmental Considerations	397
16.1 Introduction	397
16.2 Solid Waste Concerns	398
16.3 Source Reduction and Reuse	402
16.4 Recycling of Plastic Packaging	403
16.4.1 Collection of Packaging Materials for Recycling	404
16.4.2 Recycling Rates for Plastics Packaging	405
16.4.3 Processing of Collected Plastics	407
16.4.3.1 Size Reduction	407
16.4.3.2 Cleaning	407
16.4.3.3 Sorting	408
16.4.3.4 Extrusion and Pelletizing	410
16.4.4 Feedstock Recycling	410
16.5 PET Recycling	411
16.6 HDPE Recycling	412
16.7 LDPE Recycling	414
16.8 Recycling of PS, PP, and PVC	415
16.9 Recycling of Commingled Plastics	416
16.10 Biodegradable Plastics	417
16.10.1 PHAs	418
16.10.2 Polylactides	418
16.10.3 Other Polyesters	418
16.10.4 Starch-Based Plastics	419
16.10.5 Other Biodegradable Plastics	420
16.11 Other Environmental Concerns	420
16.11.1 Resource Depletion and Energy Efficiency	420
16.11.2 Pollution	421
16.11.3 Climate Change	421
16.12 Lifecycle Assessment	422
References	423
Study Questions	424
Additional Reading	427
Index	433

1 Introduction

1.1 Historic Note

The first man-made plastic, a form of cellulose nitrate, was prepared in 1838 by A. Parker and shown at the Great International Exhibition in London in 1862. It was intended to be a replacement for natural materials such as ivory and was called parkesine. In 1840, Goodyear and Hancock developed the "vulcanization" procedure that eliminated tackiness and added elasticity to natural rubber. The change in the properties of the natural rubber was obtained by the addition of sulfur powder that produced additional chemical bonds in the bulk of the rubber.

In 1851, hard rubber, or ebonite, was commercialized. In 1870 a patent was issued to J. Hyatt, of New York, for celluloid, a type of cellulose nitrate with low nitrate content produced at high temperature and pressure. This was the first commercially available plastic, and the only one until the development of Bakelite by Baekeland in 1907. Bakelite is the oldest of the purely synthetic plastics and consisted of a resin obtained by the reaction of phenol and formaldehyde.

The exact nature of plastics, rubber, and similar natural materials was not known until 1920, when H. Staudinger proposed a revolutionary idea: all plastics, rubber, and materials such as cellulose were polymers, or macromolecules. Before Staudinger's theory, the scientific community was very confused about the exact nature of plastics, rubbers and other materials of very high molecular weight. To most research workers in the 19th century, the finding that some materials had a molecular weight in excess of 10,000 g/mol appeared to be untrustworthy. They confused such substances with colloidal systems consisting of stable suspensions of small molecules.

Staudinger rejected the idea that these substances were organic colloids. He hypothesized that the high molecular weight substances known as polymers were true macromolecules formed by covalent bonds. Staudinger's macromolecule theory stated that polymers consist of long chains in which the individual monomers (or building blocks) are connected with each other by normal covalent bonds. The unique polymer properties are a consequence of the high molecular weight and long chain nature of the macromolecule. While at first his hypothesis was not readily accepted by most scientists,