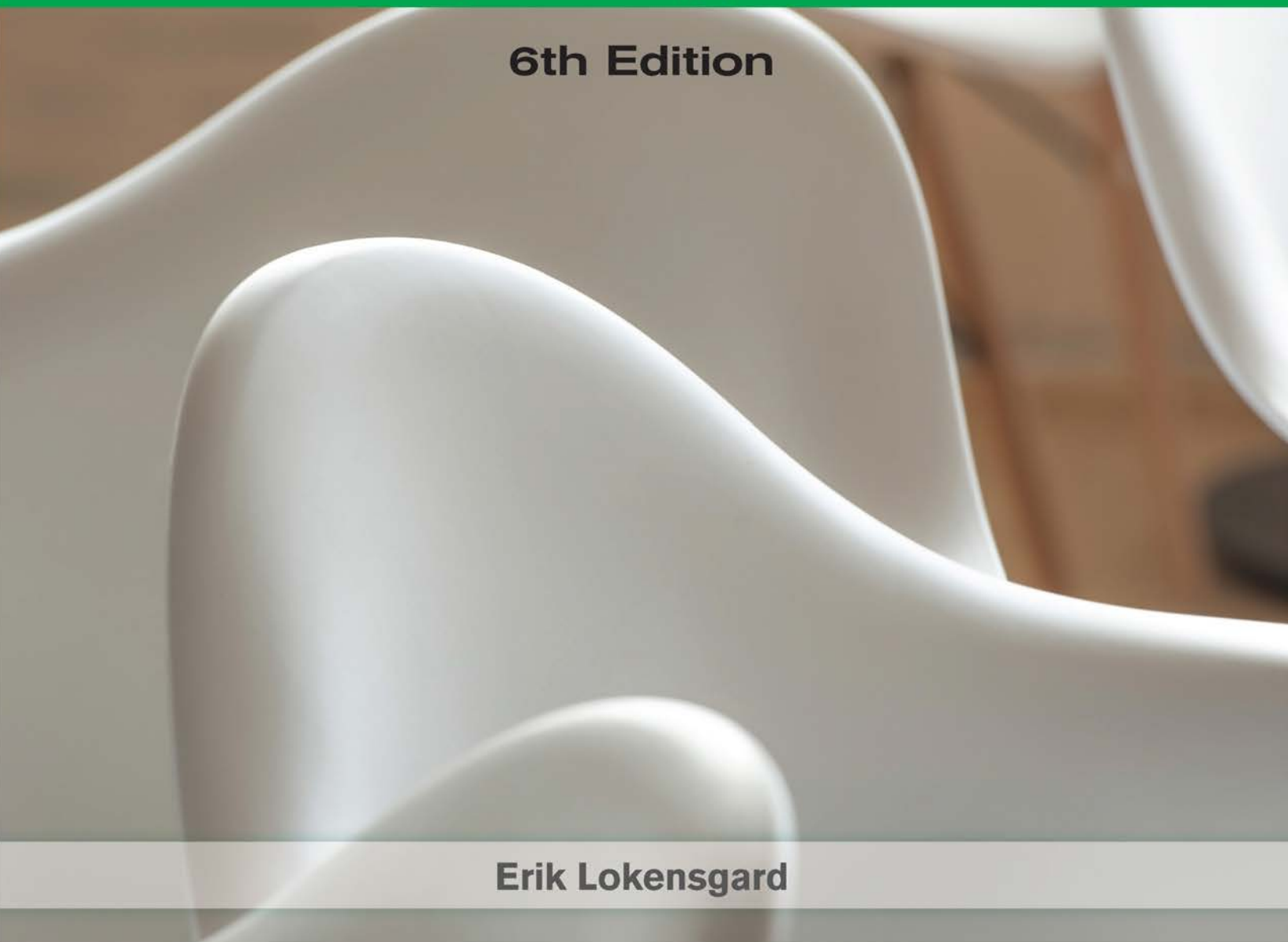
INDUSTRIAL PLASTICS

Theory and Applications

6th Edition



Erik Lokensgard

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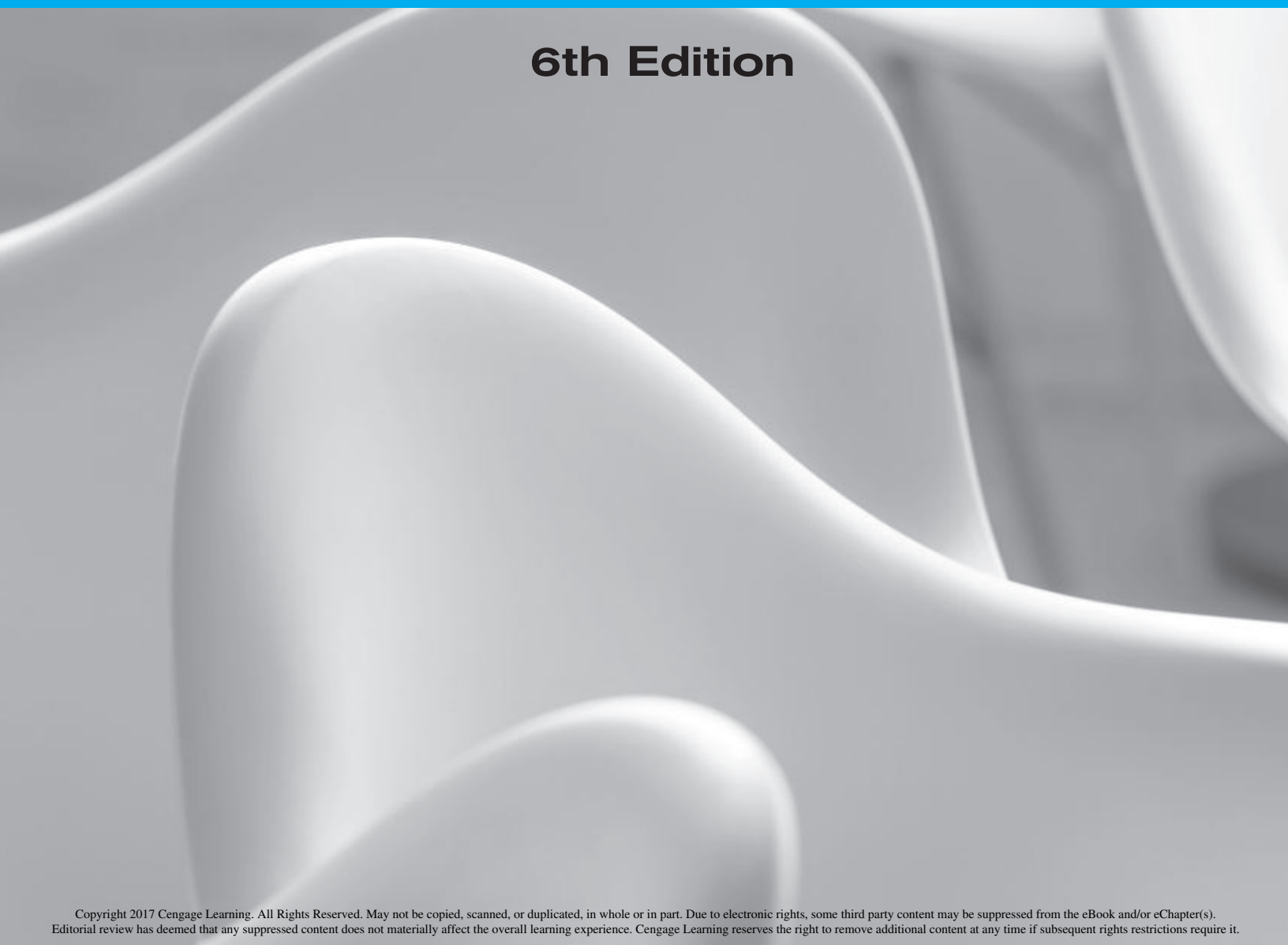

INDUSTRIAL PLASTICS

Theory and Applications

6th Edition

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Industrial Plastics: Theory and Applications, Sixth Edition
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PREFACE

INTENDED USE

Industrial Plastics: Theory and Applications, Sixth Edition, covers all facets of industrial plastics technology as well as major manufacturing processes, serving as an indispensable resource for those individuals enrolled in polymer technology or plastics technology programs at community colleges, technical colleges, and universities. Comprehensive in nature, this text will also be useful to professionals who wish to review the basics and remain up to date on the latest technology in plastics manufacturing.

TEXT LAYOUT

Presented in a logical sequence, *Industrial Plastics* builds topics from the ground up—covering everything from the history of plastics to the running of a successful plastics business.

CHAPTER 1, provides a historical introduction to plastics.

CHAPTER 2, includes extensive updates on the current status of the plastics industry. It features US consumption of major plastics materials, recycling, disposal, and significant organizations within the industry.

CHAPTER 3, treats elementary polymer chemistry. It attempts to present basics about plastics and polymer chemistry in a practical context.

CHAPTER 4, on health and safety, reflects the organization in material safety data sheets. The intent of this chapter, which has been updated to reflect current standards, is to assist students in becoming adept at reading and understanding MSDSs for plastics.

CHAPTER 5, on elementary statistics, relies on graphical techniques rather than hypothesis testing.

CHAPTER 6, on properties and tests, has been updated to show current varieties of testing equipment.

CHAPTER 7, on ingredients of plastics, includes a new section on nanocomposites.

CHAPTER 8, on the selection of plastics for specific applications, has the intent of explaining the differences between various grades of plastics.

CHAPTER 9, on machining and finishing, treats common processes for shaping and polishing plastics products.

CHAPTER 10, on molding processes, includes a new section on all-electric and hybrid injection-molding machines. It continues to feature thorough treatment of injection-molding safety.

CHAPTER 11, on extrusion, now includes several recent photos of multilayer blow-molding equipment and blown film equipment.

CHAPTER 12, on laminating processes, discusses layers of plastics, paper, glass fibers, and metal.

CHAPTER 13, on reinforcing processes, includes numerous processes to create a matrix of fibrous reinforcements and plastics.

CHAPTER 14, on casting processes, includes several new photographs of large rotational molding equipment.

CHAPTER 15, on thermoforming, treats the major methods to form sheet materials with vacuum, pressure, and mechanical forces.

CHAPTER 16, on expansion processes, discusses techniques to create foamed materials. It includes several new photographs of synthetic turf.

CHAPTER 17, on coating processes, concerns the application of coatings onto plastics substrates and the application of plastics onto non-polymeric substrates.

CHAPTER 18, on fabrication, treats both mechanical and chemical techniques.

CHAPTER 19, on decoration processes, includes updated information on hot-foil stamping, as well as other decorating techniques.

CHAPTER 20, on radiation processes, treats growth in the use of radiation processing.

CHAPTER 21, on design, includes a new section on stereolithography.

CHAPTER 22, on tooling and mold making, covers major machining techniques.

CHAPTER 23, on commercial considerations, provides updated coverage of auxiliary equipment.

APPENDIX A, the glossary, provides definitions of terms.

APPENDIX B, on abbreviations, includes chemical or generic names for an updated list of abbreviations.

APPENDIX C, on trade names, provides trade names, the corresponding name of the plastics, and the manufacturer.

APPENDIX D, on material identification, offers several methods to identify unknown plastics.

APPENDIX E, on thermoplastics, contains extensive material and a thorough list of thermoplastics.

APPENDIX F, on thermosets, treats most major thermoset materials.

APPENDIX G, provides useful tables showing conversions of various units.

APPENDIX H, provides contacts for many organizations and also a selected bibliography.

The new and updated sixth edition of *Industrial Plastics* will further enhance the ease of use and the depth of content.

NEW TO THIS EDITION

The Latest Technology

The sixth edition of *Industrial Plastics: Theory and Applications* provides updated materials on websites in all chapters, current data on the plastics industry, and expanded treatments of emerging technologies, in particular, nanoplastics, and bioplastics.

Related Internet Sites

A list of Internet sites at the end of each chapter guides students to find more information on specific topics. Each site relates to the material found in the chapter and further enhances learning for the reader. Many of these companies provide extensive discussions of their materials, processes, and products on their websites. The more elaborate related Internet sites also include photos, video, and audio presentations.

OTHER FEATURES

Lab Activities

Where applicable, lab activities are included at the end of the chapter. The philosophy embedded in the laboratory activities is that practical applications are essential for thorough understanding of many theoretical concepts. The activities contain tried approaches but also include suggestions for further investigations. It is hoped that students and instructors will build on the laboratory activities and customize them for available equipment and materials.

*The confidential and proprietary details outlined or other information provided are intended only as a guide. They are not to be taken as a license under which to operate or as a recommendation to infringe on any patents.

Chapter Review

All chapters provide vocabulary lists and review questions for students to use as a self-study guide and to test their knowledge of important concepts.

SUPPLEMENTS

Instructor Resources

The Instructor Resources, now available online, contain a thorough classroom guide for instructors, including answers to all end-of-chapter questions, chapter tests powered by Cognero with hundreds of test questions, and an image gallery with all photos and illustrations from the text.

To access these Instructor Resources, go to login.cengagebrain.com, and create an account or log into your existing account.

ABOUT THE AUTHOR

Erik Lokensgard is a professor at Eastern Michigan University in the School of Engineering Technology. In addition to teaching, he has been active with the Detroit Section of the Society of Plastics Engineers and has provided training for several plastics companies in the Detroit area.

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HISTORICAL INTRODUCTION TO PLASTICS

CHAPTER 1

INTRODUCTION

Life without plastics is rather hard to imagine. In everyday activities, we rely on plastic items such as milk jugs, eyeglasses, telephones, nylons, automobiles, and videotapes. However, not much more than one hundred years ago, the plastics taken for granted today did not exist. Long before the development of commercial plastics, some existing materials displayed unique features. Although they were strong, translucent, lightweight, and moldable, only a few substances combined these qualities. Today, these materials have the name **natural plastics**. They provide the starting point for a brief history of plastics materials.

This chapter will provide information about advantages of early plastics and the difficulties encountered during their manufacturing. It sets modern materials and processes in a historical context and demonstrates the powerful influence of pioneers in the plastics industry. The topics included are listed here:

- **I. Natural plastics**
  - **A. Horn**
  - **B. Shellac**
  - **C. Gutta percha**
- **II. Early modified natural materials**
  - **A. Rubber**
  - **B. Celluloid**
- **III. Early synthetic plastics**
- **IV. Commercial synthetic plastics**

NATURAL PLASTICS

The starting point for this section is set in Medieval England. In medieval times, English surnames—last names—indicated professions. Some of these professions are easily recognized today. Occupational references for names such as Smith, Baker, Carpenter, Weaver, Taylor, Cartwright, Barber, Farmer, and Hunter are obvious. Occupational origins of other names, such as Fuller, Tucker, Cooper, and Horner, are less familiar.

> Little Jack Horner
> Sat in a corner
> Eating his Christmas pie;
> He put in his thumb
> And pulled out a plum,
> And said, "What a good boy am I."

This rhyme implies that Jack was not hungry or poor and did not have to share his Christmas treat with other family members. He enjoyed a special treat alone. Apparently, Jack's father had a comfortable income. What did Jack's father, or perhaps grandfather, do? He was a horner—a man who made small items from horns, hooves, and occasionally from tortoiseshells.

A typical response to horn working is to dismiss it as quaint, irrelevant, or disgusting. The horner's craft was smelly and often unpleasant. Today, horners can only be found in rare historically oriented craft museums. However, horn working is not irrelevant with relation to the plastics industry. The unique properties of horn inspired a search for substitutes. The quest for synthetic horn led to the production of early plastics and the beginnings of the modern plastics industry.

Horn

Spoons, combs, and lantern windows were common products made by horners in England and Europe during the Middle Ages. Horn spoons were strong and lightweight. They did not

rust, corrode, or give an undesirable taste to food. Horn combs were flexible, smooth, glossy, and often decorative. As seen in Figure 1-1, lantern windows exploited the translucent quality of horn. They also flexed without shattering and withstood some impact. No other material provided this combination of properties.

Making utilitarian objects from natural polymers did not begin in the Middle Ages. One of the oldest known uses of horn dates from the times of the pharaohs of Egypt. Approximately 2000 BC, ancient Egyptian craftsmen formed ornaments and food utensils by softening tortoiseshells in hot oils. When the shell was sufficiently pliable, they pressed it into the desired shape. They trimmed any rough shapes, scraped, sanded, and finally polished them to a high luster with fine powders.

Little Jack Horner's forefather worked in a manner similar to the ancient Egyptians. He softened pieces of cow horn by either boiling them in water or soaking them in alkaline solutions and pressing the pieces flat. Some horns were delaminated along growth lines, which yielded thin sheets. If thicker pieces were needed, several thinner sheets were welded together. After creating the desired thickness, horn pieces were squeezed into molds to create a useful shape. Sometimes, horners dyed the pieces to make them look like expensive tortoiseshell.

Two items are particularly important for this history because they are made using different techniques: combs and buttons.

From the Collections of the Henry Ford Museum and Greenfield Village

Figure 1-1. This candle lantern displays horn windows.

Combs. Some English horners emigrated to the American colonies and established small businesses. By 1760, horn workers were well established in Massachusetts. Leominster, Massachusetts, became a center for the comb business and earned the name "Comb City."

In comb factories, craftsmen sawed flattened horn pieces to size, cut in teeth with fine saws, smoothed rough edges, colored, and polished the combs. The final operation was called bending. A contoured wooden form imparted a curve to a softened comb and maintained the shape as the comb cooled.

Figure 1-2 shows a photograph of a comb made from tortoiseshell. Notice that several teeth are slightly warped. Even in the most carefully made combs, thin teeth were easily broken. Notice also that the comb is generally uniform in cross section. Usually, combs were not embossed with raised artistic motifs because shell and horn do not flow easily.

Although comb makers in Massachusetts developed machines to mechanize manufacturing, they could not establish stable production. This was not the fault of the machines, but of the material. Clamping fixtures and cutter movements required uniform, flat workpieces. Horn was neither flat nor uniform in size and flexibility.

The lack of dimensional consistency, low "flow ability," and inherent waste caused by the shape of horn encouraged comb manufacturers to search for substitutes.

Buttons. Horn button makers faced a different set of problems. Flat, utilitarian buttons were molded from horn pieces, cut out in pre-sized blanks, and then pressed into heated molds. However, customers also wanted decorative buttons to complement fine garments. Hand-carved buttons of ivory

From the Collections of the Henry Ford Museum and Greenfield Village

Figure 1-2. This well-preserved tortoiseshell comb shows only one broken tooth.

had been available for centuries, but they were expensive and one of a kind. In order to make embossed and raised motifs, the molding material had to flow easily in the mold. To achieve this, the horners developed molding powders of ground horn. Horn buttons often consisted of ground cow hooves colored with a water solution. The horn powder was poured into molds and compressed or rolled out into sheets. The sheets were cut into small blanks with tools similar to small cookie cutters. The blanks were then compressed into a mold to achieve three-dimensional surfaces. Figure 1-3 shows two horn buttons—one with a prominent relief.

Buttons required rather undemanding physical properties. They were thick enough to be strong and devoid of fragile teeth. The impetus to seek alternatives came from the actual working of the horn. Removing the tissue mass and cleaning the slimy membrane from the inside of the horn was dirty work accompanied by strong odors from boiled horns. When shellac became readily available, horners carefully evaluated its qualities.

Shellac

In about 1290, when Marco Polo returned to Europe from his travels in Asia, he brought back shellac. He had found shellac in India, where people had been using it for centuries. They had discovered the unique properties of a natural polymer that came from insects rather than cow horn.

The insect that produces a polymer is a small bug called the **lac**, native to India and southeast Asia. A female lac inserts a stinger-like proboscis into the twig or small branch of a tree. She lives off the sap drawn from the host plant, and exudes a thick liquid, which dries slowly. As the deposit of hardened liquid grows, the insect becomes immobilized. After the male lac fertilizes the female, she increases the juice excretions and is totally covered. Inside this deposit, she lays hundreds of eggs and eventually dies. When the eggs hatch, the young insects eat their way out of the covering and go off to repeat the cycle.

The hardened excretion has unique properties. When cleaned, dissolved in alcohol, and applied to a surface, it makes a shiny, almost transparent coating. The name **shellac** was descriptive because it came from the *shell* of the *lac*. In addition to being used as a protective coating for furniture and floors, solid shellac was moldable.

Under heat and pressure, shellac will flow into the recesses of intricate and detailed molds. Because pure shellac is brittle and weak, compounds containing various fibers were developed to give the moldings some strength. An early product made from molded shellac was the daguerreotype case, seen in Figure 1-4. Their manufacture in the United States began about 1852.

In addition to such cases, shellac was molded into buttons, knobs, and electrical insulators. By 1870, the shellac molding business was well established. The business got a big boost when phonograph records were made from shellac. Shellac molding materials could accurately reproduce the intricate detail needed for sound. Molded shellac parts maintained a niche in the growing plastics industry until the 1930s, when synthetic plastics finally surpassed their qualities.

Several undesirable traits offset the desirable characteristics of this material. The amount and quality of the lac harvest were affected by predator insects, insufficient rain, wide temperature variations, hot winds, and the geographic regions of India. In a drought, farmers harvested twigs hosting live lac and eggs. They stored the lac brood in pits and kept the sticks and twigs wet with cool water. If they did not continue this burdensome task, the death of the lac brood stock would result.

Under normal conditions, the farmers collected the encrusted twigs after the larva left the sheltering deposit. Next, they then scraped the hardened residue off and cleaned it. Cleaning was

From the collection of Evelyn Gibbons

Figure 1-3. These black horn buttons show the three-dimensional relief possible with horn-molding compounds.

Figure 1-4. This daguerreotype case, molded in about 1855, contains shellac and wood flour. The detail is remarkable.

not a simple process, due to sand, dirt, dead lac bodies, leaves, and wood fibers.

After the shellac was ready for use as a coating or a molding powder, problems still persisted. The largest problem was moisture absorption. When a shellac molding or coating gets wet, it absorbs water. If soaked for 48 hours, it will absorb up to 20% water and change to a whitish color. Antique furniture suffered from water rings caused by condensation on containers of ice water. Shellac also takes on moisture from the atmosphere. In high-humidity environments, enough water will be absorbed to whiten shellac finishes. In moldings, moisture absorption could lead to cracking. Even such stable forms as buttons cracked due to moisture absorption.

The color of shellac was not consistent. The most common colors—yellow and orange—depended on the type of tree the lac infested. To create white shellac, chlorine bleaches were used to lighten the natural color. However, the bleaching process also affected its solubility in alcohol. Bleached shellac often coalesced into a gummy, worthless lump.

Another problem involved aging. Shellac finishes and moldings darkened with age. Old shellac became insoluble in alcohol. Shellac finishes stored in steel cans also absorbed iron, which caused the finish to turn gray or black.

These problems caused manufacturers to seek alternatives. During the 1920s and 1930s, new plastics began replacing shellac. In response, shellac producers tried to improve its qualities. Because shellac contained several polymers, they hoped to separate the most desirable portion by fractional distillation. However, this effort did not result in a material that could withstand the competition from the synthetic plastics.

Gutta Percha

Gutta percha is a natural polymer with remarkable properties. It is produced by the Palaquium gutta trees indigenous to the Malay peninsula. In 1843, William Montgomerie reported that in Malaya, gutta percha was used to make knife handles. The material was softened in hot water and pressed by hand into a desired shape. His report stirred interest in the material and led to the formation of the Gutta Percha Company, which remained active until 1930. This company manufactured molded items.

The characteristics of gutta percha are unusual. At room temperature, it is a solid. It can be dented but does not break easily. When heated, it can be drawn out into long strips that will not rebound like rubber. Gutta percha is highly inert and resists vulcanization. Its resistance to chemical attack made it an excellent insulator for electric wires and cable. When long strips of extended gutta percha were wound tightly around a wire, the resulting cable was flexible, waterproof, and impervious to chemical attack.

The first underwater telegraph cable ran across the English Channel from Dover to Calais. Its success was due to gutta percha insulation. In the United States, the Morse Telegraph Company laid a cable insulated with gutta percha across the Hudson River in 1849. Gutta percha also protected the first transatlantic cable laid in 1866. Figure 1-5 shows the use of gutta percha in the first transatlantic cable.

Like other natural materials, gutta percha was inconsistent. Contamination created regions in the insulation that were low in resistance to electricity. These areas eventually lost the ability to insulate, which led to the shorting out of electric circuits. Despite these problems, it remained unsurpassed as an insulator until the development of synthetic plastics in the 1920s and 1930s. Only then did gutta percha become less important in electrical applications.

EARLY MODIFIED NATURAL MATERIALS

It was difficult to harvest, gather, or purify natural plastics. Using these materials in manufacturing processes was arduous. Virtually any material that held potential as a substitute for horn and shellac received attention. Many materials were

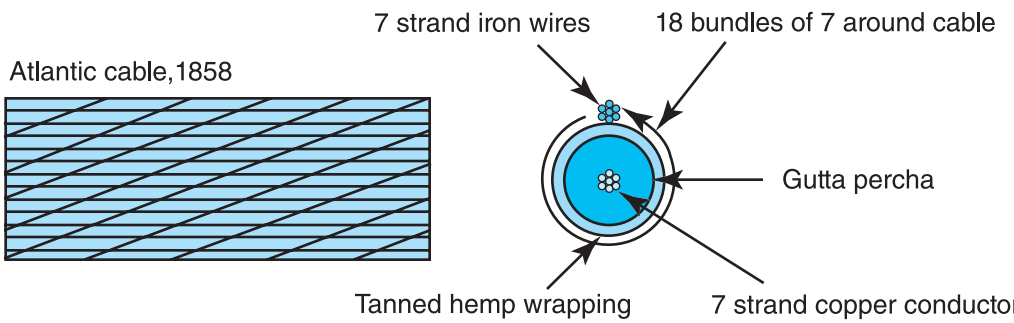


Figure 1-5. The first transatlantic cable had an overall diameter of 0.62 inches and contained 1 pound of gutta percha in every 23 feet of cable. The amount of gutta percha used for the entire cable was over 260 tons.

complete failures. Others failed in their natural condition but became useful when chemically altered.

Casein, a material made from milk curd, appeared to have some value as artificial horn. Dried milk curds were ground into powder and plasticated with water. The resulting dough was molded into various shapes. This attempt met failure because the molded items dissolved when wet. Casein held no significance as a rival to horn until 1897. In that year, a German printer, Adolf Spitteler, learned how to harden the casein dough with formaldehyde. The hardened casein was called **Galalith**, which means "milkstone." It was a moldable plastic used for buttons, umbrella handles, and other small items.

Galalith is important because it exemplifies a group of materials that originate in nature and become useful for manufacturing only after chemical modification. One of the earliest and most important materials in this category is rubber.

Rubber

Natural rubber, also called **gum rubber**, is a natural latex. It is found in the sap or juice of many plants and trees. The white, sticky juice of the milkweed plant is rich in latex. Several trees also produce natural latex in great quantities. For example, the rubber tree (*Hevea brasiliensis*), a prolific producer of latex, was cultivated in large plantations in India.

Compared to gutta percha, natural rubber had little industrial significance. Natural rubber is extremely sensitive to temperature. When the weather is hot, it becomes very soft. When the ambient temperature is cool or cold, it becomes stiff. One of the first uses of gum rubber was to make cloth waterproof.

In 1823, Charles Mackintosh got a patent for waterproof cloth. By pressing a layer of rubber between two pieces of cloth, he solved one problem. In comfortable temperatures, gum rubber becomes tacky. However, when rubber is placed between two pieces of fabric, it no longer has a tacky feeling. Some waterproof jackets called Mackintoshes were manufactured, but they had all the problems of gum rubber. In cold weather, the jackets were stiff and frequently cracked. When it was hot, the jackets melted. In addition to getting sticky in warm weather, gum rubber decomposed easily, creating a strong, foul odor.

In 1839, Charles Goodyear discovered that kneading powdered sulfur into rubber tremendously improved its characteristics. His finding did not happen easily. Goodyear spent years trying to alter gum rubber. He tried blending it with ink, castor oil, soup, and even cream cheese. He finally mixed gum rubber with powdered sulfur and heated the blend. The resulting rubber was stronger, tougher, less sensitive to temperature, and more resilient than before. He had learned how to **vulcanize** the gum rubber. Kneading in small amounts of sulfur produced flexible rubber. Large amounts of sulfur—up to 50%—yielded **ebonite**, a rubber so hard it could shatter like glass.

In 1844, Goodyear received an American patent for his discovery. He hoped that a large display at the London Exhibition of 1851 would send him on the road to riches. Goodyear put considerable effort into his display, which was called the Vulcanite Court. Its walls, roof, and furniture were made of rubber. His display included combs, buttons, canes, and knife handles molded of hard rubber. His products of flexible rubber featured large rubber balloons and a rubber raft. Goodyear also set up an exhibit in 1855 at the Paris Exposition. Here he featured electric wires insulated with hard rubber, toys, sporting equipment, dental plates, telegraph equipment, and fountain pens.

These displays convinced many people that vulcanized rubber held immense commercial potential. However, before Goodyear could win personal wealth from his idea, he died in 1860. He did not live to see the rise of the rubber industry, which became significant during the Civil War. During that period, the Union Army purchased rubber products valuing $27 million. The Goodyear Company moved into the forefront of the new rubber industry.

Horners were particularly interested in hard rubber as a substitute for horn. In England, comb makers purchased tons of hard rubber. They preferred it to both horn and tortoiseshell because it reduced waste.

Although rubber was less wasteful, it did not have an advantage in appearance. The highly sulfur-loaded material was usually black or dark brown. It could not replace the many horn products that imitated tortoiseshell or ivory. This appearance limitation prevented ebonite from sweeping other materials aside.

Vulcanized rubber was one of the first modified natural polymers. Without vulcanization, gum rubber was of limited utility. Vulcanized rubber was both flexible and hard, making it a very significant industrial material.

Celluloid

To produce celluloid, cellulose, in the form of cotton linters, underwent a series of chemical modifications. One alteration was the conversion of cotton into **nitrocellulose**. In 1846, a Swiss chemist, C. F. Schönbein, discovered that a combination of nitric acid and sulfuric acid transformed cotton into a high explosive. Explosive nitrocellulose is highly nitrated. Moderately nitrated cellulose is not explosive but is useful in other ways.

Moderately nitrated cellulose is called **pyroxylin**, a material that dissolves in several organic solvents. When applied to a surface, the solvents evaporate and leave behind a thin, transparent film. This film was named **collodion**. Collodion found widespread use as a carrier for photosensitive materials. Anyone

familiar with the photographic processes common in the 1850s and 1860s observed dried collodion. When a thick layer of collodion dried, the resulting material was hard, water resistant, somewhat elastic, and very similar to horn.

Alexander Parkes, a British businessman, decided to focus his efforts on developing collodion into an industrial material. Parkes lived in Birmingham, England, and had considerable experience in working with natural polymers. He had worked with gum rubber, gutta percha, and chemically treated gum rubber. He understood the qualities of natural plastics and their limitations. In 1862, he announced a new material, which he called **Parkesine**.

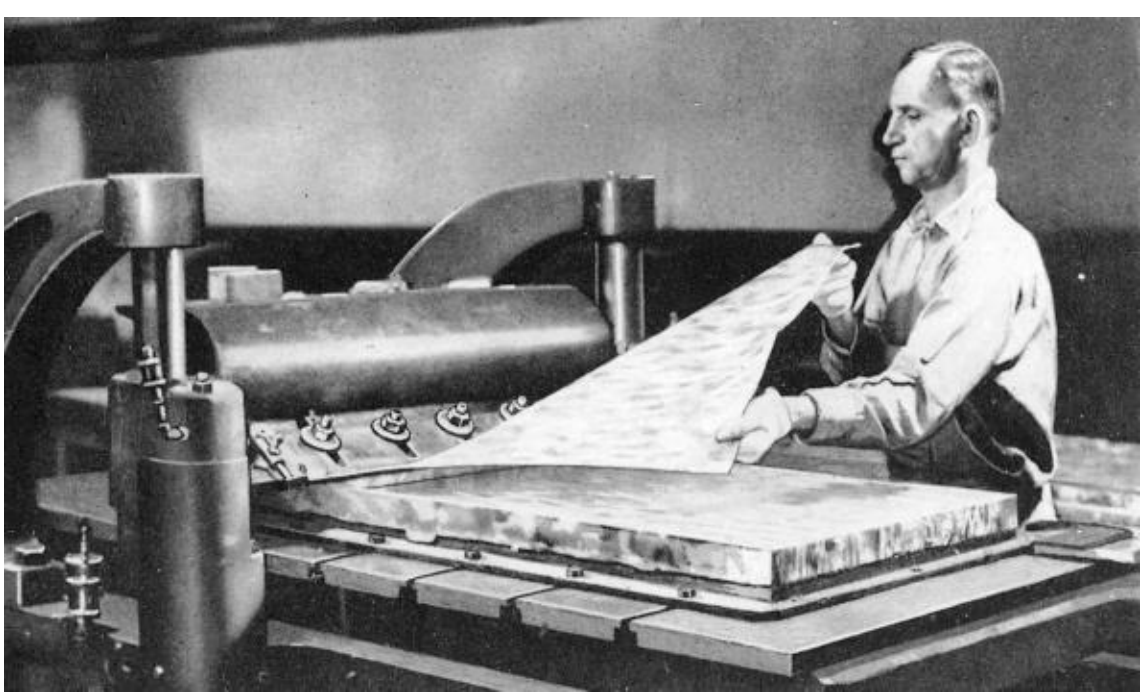
He claimed that Parkesine was a substance "partaking in a large degree of the properties of ivory, tortoiseshell, horn, hardwood, India rubber, gutta percha, etc., and which will . . . to a considerable extent, replace such materials." In 1866, he founded a company that would sell his new material, but his expectations did not match reality. When mixing pyroxylin with various stiff oils, he used several solvents. When the solvents evaporated, the new plastic shrunk excessively. Combs became so warped and twisted that they were useless. Parkes did not find buyers flocking to his door to purchase his material, and his company failed in two years.

Parkes's failure did not turn others away from the effort to convert hardened collodion into an industrial material. An American, John W. Hyatt, also turned his attention to the problem. In 1863, he decided to try for a $10,000 reward promised to anyone who could find a substitute for ivory billiard balls. Hyatt made a few billiard balls out of shellac and wood pulp, similar to the material used for daguerreotype cases. However, these were poor substitutes because they lacked the elasticity of ivory.

Hyatt then set out to make a solid material from pyroxylin. In 1870, he received a patent on the process for making a new material he called **celluloid**. He mixed powdered pyroxylin with pulverized gum camphor. Hyatt wet the mixture to evenly disperse the powders. He then removed the water by pressing it with blotting paper. The material, by then a fragile block, was placed in a mold, heated, and pressed. This resulted in a block of material that was uniform throughout. This block could be used as a molding compound but was usually shaved into sheets that needed seasoning to remove residual water. Figure 1-6 shows the shaving of a large block of celluloid into sheets.

John and his brother, Isaiah S. Hyatt, established a few companies to use their new material. The first was the Albany Dental Plate Company, established in 1870. Next, they formed the Albany Billiard Ball Company. In both cases, the applications they selected for celluloid were failures. Dental plates were a very poor choice because they tasted of camphor. Some dental plates softened, warped, or flaked. They were not nearly as good as dental plates made with hard rubber and never seriously competed with them for the market. The celluloid billiard balls, pictured in Figure 1-7, had the same problems as shellac balls. Hyatt's company abandoned dental plates and billiard balls, and focused on horn products.

Celluloid was a very good substitute for horn. It easily imitated ivory, tortoiseshell, and horn. Celluloid became a commercial success, and the Celluloid Manufacturing Company brought the Hyatts substantial profits. By 1874, celluloid combs and mirrors



Solutia, Inc.

Figure 1-6. This machine shaved sheets of celluloid from large blocks. The block shown contains spots of various colors to make the celluloid appear like tortoiseshell.

Ticona, the technical polymers business of Celanese AG

Figure 1-7. The Hyatt billiard ball, an early celluloid product.

were readily available. Between 1890 and 1910, comb manufacturers in Leominster, Massachusetts, switched almost completely to celluloid. Figure 1-8 shows these products.

Instead of trying to monopolize celluloid manufacturing, the Hyatts licensed a number of companies to use their material. Between 1873 and 1880, they began affiliations with the Celluloid Harness Trimming Company, the Celluloid Novelty Company, the Celluloid Waterproof Cuff and Collar Company, the Celluloid Fancy Goods Company, the Celluloid Piano Key Company, and the Celluloid Surgical Instrument Company. As this list indicates, celluloid products were generally small items related to clothing or novelties.

Celluloid was not adequate for most industrial applications. One example of its failure in the engineering materials market was safety glass. Layers of celluloid were placed between two pieces of glass to make safety glass for automobiles. The problem was that exposure to sunlight caused yellowing and deterioration. Celluloid did meet the needs of one major application that could never have been filled by ivory, tortoiseshell, horn, or hard rubber—it was used for photographic film.

Ticona, the technical polymers business of Celanese AG

Figure 1-8. A comb and brush produced from celluloid in 1880.

By 1895, motion pictures based on celluloid roll film were available to some audiences. Celluloid made possible the early silent films and famous celluloid personalities. The biggest problem with celluloid film was flammability. Carbon arcs provided light for projection, but when films jammed in the projector, the intense heat caused the ignition of film. Hundreds of people lost their lives in disastrous theater fires. However, those deaths did not limit the use of celluloid for motion pictures. No other material could perform like celluloid. Not until safety film was invented in the 1930s was a photographic base available that eliminated the fire hazard.

The consumption of celluloid rose until the mid-1920s. It did not mold easily and was used mainly as a fabricating material. Therefore, moldings of plastics continued to be dominated by shellac. Starting in the 1920s, more robust synthetic polymers took over celluloid applications. Table tennis balls are one of the few remaining products made of celluloid.

EARLY SYNTHETIC PLASTICS

Dr. Leo H. Baekeland was a research chemist who searched for a substitute for shellac and varnish. In June 1907, when working with the chemical reaction of phenol and formaldehyde, he discovered a plastic material that he named **Bakelite**. Phenol and formaldehyde came from chemical companies rather than nature. This marked a major difference between Bakelite and modified natural plastics.

In his notebook, Baekeland wrote that, with some improvements, his material might be "a substitute for celluloid and hard rubber." In 1909, he reported his finding to the New York section of the American Chemical Society. He claimed that Bakelite made excellent billiard balls because its elasticity was very similar to that of ivory.

The General Bakelite Company was established in 1911. Bakelite use grew rapidly. In contrast to celluloid, it found applications beyond the area of novelties and fashion apparel. Other companies began production of **phenolics**, plastics very similar to Bakelite. By 1912, the Albany Billiard Ball Company, a company founded by J. W. Hyatt, adopted Bakelite for billiard balls. In 1914, Western Electric began to use phenolic resins for the telephone earpiece. That same year, Kodak cameras used phenolic for end panels.

In 1916, Delco began to use phenolics for molded insulation in automotive electrical systems. By 1918, molded phenolic resins appeared in dozens of automotive parts. During World War I, aircraft and communication systems increasingly used

molded phenolics parts. Phenolics are not obsolete. In 1991, the US plastics industry used 165 million pounds of phenolics.

With Bakelite, a new era began in plastics. Previously, plastics were either natural or chemical modifications of natural materials. The production of Bakelite proved that it was possible to do in a laboratory or factory what the lac insects and rubber trees did in nature. In fact, the controlled conditions of a factory allowed the production of purer and more uniform materials than those produced from trees, insects, or horns.

COMMERCIAL SYNTHETIC PLASTICS

Bakelite was the first in a long, continuing stream of new plastics. Pioneers in the development of early commercial synthetic plastics struggled with two basic problems—one theoretical and one practical. The theoretical problem was that they did not have a clear understanding of the chemical and structural nature of plastics. This confusion continued until 1924, when Herman Staudinger claimed that polymers were long linear molecules consisting of many small units held together by chemical bonds. This idea served as the starting point for the development of many plastics. The practical problem involved the purity of the chemicals required for sustained chemical reactions in making plastics. After many failed attempts, chemists understood that the purity requirements far exceeded their expectations. Consequently, polymer-grade chemicals became synonymous with the highest purity commercially available.

During the 1930s, the solutions to these two problems became rather clear. The needs of World War II also contributed to a surge in the development of new plastics. Table 1-1 provides a partial chronology of the growth of plastics. The period between 1935 and 1945 stands out because many of the materials developed at that time received wide use and continue today as major industrial materials. Details about many of the materials in this list are available in Appendixes E and F.

Table 1-1. Chronology of Plastics

Date	Material	Example
1868	Cellulose nitrate	Eyeglass frames
1909	Phenol-formaldehyde	Telephone handset
1909	Cold molded	Knobs and handles
1919	Casein	Knitting needles
1926	Alkyd	Electrical bases
1926	Analine-formaldehyde	Terminal boards
1927	Cellulose acetate	Toothbrushes, packaging
1927	Polyvinyl chloride	Raincoats
1929	Urea-formaldehyde	Lighting fixtures
1935	Ethyl cellulose	Flashlight cases
1936	Acrylic	Brush backs, displays
1936	Polyvinyl acetate	Flashbulb lining
1938	Cellulose acetate butyrate	Irrigation pipe
1938	Polystyrene or styrene	Kitchen housewares
1938	Nylon (polyamide)	Gears
1938	Polyvinyl acetal	Safety glass interlayer
1939	Polyvinylidene chloride	Auto seat covers
1939	Melamine formaldehyde	Tableware
1942	Polyester	Boat hulls
1942	Polyethylene	Squeezable bottles
1943	Fluorocarbon	Industrial gaskets
1943	Silicone	Motor insulation
1945	Cellulose propionate	Automatic pens and pencils
1947	Epoxy	Tools and jigs
1948	Acrylonitrile-butadiene styrene	Luggage
1949	Allylic	Electrical connectors

1954	Polyurethane or urethane	Foam cushions
1956	Acetal	Automotive parts
1957	Polypropylene	Safety helmets
1957	Polycarbonate	Appliance parts
1959	Chlorinated polyether	Valves and fittings
1962	Phenoxy	Bottles
1962	Polyallomer	Typewriter cases
1964	Ionomer	Skin packages
1964	Polyphenylene oxide	Battery cases
1964	Polyimde	Bearings
1964	Ethylene-vinyl acetate	Heavy-gauge flexible sheeting
1965	Parylene	Insulating coatings
1965	Polysulfone	Electrical and electronic parts
1965	Polymethylpentene	Food bags
1970	Poly(amide-imide)	Films
1970	Thermoplastic polyester	Electrical and electronic parts
1972	Thermoplastic polyimides	Valve seats
1972	Perfluoroalkoxy	Coatings
1972	Polyaryl ether	Recreation helmets
1973	Polyethersulfone	Oven windows
1974	Aromatic polyesters	Circuit boards
1974	Polybutylene	Pipes
1975	Nitrile barrier resins	Packaging
1976	Polyphenylsulfone	Aerospace components
1978	Bismaleimide	Circuit boards
1982	Polyetherimide	Ovenable containers
1983	Polyetheretherketone	Wire coating
1983	Interpenetrating Networks (IPN)	Shower stalls
1983	Polyarylsulfone	Lamp housings
1984	Polyimidesulfone	Convey links
1985	Polyketone	Automotive engine parts
1985	Polyether sulfonamide	Cams
1985	Liquid crystal polymers	Electronic Components
1986	Polycarbonate/ABS blends	Automotive parts
1987	High-purity polyacetylene	Electrical conductors
1991	Metallocene polyethylene	Packaging films
1992	Linear low density polyethylene	Packaging films
1992	Syndiotactic polystyrene	Thinwall electrical parts
1992	Syndiotactic polypropylene	Automotive interior parts
1992	Cyclic olefin copolymers	Appliance parts
1998	Ethylene-styrene copolymers	Toys
1998	Nanocomposites	Truck body parts
2001	Transparent polyester/polycarbonate alloys	Sunglasses
2005	Polylactic Acid	Compostable packaging

SUMMARY

For centuries, natural plastics combined light weight, strength, water resistance, translucency, and moldability. Their potential was obvious, but the materials were difficult to gather, or they were only available in limited volumes or sizes. All over the world, people tried to improve natural plastics or find substitutes.

The manufacture of modified natural plastics converted natural raw materials, such as cotton linters or gum rubber, into new and better forms. Celluloid had many qualities that surpassed horn. However, modified materials still relied on natural sources for their prime ingredient. Not until the development of Bakelite was it possible to create a material that rivaled nature in a factory. Bakelite opened the door to the development of a host of synthetic polymers tailored to meet specific requirements.

The search for improved materials continues today. Many modern fibers are a result of attempts to create artificial silk. Composite materials are now taking over applications previously reserved for metals. The possibilities for new substitutes seem endless. Leo Baekeland saw boundless potential in phenolic plastics and used the infinity symbol to represent its uses. That symbol applies today to the unlimited future facing those who strive to find and use new polymers.

RELATED INTERNET SITES

- **www.americanchemistry.com.** The American Chemistry Council's home page lists "Products and Technology" as a main selection. Under that section, choosing "Plastics" leads to a list containing "Education and Resources." Within "Education and Resources," there are a number of documents, including "Plastics 101" and "Hands on Plastics."
- **http://museo.cannon.com.** The Sandretto Plastics Museum in Italy offers a guided tour of the museum, which is dedicated to plastics products. The site also includes an extensive section on the history of plastics.

VOCABULARY

The following vocabulary words are found in this chapter. Use the glossary in Appendix A to look up the definitions of any of these words you do not understand as they apply to plastics.

Bakelite
casein
celluloid
collodion
ebonite
Galalith
gum rubber
gutta percha
lac
natural plastics
natural rubber
nitrocellulose
Parkesine
phenolics
pyroxylin
shellac
vulcanize

QUESTIONS

1-1. Why was machine manufacture of horn combs often unsuccessful?

1-2. Why weren't daguerreotype cases made from horn or horn powders?

1-3. Casein comes from _____.

1-4. Moderately nitrated nitrocellulose is called _____.

1-5. What is the difference between collodion and moderately nitrated nitrocellulose?

1-6. What is the difference between Parkesine and celluloid?

1-7. Bakelite comes from a chemical reaction between _____ and _____.

ACTIVITIES

1-1. Write a report tracing the development of one piece of sporting equipment that has a long history. Examples include golf clubs, tennis rackets, tennis balls, snow skis, tennis shoes, billiard balls, and fishing rods. Try to gather information on the manufacturing processes involved.

As an example of the changes in sports equipment, the following section begins to treat golf balls:

> Golf balls began as ovals or spheres of wood, ivory, or iron. Featheries, which were leather pouches tightly stuffed with feathers, replaced the solid balls. Featheries could not withstand moisture and prevented any play on wet grass or in rain.
>
> Between 1846 and 1848, balls of solid gutta percha began to replace featheries. They were fine in the rain but fractured on cold days. However, the pieces could be remolded into a usable ball. Figure 1-9 shows a mold for balls of gutta percha.
>
> In about 1899, a new ball made gutta percha balls obsolete. It consisted of stretched elastic thread wound into a sphere and covered with gutta percha or *balata*, a natural rubber that could be vulcanized. These balls required high-quality elastic thread and the

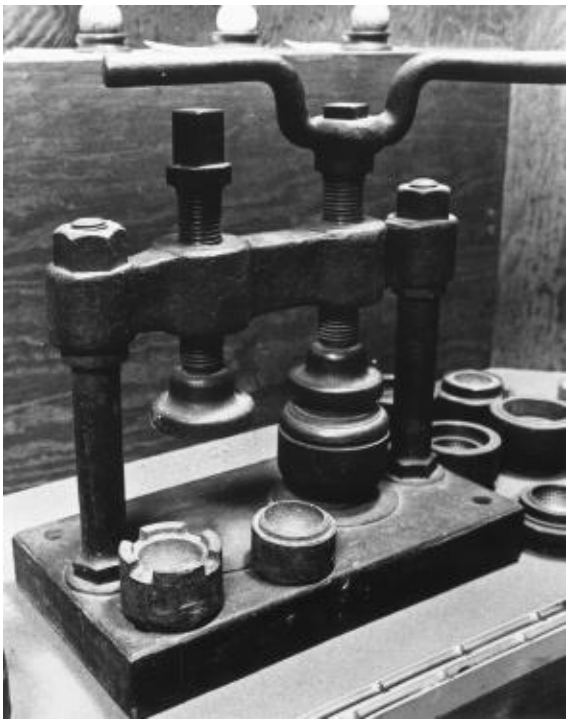

U.S. Golf Association Museum

Figure 1-9. This mold shaped gutta percha into golf balls.

equipment to tightly and uniformly wind the balls. The new balls were much more elastic and could be hit further.

In 1966, the balls of wound elastic thread became outdated when a ball molded of a solid synthetic type of rubber came to the market. It was much tougher than the previous balls and depended on new materials that were just being developed by chemical companies. Since then, new outer coverings have been developed that are almost impossible to cut with a golf club.*

1-2. Trace the development of a plastics manufacturing company that has a long history. Companies like DuPont, Celanese, and Monsanto have ties to companies that used or manufactured celluloid. Companies that had factories in Leominster, Massachusetts, often have ties to horn comb making. For example, the Foster Grant company, famous for its sunglasses, began operations in Leominster to make plastic combs. Many of its early employees had likely been horn workers.

1-3. Investigate natural plastics.

Equipment. Heated platen glass or unheated press, saws, polished plates, or stainless steel mirror stock.

! CAUTION

Perform activities in a laboratory environment under supervision.

Solid horn

Note: *This activity does not reflect current practices in the plastics industry. It does demonstrate the qualities of molded horn.*

a. Acquire cow horns from your local pet store. If they are fresh, boil them for about 30 minutes to prevent decay. Saw the horns and remove the tissue mass. Scrape the membrane from the inside of the horn pieces. When finished, the half horn will appear as shown in Figure 1-10.

b. Cut a small piece, about 1 inch square. Measure length, width, and thickness. Soak in boiling water for about 15 minutes. Place between polished plates and squeeze in a platen press. If heated, keep heat about 250°F (121°C). Keep pressed and let cool. Examine the resulting horn piece. If the original piece appears off-white in color, the flattened and thinned piece should be quite transparent. Figure 1-11 shows some rather transparent pieces of flattened horn. The relative smoothness of the press plates will affect the transparency of the horn.

c. Measure the flattened horn.

d. Resoak in boiling water.

e. Remeasure. Did the horn return to its original dimensions?

f. Put food coloring in the water to see how readily the horn takes dye.

g. Examine the eggcup spoons made from horn, available at some kitchen utensil retailers. Make a wooden form for a similar spoon. You may have seen a shoehorn like the one shown in Figure 1-12.

Figure 1-10. This half horn is ready for cutting and flattening.

Figure 1-11. This photograph demonstrates the transparent qualities of horn.

Figure 1-12. Molding altered the shape and surface finish of this shoehorn.

Powdered horn or hoof. Cow hooves are available in pet stores for dog chews.

- **a.** Make powder by filing with a coarse file.
- **b.** Compact with a plunger in a cylinder, as seen in Figure 1-13. The rectangular piece of material is a rubber bumper.
- **c.** Explore the surface detail by pressing it against a coin. See how well the detail transfers.
- **d.** Experiment with colors.

Shellac. It is available in stick form for furniture scratch repair or as flake from fine woodworking supply stores (see Figure 1-14).

- **a.** Do simple moldings using cylinder, plunger, and a coin. Figure 1-15 shows a shellac molding using a quarter as the impression. Note the reproduction of details. Shellac will flow at a temperature just above 212°F (100°C). Without a device to apply pressure to the cylinder, the shellac will raise the cylinder and flash excessively. The rubber "bumper" keeps pressure on the cylinder during compression.

Figure 1-13. This type of simple cylinder and plunger can mold shellac and horn powders.

Figure 1-14. Shellac in flake form is rather rare, but it is still available.

Figure 1-15. This shellac molding, made with a quarter as the impression piece, indicates the fine detail possible with molded shellac.

- **b.** Compare powdered hoof moldings to shellac moldings.
- **c.** Investigate the effect of fibers.
  - **(1)** Create a sandwich of paper towels and shellac.
  - **(2)** Press the sandwich in a heated platen press.

(3) Does shellac flow through paper? How much does paper improve the strength of shellac? Figure 1-16 shows a thin laminate, containing two layers of paper toweling and a small amount of shellac.

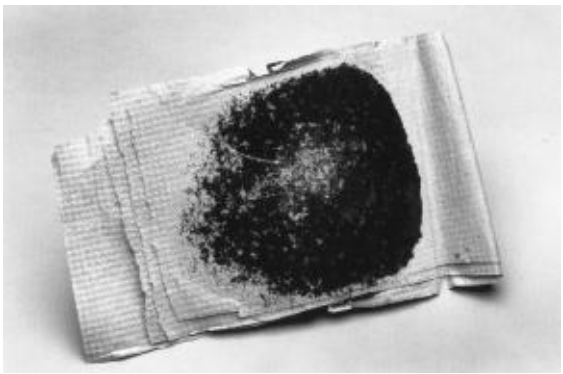


Figure 1-16. This thin laminate is significantly more flexible than a similar sheet of unreinforced shellac.

(4) Create a molding compound using powdered shellac and glass or cotton fibers. How greatly do the fibers improve the physical properties of the moldings?

Casein. Casein, a natural plastic made from milk curds, was molded into various shapes in the 1800s. Because the finished objects would dissolve when wet, casein did not gain industrial importance. To make casein:

a. Slowly warm ½ cup of heavy cream (or milk). Do not boil.

b. When the cream begins simmering, stir in a few spoonfuls of vinegar or lemon juice.

c. Continue to slowly add vinegar until it begins to gel.

d. Cool the mixture and remove the "blob."

e. Wash the "blob" with water, revealing little plastic curds.

f. Mold the material into a shape and let it solidify for a few hours.

CURRENT STATUS OF THE PLASTICS INDUSTRY

CHAPTER 2

INTRODUCTION

Chapter 1 used the words *polymers, rubber*, and *plastics* without providing thorough definitions. **Polymers** are natural or synthetic organic compounds. Natural polymers include horn, shellac, gutta percha, and gum rubber. Synthetic polymers appear in thousands of plastics products, clothing, automobile parts, finishes, and cosmetics. Whether natural or synthetic, polymers have chemical structures characterized by repeating small units called *mers*. In order for a compound to be a polymer, it should have at least 100 mers. Many polymers found in plastics products have 600 to 1000 mers.

The word **plastics** comes from the Greek word *plastikos*, which means "to form or fit for molding." A more definitive explanation comes from The Society of the Plastics Industry. It identifies plastics as follows:

> Any one of a large and varied group of materials consisting wholly or in part of combinations of carbon with oxygen, nitrogen, hydrogen, and other organic or inorganic elements which, while solid in the finished state, at some stage in its manufacture is made liquid, and thus capable of being formed into various shapes, most usually through the application, either singly or together, of heat and pressure.

In this book, the word *plastics* will always end with an *s* when it refers to a material. The word *plastic*, without an *s*, will be considered an adjective meaning formable. Because plastics are closely related to resins, the two are often confused. **Resins** are gumlike solid or semisolid substances used in making such products as paints, varnishes, and plastics. A resin is not a plastics unless it has become a "solid in the finished state."

The English chemist Joseph Priestley coined the word **rubber** after he noticed that a piece of natural latex was good to rub out pencil marks. Natural rubber is one material in a group called elastomers. **Elastomers** are natural or synthetic polymeric materials that can be stretched to at least 200% of their original length and, at room temperature, return quickly to approximately their original length.

Although elastomers and plastics have been considered as separate categories of materials, the distinction between them has eroded significantly. In the early development of plastics and rubber materials, the plastics tended to be stiff, whereas the rubbers tended to be flexible. Now many plastics exhibit characteristics traditionally available only in rubber. Although rubbers still have unique characteristics—especially the ability to retract rapidly—the categories now partially overlap.

In recent years, a family of materials called **thermoplastic elastomers (TPEs)** have partially bridged the gap between traditional rubbers and plastics. Within the TPEs, subsets include thermoplastic elastomers based on urethanes, polyesters, styrenics, and olefins. By far the most dominant are the **thermoplastic olefin elastomers (TPOs)**. They have replaced many grades of rubber, particularly in automotive parts. The TPEs have supplanted many traditional rubber products because of their ease of processing (see Figure 2-1).

Plastics and elastomer products do not contain 100% polymer. They generally consist of one or more polymers plus various additives (see Chapter 7 for discussion of additives and their effects). The relationship between these basic terms appears in Figure 2-2. Note that polymers is the umbrella category. With the presence of additives, some polymers become plastics or elastomers.

Courtesy of Ciba Specialty Chemicals

Figure 2-1. TPO bumper fascia must withstand sunlight, heat, and impact from stones.

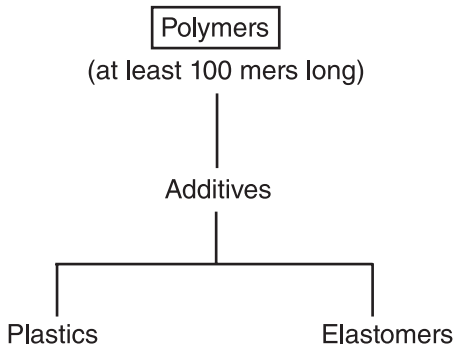


Figure 2-2. Plastics and elastomers contain additives to make them reliable in a wide variety of environments. Even natural-color plastics contain additives.

This chapter presents the current status of the plastics industry, with emphasis on the United States. The content outline is presented here:

MAJOR PLASTICS MATERIALS

The plastics industry plays a major role in the economy of the United States. In 2010, the US plastics industry provided employment to about 900,000 people. This was lower than the 1.1 million employed in 2005, when the industry ranked as the third largest manufacturing industry in the country.

Although the production of plastics in the United States grew steadily in the 1980s and 1990s, since 2000 the growth has been less steady. A number of factors contribute to that development. The destruction of the World Trade Center on September 11, 2001; the wars in Afghanistan and Iraq; problems with some mortgage financing; and growing global demand for crude oil have all influenced the plastics industry. The financial crisis that started in 2008 led to a steep drop in plastics production. As seen in Figure 2-3, the US production is now growing slowly after the lowest point in 2009. Although the financial crisis hurt the plastics industry, much

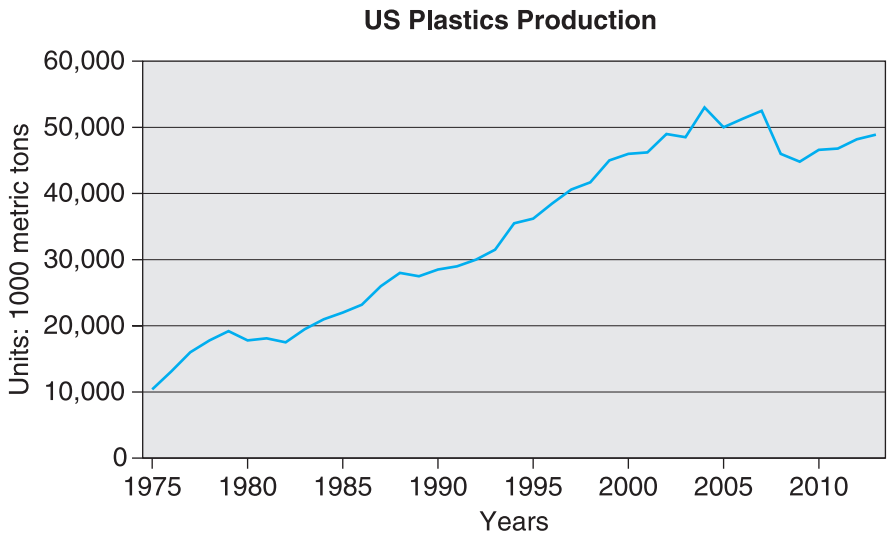


Figure 2-3. US production of plastics is recovering from a sharp drop in 2008 and 2009.

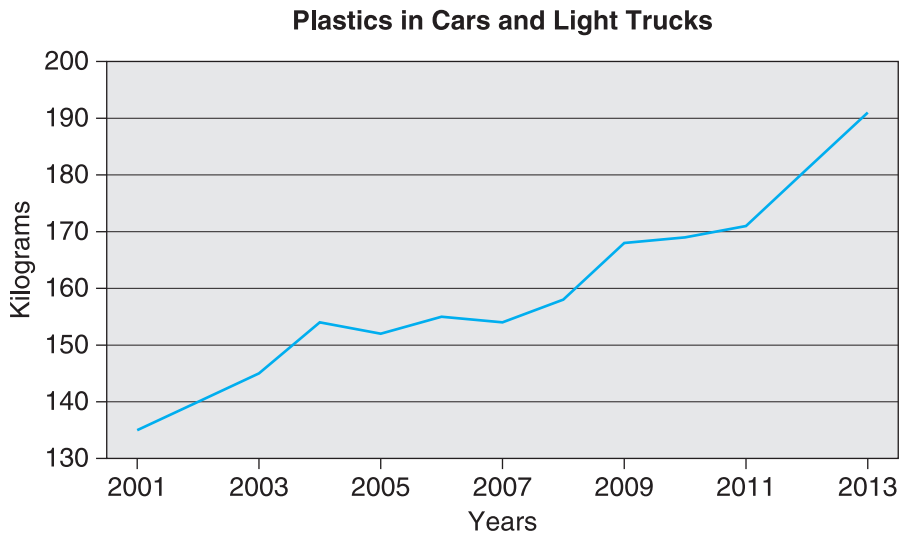


Figure 2-4. Plastics steady growth in cars and light trucks.

of the decrease was not inherent to the industry, but derived from national and international markets. The use of plastics in cars and light trucks continued to increase slowly during the financial crisis, as shown in Figure 2-4. The projections for 2020 have been based on growth of plastics in the automotive industry.

The commodity thermoplastics, which includes six plastics, accounted for 57% of the total production:

Polypropylene (PP)	7065
High-density polyethylene (HDPE)	6458
Polyvinyl chloride (PVC)	4024
Linear low-density polyethylene (LLDPE)	4586
Low-density polyethylene (LDPE)	2473
Polystyrene (PS)	2093
Total	26,699
Units: 1000 metric tons	

Figure 2-5 shows the percentages of the total production by material type.

Figures 2-6 through 2-11 provide graphic representation of the expected utilization of six thermoplastics in the year 2012.

The overall growth of plastics sales reflects the ability of plastics products to fulfill an increasing number of consumer demands. The increasing utilization of plastics has also caused concern for the role of plastics in environmental pollution.

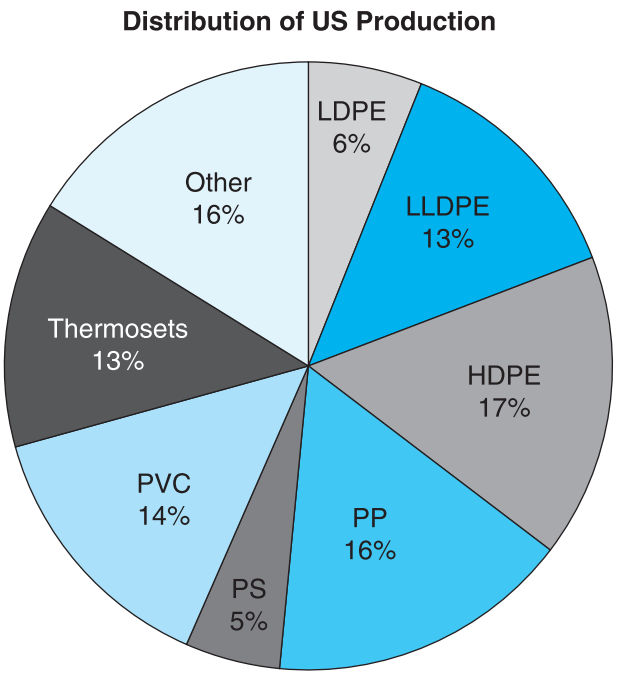


Figure 2-5. US production by types of plastics.

RECYCLING OF PLASTICS

The first Earth Day, which occurred in 1970, signaled the development of a new level of awareness and concern about the environment. During the 1970s, a number of antilitter campaigns sprang up. In 1976, the federal government passed the **Resource Conservation and Recovery Act (RCRA)**. It promoted reuse, reduction, incineration, and recycling of materials. The combined effects of public concern and legislation created major changes in two arenas: hazardous waste management and recycling of nonhazardous materials. Treatment of hazardous materials in the plastics industry appears in Chapter 4.

Recycling is a term generally reserved for postconsumer waste materials. In contrast, reuse or reprocessing usually handles waste materials generated during manufacturing. Plastics industries have for decades reused the materials in defective parts, trimmings, and other manufacturing scrap. This usage

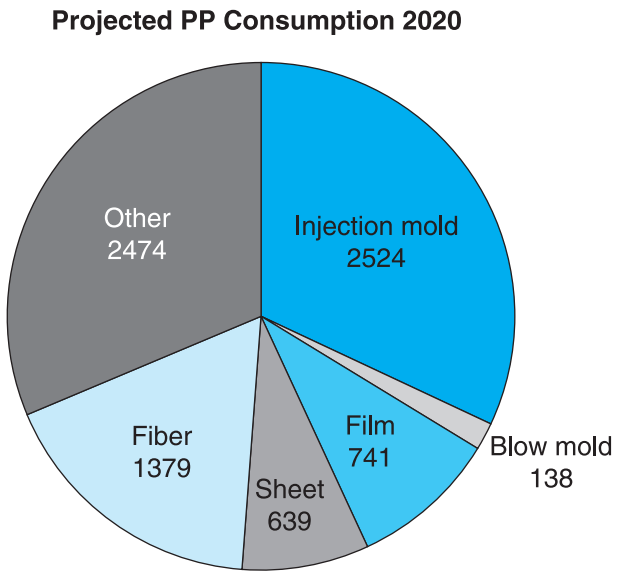


Figure 2-6. Expected polypropylene (PP) usage for the year 2020.

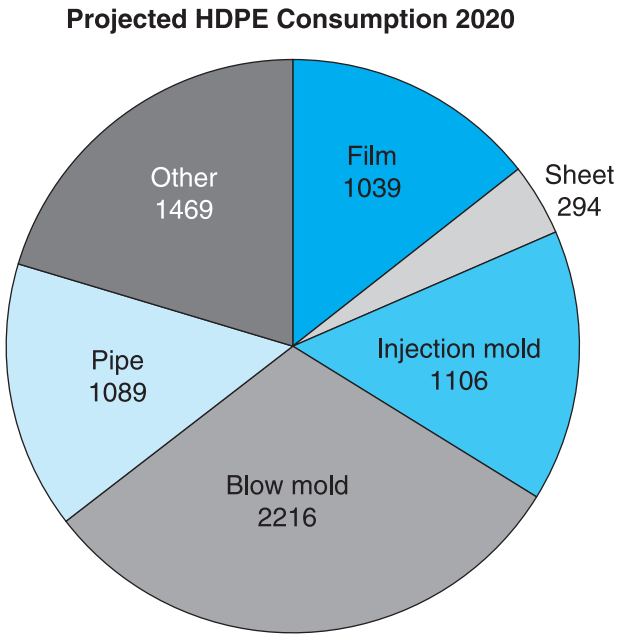


Figure 2-7. Expected HDPE usage for the year 2020.

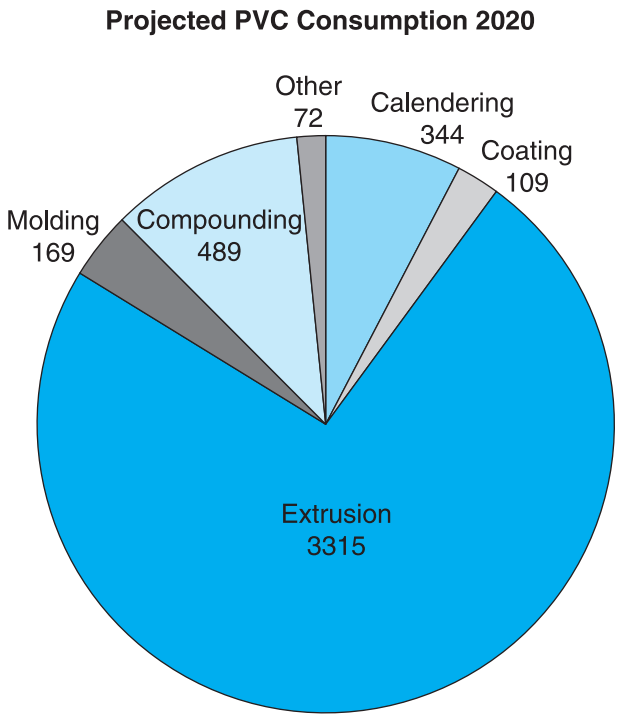


Figure 2-8. Expected polyvinyl chloride (PVC) usage for the year 2020.

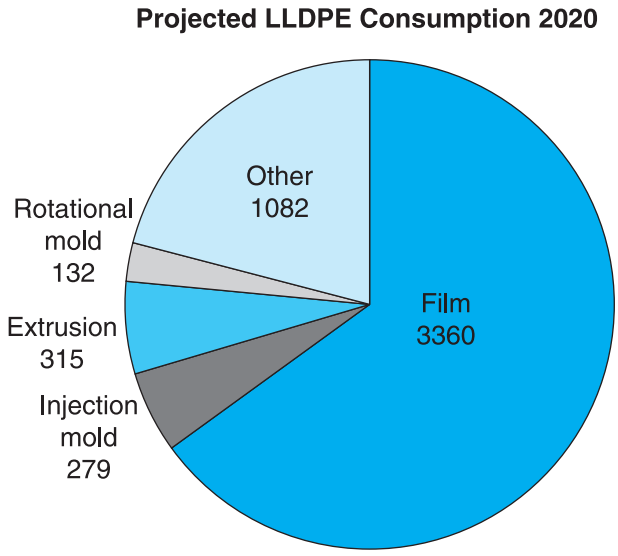


Figure 2-9. Expected LLDPE usage for the year 2020.

ranges from very small-scale reprocessing in small companies to huge programs that generate thousands of tons of reprocessed materials. Systematic recycling of postconsumer plastics occurs through three main channels: bottle returns for deposits, drop-off stations, and curbside pickup programs.

Bottle Deposit Laws and Their Effect

Efforts to encourage or force recycling of bottles have involved state laws, federal proposals, and state mandates. The recycling of PET (polyethylene terephthalate) containers reflects the effectiveness of these efforts.

State legislation. During the 1970s, five states enacted bottle deposit laws. In chronological sequence, they were Oregon, Vermont, Maine, Michigan, and Iowa. In the 1980s, five more states required deposits: Connecticut, Delaware, Massachusetts, New York, and California. The first deposit law took effect in 1972 in Oregon, and the latest occurred in 1987

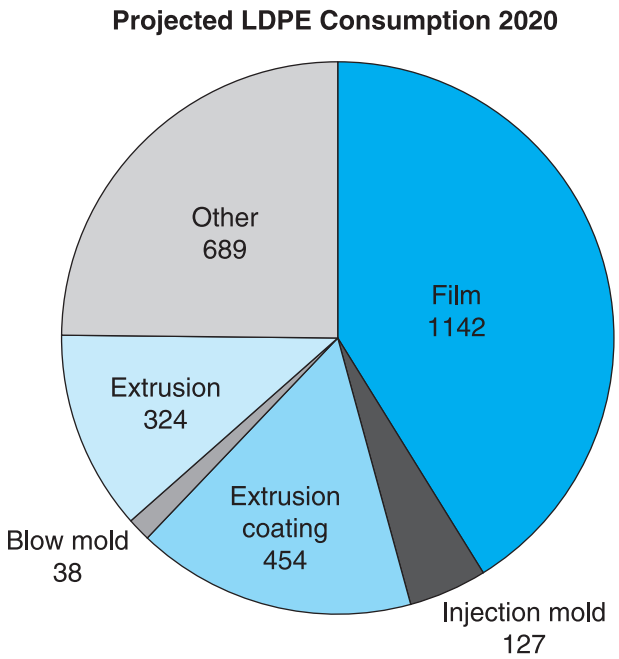


Figure 2-10. Expected LDPE usage for the year 2020.

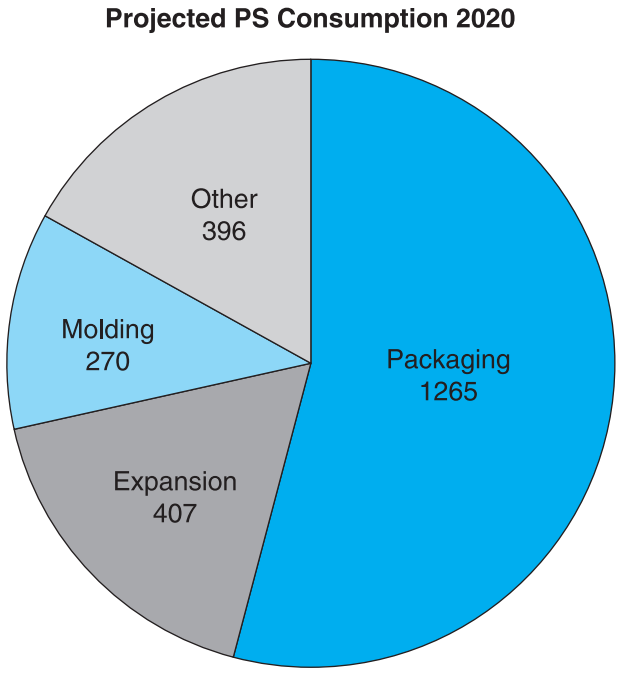


Figure 2-11. Expected polystyrene usage for the year 2020.

in California. The deposit law states require 5 cents deposit per bottle or can, except Michigan, which requires 10 cents.

Since 1987, bottle deposit legislation has been introduced annually in about 25 states, but no additional states have enacted deposit laws. This is explained by the powerful opposition of major soft drink manufacturers such as Coca-Cola® and Pepsi-Cola® companies. They view bottle deposits as an unfair tax and a hardship for beverage retailers. In 2015, 11 states have bottle deposit laws, and the other states remain without deposit laws.

Because Michigan was the only state to charge more than cents, it has held a rather unique position in bottle recycling efforts. The Michigan Department of Natural Resources indicated that the deposit law caused a 90% reduction in litter along highways and parks. In addition, the deposit law led to the annual recovery of about 18,000 metric tons of plastics—almost entirely PET. In 2011, Michigan recovered about 97% of the plastics bottles covered by this law. In contrast, states with deposits of five cents recover about 85%. States with no bottle deposit law recover about 20% of the containers.

Federal legislation. Concurrent with the initiation of state laws, federal legislators and officials investigated deposit laws. In 1976, a Federal Energy Administration study recommended a nationwide deposit law. In 1977, the General Accounting Office favored deposits. In 1978, the Office of Technological Assessment issued a report favoring deposits. In 1981, Senate Bill 709 for deposits received hearings—but no action. In 1983, Senate Bill 1247 and House of Representatives Bill 2960 proposed a 5-cent deposit on carbonated beverages. No action was taken. In 2007, H.R. 4238, Bottle Recycling Climate Act, was introduced but did not pass. Consequently, bottle deposit laws have remained at the state level.

State recycled content mandates for bottles. Because of pressure from the federal government and concern at the state level, by the end of 1994, 40 states had established legislated goals for litter control or recycling. In an effort to force more thorough recycling, some states also passed recycling content mandate laws. These laws often replaced laws enacted in the early 1990s that subjected various plastics to bans. For example, some states placed polystyrene foam packaging under a ban. In many cases, these laws were not enforced.

A differing legislative approach was to mandate recycling rates or percentages of postconsumer recycled (PCR) content used in "new" containers. These laws usually specify the percentage of PCR of various types of containers. Starting in 1994, Florida sought a rate of 25% PCR in bottles and jars and planned to require wholesale distributors to pay an advanced deposit fee if containers did not contain this percentage. Oregon had a similar rule, expecting 25% PCR in rigid containers.

These regulations did not lead to compliance. The history of California reflects some of the problems with such mandates. In California, a law offered three alternatives. First, rigid plastic containers were to contain 25% PCR by 1995. Second, containers that could be reused or refilled five times were exempt. Third, the recycling rate of containers had to be at least 45%. If the recycling rate fell below 25%, California was to begin vigorous enforcement.

The beverage industry did not meet these mandates. Therefore, in 1997 the State of California decided not to enforce its laws and to give the industry time to comply voluntarily. One major problem concerned the cost and availability of PCR supplies. In some cases, recycled material became more expensive than new plastics. Some of the PET collected in California did not go into reprocessing in the United States. It was sold to Asia because shipping costs were lower to Asia than to the East Coast of the United States.

However, in July 2001, the state recycling board declared the recycling rate for rigid plastic containers was below 25% in 1999 and 2000. If California chose to enforce its laws, significant changes would be required by the beverage manufacturers.

Several groups have tried to push Coca-Cola and Pepsi-Cola to use more aggressive actions to promote recycling. In April 2001, Coca-Cola announced plans to include 10% recycled content in all its PET bottles by 2005. This announcement was a partial answer to a group of shareholders who supported a resolution asking Coca-Cola to set a rate of 25% recycled content and a target of 80% recycling rate. The problem with this announcement was that in the early 1990s, Coca-Cola had announced its intention to use 25% recycled content in its bottles and later backed away from that pledge. In 2012, a state in Australia instituted a 10-cent bottle deposit program. Coca-Cola has sued to stop the program. An environmental organization, SumOfUs.org, has created a petition campaign to get Coca-Cola to end its opposition to public recycling programs.

PET bottle recycling. In states with bottle deposits, consumers return bottles to the stores, often using reverse vending machines to claim their refund. Stores sort the bottles for pickup by the distributors. The distributors then sell the materials to the recycling market. To make shipping more cost-effective, densification equipment squeezes the bottles into bales, which are sold to recycling companies. The recyclers unbale the containers, chop them into flakes, clean, wash, dry, and in some cases reprocess the materials. Table 2–1 shows the growth of PET recycling. In 2011, the recycling rate reached a new high, in part due to increases in collection in California and a ban on plastic bottles in landfills in North Carolina. Budget concerns caused decreases in collections by discontinuing or curtailing some collection programs. However, these decreases did not match the increases.

Finding uses for the recycled PET has not always been an easy task. For years, the US Food and Drug Administration (FDA) did not allow recycled materials to be used in food-contact applications. Consequently, PET had to be used in nonfood applications. A major use for recycled PET was as fiber. For example, 35 soft drink bottles provide enough material for the fiberfill used in one sleeping bag. Other significant uses are the production of strapping, film/sheet, beverage containers, and polyester fabrics for clothing.

Another possibility was to make multilayer containers, with an inner layer of virgin material, a middle layer of recycled material, and an outer layer of virgin material. Figure 2-12 shows a sketch of this style container. This allows use of recycled material, yet provides control of the food-contact layer and the outer or show surface.

Yet another possibility was to chemically depolymerize the PET, and then use the resulting materials for polymerization into "new" PET. This option has found limited success because it produces PET that is more expensive than newly manufactured PET. According to one estimate in 1994, recycled PET made by depolymerization cost 20 to 30 cents per pound more than virgin material.

In an important decision made in August 1994, the US Food and Drug Administration approved the use of 100% recycled PET for food-contact packaging. This was the first time the FDA approved 100% recycled content in food and beverage packaging. That means that PET soft drink bottles could be reprocessed into new food-use bottles.

To win this approval, a recycling facility in Michigan had to develop new ways of thoroughly cleaning the recycled material. The new process features high-intensity washing, temperatures of about 500°F (260°C), and other cleaning techniques. Since the first approval of bottle-to-bottle recycling, several other companies have developed comparable systems. In 2001, a company in Holland, Ohio, received FDA approval to produce

Table 2-1. Recycling of PET

1982	1989	1993	1999	2006	2011	2013
18	88.5	203.5	336	578	729	817

Units: 1000 metric tons

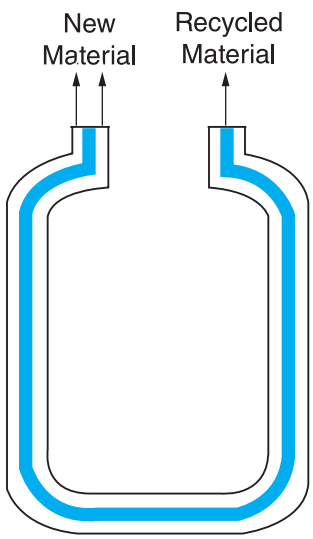


Figure 2-12. An inner layer of recycled material is sandwiched between two layers of prime material.

100% recycled PET bottles from curbside collection. Another company, which owns about 10% of the worldwide PET production capacity, opened a recycling facility in West Virginia in 2001. The company hopes to process more than 10,000 metric tons of PCR PET per year.

In 1993, the recycling rate for all PET packaging was approximately 30%. In states with bottle deposit laws, the containers covered by deposits are returned at a rate of about 95%. Because deposit laws cover 18% of the American population, that means that the one-fifth of the population under deposit laws accounts for about 60% of the total recycled PET bottles. Although these figures might indicate support for bottle deposits, opponents assert that comprehensive waste-management programs are far more effective than forced deposits.

The Association of Postconsumer Plastic Recyclers (APR) is an organization whose members represent more than 90% of the companies and organizations involved in recycling in North America. In 2006, the APR issued a position statement supporting the expansion of bottle deposit laws to include noncarbonated as well as carbonated beverage bottles. That move is partially a reflection of the growth in sales of bottled water and juices. *The New York Times* estimated that Americans consumed 30 billion single-serving bottles of water in 2007. Because the large beverage companies continue to oppose bottle deposits in any form, the APR realizes that new and expanded bottle deposit laws will be difficult to enact.

The statistics about recycling indicate the magnitude of the problem. The 2005 Report on Postconsumer PET Container Recycling Activity from the National Association for PET Container Resources (NAPCOR) and the APR indicates that in 2005, 5.075 billion pounds of PET were made into bottles in the United States. Of that amount, only 1.17 billion pounds came into recycling facilities. That amounts to a gross recycling rate of 23.1%. Although the total number of pounds of recycled PET has grown every year since 1997, the gross recycling rate declined from 27.1% in 1997 to 23.1% in 2005. Since 2005, the gross recycling rate has grown slightly, and in 2010 reached 29%. The lowest percent was in 2003, with 19.6% as the gross recycling rate. For several years, the largest uses for the recycled PET were for fiber, strapping, and food and beverage bottles.

Curbside Recycling

During the early 1990s, the number of US communities that offered drop-off stations or curbside recycling grew significantly. Since 1997, the growth of these opportunities has been very slow. By the year 2000, over 7000 communities offered curbside recycling to about 52% of the US population. By 2009, 9000 programs existed. Over 80% of the population has access to drop-off stations or curbside recycling. In small communities, the programs tend to be managed by companies or agencies established to fill that need. Many medium to large communities hire a nationwide solid-waste management company to organize the collection, establish and maintain facilities, and locate buyers for recycled materials. Although curbside recycling is helping in the reclamation of plastics, in 2009, 2.12 million tons of plastics was recycled. However, that represented only 7% of the total production.

Identification coding. Unlike bottle deposit materials, in which the type of plastics was clearly known, it was difficult to distinguish the types of plastics obtained in the curbside recycling programs. In some cases, mistaken identity of a few containers could ruin a large amount of otherwise useful material. For example, PET bottles and PVC bottles are often impossible to distinguish by appearance. If a small amount of PVC is mixed into a large batch of PET, the PET will be ruined.

To avoid this and other similar problems, the Plastic Bottle Institute of the Society of the Plastics Industry established a system for identifying plastics containers in 1988. Each code has a number in the triangular symbol and an abbreviation below it, as shown in Figure 2-13.

The "chasing arrows" symbol has come to imply recycling. Some individuals and organizations feel that the recycling symbol is deceptive, for when they tried to recycle containers marked 3 or 6, they frequently found no one who would accept those materials. They thought the symbol implied recycling, not just the capability of the material to be recycled. However, systematic and widespread recycling of plastics will require

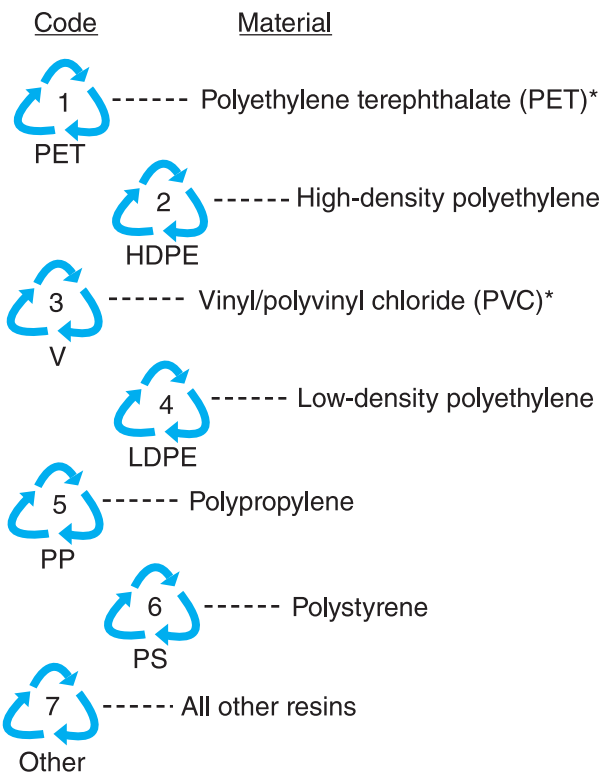


Figure 2-13. These codes were recommended by the Plastic Bottle Institute.

some identification system, with or without the chasing arrows symbol.

Collection. Most recycling programs accept metals, plastic, and paper/cardboard. Some programs require residents to extensively separate the materials. For the plastics, the residents look at the recycling codes and sort plastics into selected groups. During pickup, the materials go into bins or containers to preserve the sorting. Most programs accept plastics number 1 (PET) and 2 (HDPE). Requiring residents to sort the plastics containers has two major drawbacks. First, they often make mistakes in sorting. Second, and often more important, the pickup drivers need more time to place the sorted materials into appropriate containers. Some cities have found that a central sortation line is much more efficient. One very basic manual sorting line requires six employees working only 3.5 hours to process the containers from 5000 houses.

Because of the efficiency of centralized sorting, many large communities accept commingled materials. Residents in many cities throw plastics 1, 2, and 6, plus aluminum and steel cans, newsprint, cardboard, scrap metal, and other paper, into one large container. The importance of compaction affects the decision to accept commingled materials. Uncompacted materials can occupy 10 cubic yards, but if the items are compacted, they need only 3 cubic yards. Compaction in the collection truck can result in savings, primarily in transportation costs. Some trucks can compact paper and cardboard—leaving glass, metal, and plastics loose.

The American Plastics Council promoted "all-bottle" recycling as an alternative to bottle deposits. It conducted studies that indicate an all-bottle approach can boost the amount of containers collected by about 12%. In 2001, only 10% of US communities participated in all-bottle collections. Although most material recovery facilities are not equipped to handle all types of bottles, Waste Management, Inc. (WMI) plans to create a facility near Raleigh, North Carolina, that will allow it to gather and sort plastic containers from all resin types. The biggest concern for the company is whether recycling PVC, LDPE, PS, and PP will be economical.

Figure 2-14 shows a collection truck. This style features two large bins, one for paper and cardboard, the other for commingled containers. Figure 2-15 shows the dumping of the commingled containers.

Because the plastics containers account for the most volume, some trucks are outfitted with special compacting equipment. Figure 2-16 shows a small compaction bin for crushing plastics containers, particularly milk jugs. Without the ability to compact milk jugs, the drivers would have to make more trips to unload.

Sortation. The collection trucks deliver materials to a **materials recovery facility (MRF)**. In 1995, about 750 MRFs were operating in the United States. Only about 60 had automatic sortation lines, and almost 700 had mostly manual procedures. Between 1995 and 2000, some MRFs closed and diverted materials to larger facilities. In 1999, 480 MRFs were operating

Courtesy of the City of Ann Arbor, Solid Waste Dept.

Figure 2-14. The bins in this style truck allow separation of paper from mixed containers.

Courtesy of the City of Ann Arbor, Solid Waste Dept.

Figure 2-15. The plastics containers consume far greater volume than steel or glass containers.

Courtesy of the City of Ann Arbor, Solid Waste Dept.

Figure 2-16. The compaction bin reduces the volume of collected plastics bottles.

in the United States, with a daily throughput of 50,000 metric tons per day. Although there is interest in automatic sortation, many new facilities have manual techniques. Even low-level automatic systems, which can handle only a limited stream of waste plastics, cost about $100,000.

Trucks tip the collected materials into initial sorting equipment. Figure 2-17 shows a conveyor that delivers the commingled containers into the sorting equipment. Many of the manual MRFs can magnetically separate all ferrous containers. Manual sortation can be a very simple process that involves depositing various materials into bins or tubs. Manual sortation can also occur on a picking line. **Picking lines** feature conveyor belts that move recycled materials past employees who sort them into various categories.

Some recycling facilities accept foamed polystyrene. Foamed PS presents several problems. Because its bulk density is so low, the initial storage point must be rather large. Figure 2-18 shows an 8-foot-tall metal storage container. A full semitrailer load of PS foam for recycling will weigh about 1500 lb. Even bales of foamed PS are very light. Figure 2-19 shows a bale of PS foam. These bales weigh from 80 to 90 lb. In contrast, a similarly sized bale of HDPE weighs about 450 lb.

Courtesy of the City of Ann Arbor, Solid Waste Dept.

Figure 2-17. To remove the steel from the mixed container stream, a magnetic drum pulls cans out of the main flow.

Figure 2-18. This enclosed bin protects scrap PS foam from the elements. When full, a truck delivers the foam to an MRF for baling.

Figure 2-19. This tightly packed bale of PS foam came from a vertical-style baler.

Recycling of PCR HDPE

Because HDPE containers do not fall under bottle deposit laws, the effectiveness of recycling depends on curbside recycling and drop-off stations. HDPE bottles were recycled at a rate of about 38% in the year 2000. By 1999, HDPE recycling reached 346,000 metric tons. Table 2-2 shows the growth of HDPE recycling.

The recovery rate on natural HDPE bottles (predominantly 1-gallon and 1-half-gallon milk jugs) was slightly less than 25% in 1993. In contrast, the rate for all HDPE packaging was about 10%. The total packaging sales in 1993 was 1,929,000 metric tons. The total sales of HDPE for the same year was 4,820,000 metric tons, which indicated that packaging of the type that appears in the postconsumer waste stream is only 25% of the total sales. The other products eventually find their way to landfills or incinerators.

In 1995, the demand for recycled materials was up, and the recycling companies were making profits. The recycled HDPE, number 2, had a demand of 500 million pounds in 1994, which was about one-third more than what came through recycle streams. Because of this high demand, a number of major manufacturers began to market materials containing recycled postconsumer plastics. Among these companies were Dow, Eastman Chemical, and Ticona.

Table 2-2. Recycling of HDPE

	1982	1989	1993	1999	2005	2011
HDPE	–	59	216.4	346.0	449	443
Units: 1000 metric tons						

Courtesy of the City of Ann Arbor, Solid Waste Dept.

Figure 2-20. When the bin is full, this pile of mixed-color HDPE will go to the baler.

Courtesy of FCR Inc.

Figure 2-21. The conveyor lifts the containers to the top of the baling chamber.

Courtesy of FCR Inc.

Figure 2-22. This photo shows a bale of PET exiting the baling machine.

Although only a limited number of MRFs handle polystyrene foams, almost all accept PET, natural HDPE, and mixed colored HDPE. Picking lines and automatic sorting equipment separate natural from colored HDPE. When the volume of either type is great enough, the stored containers will go to a baling machine. Figure 2-20 shows a view of a large bin of mixed color HDPE.

Balers are of two major types, horizontal and vertical. The distinction refers to the direction of movement of the ram, which compacts the containers. Vertical balers may be the simplest type that requires hand loading. Because vertical balers force the containers into a closed rectangular space, the bales so produced are often very tight.

Horizontal balers raise the containers up a long conveyor and drop them into a chamber. Figure 2-21 shows the feed conveyor of a horizontal baler. The containers fall into a chamber, and a ram presses them into a bale. Wire-tying equipment finishes the bales. In contrast to many vertical balers, which often make tight bales, some horizontal balers produce bales which are not tightly packed. This occurs because the ram on some horizontal balers pushes against the resistance provided by previously generated bales. Figure 2-22 shows bales exiting the machine. The difficulty with loose bales is that they may break up during handling with fork lifts. Figure 2-23 shows two bales of HDPE on a fork lift.

Because most MRFs do not have equipment to reprocess the plastics, they sell the bales to a reprocessing company. Transportation from the MRF to the reprocessing company generally occurs in semitrailers.

Because a reprocessing facility acquires baled HDPE from several sources, the quality differences in various types of baling equipment are apparent. Figure 2-24 shows tightly packed bales. In contrast, Figure 2-25 shows a loose bale—one in danger of breaking up before reaching the reprocessing equipment.

The first step in reprocessing is to unbale the milk jugs and feed them into a chopper. This provides an opportunity for some control on the materials going into the reprocessing system. The flakes coming from the chopper contain irregular shapes and considerable contamination. Figure 2-26 shows unwashed chopped flakes. A blower system then separates the fine pieces out, because they are too light to fall through a controlled updraft. This process is called **elutriation**. Elutriation

Courtesy of the City of Ann Arbor, Solid Waste Dept.

Figure 2-23. A forklift carries bales to a waiting semitrailer.

Courtesy of FCR Inc.

Figure 2-24. These large, tight bales promote easy handling.

Courtesy of Michigan Polymer Reclaim

Figure 2-25. This loose bale may break when moved with a forklift.

Courtesy of Michigan Polymer Reclaim

Figure 2-26. Unwashed flakes contain many types of contamination, including paper, dirt, pebbles, and undesired plastics.

refers to a purification by straining, washing, or decanting. In this context, the purification is done with air. Figure 2-27 shows the types of fines, paper, and dirt removed during the first elutriation process.

Storage bins hold the flake until it enters a washer. Figure 2-28 shows a washer for HDPE flake. After a pre-weighed charge of flakes drops into the washer, a determined amount of water enters, and a vigorous washing cycle begins. Some systems utilize detergents to assist in cleaning. Others rely on the abrasive characteristics of the flakes to scrub each other.

The washer dumps the load of water and flakes out an outlet pipe, as seen in Figure 2-29. The charge of flakes then enters a **flotation tank**. Slow-moving paddles move the flakes, which float in water, through the tank. The paddles also agitate the flakes and cause heavy particles to fall to the bottom of the tank. In the tank, dirt, sand, and most plastics, other than polyethylene and polypropylene, settle out.

The paddles of the flotation tank lift the flakes to an exit chute, which delivers them to a centrifugal dewatering device.

Courtesy of Michigan Polymer Reclaim

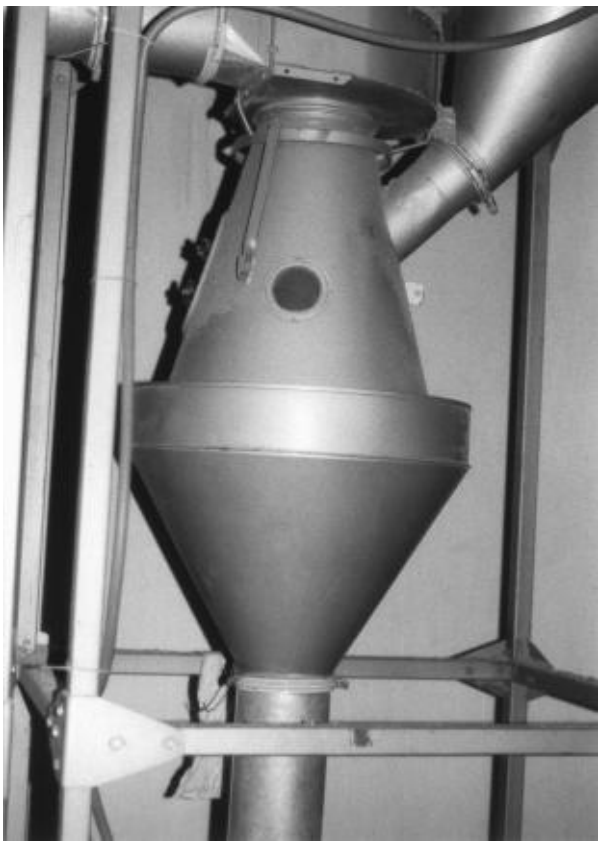
Figure 2-27. This photo reveals dust, lint, paper, and plastic films. The particles were light enough for separation by an elutriation system.

Courtesy of Michigan Polymer Reclaim

Figure 2-28. This cylindrical machine is a high-intensity washer.

Courtesy of Michigan Polymer Reclaim

Figure 2-29. The washer dumps a load of scrubbed flakes and water into the flotation tank.



Courtesy of Michigan Polymer Reclaim

Figure 2-30. This photo shows the blower unit that separates out the fines and lightweight contaminants.

Courtesy of Michigan Polymer Reclaim

Figure 2-31. This group of fines consists primarily of films used in labels on HDPE bottles.

It spins the water out of the flakes and then delivers the flakes to a rapid drying treatment. After drying, a second elutriation system creates a controlled updraft, which separates fines from the washed flakes. Figure 2-30 shows a blower used for this separation. This elutriation yields mostly label films. Figure 2-31 shows the type of fines collected by the second air sorting. Blowers deliver the clean flakes to storage bins, such as the one seen in Figure 2-32. If the storage bins are full, flakes can be stored in **gaylords**, which are large boxes containing approximately 1 cubic yard of material.

The clean flakes (as seen in Figure 2-33) then enter the feel throat of an extruder. The extruder melts the flakes and forces the melted material through a die. Figure 2-34 shows an extruder prepared for this operation. This extruder has a water-wall-type pelletizer, which chops strands of extruded material just after they exit the die. The particles are thrown into a cylindrically shaped wall of water. Figure 2-35 shows this type of pelletizer head. The pellets cool rapidly. They are then dewatered and dumped into a gaylord for shipment to a processing facility, which will make new products.

Because the HDPE found in milk jugs is blow-molding grade material, it frequently goes into additional blow-molded products.

Automatic sortation. Manual sortation has two serious limitations. It is not effective in distinguishing PVC from PET, and it becomes unworkable when the total volume

Courtesy of Michigan Polymer Reclaim

Figure 2-32. Below the storage bin is a gaylord, which can store flakes if the bin fills up. Notice the stockings hanging around the bin. The air used to deliver the flakes into the bin must escape. The stockings catch any fines in this exhaust air stream.

Courtesy of Michigan Polymer Reclaim

Figure 2-33. These are clean flakes. Notice the one dark piece. It is a portion of a milk bottle top and consists of blue polypropylene. It is a contaminant, but because PP and HDPE have similar densities, it cannot be excluded by a flotation system.

Courtesy of Michigan Polymer Reclaim

Figure 2-34. Clean flakes drop into the feed hopper at the rear of this extruder.

Courtesy of Michigan Polymer Reclaim

Figure 2-35. This photo shows a water-well-type pelletizer. It has the advantage of keeping the die hot and dry, yet cooling hot pieces of plastics in a water bath.

of materials is very high. To develop faster systems, companies have developed various types of automatic sorting devices. Many automatic systems include similar equipment to prepare the containers for identification. They all use bale loaders, unbaling machines, and screens to remove rocks, dirt, and extremely large or small containers. Great diversity occurs in the technical method used to identify various plastics. Identification systems have two major components: a method to separate and convey the containers and a method to identify the plastics.

The separation and transportation usually involve high-speed conveyors. If there is a single detector in the system, the conveyors must singulate the containers and bring them past the detector one at a time. Frequently, an air blast is used to separate one container from the next. In addition to air blasts, vibratory conveyors also aid in singulation. If a single detector fails to recognize the container, or if the container is improperly positioned for optimal recognition, it may be unidentified. To increase identification rates, some systems have multiple detectors with a singulating conveyor system. Some systems are capable of multiple containers and require multiple detectors for this application. Figure 2-36 shows several possible configurations for automatic identification.

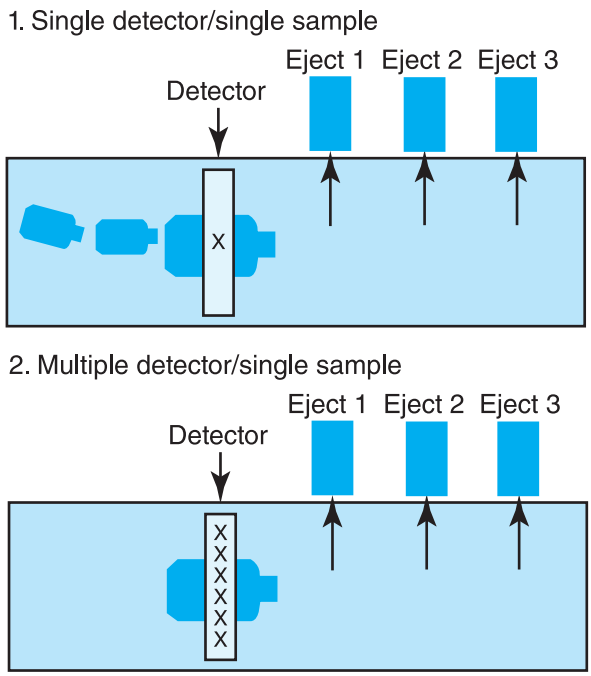


Figure 2-36. Singulating conveying systems present containers to the detection equipment one at a time.

The general purpose of the detector is to determine the chemical makeup of a container. Once that is complete, computer-based systems must track the location of the known container and then activate the air jet to eject to the appropriate takeoff conveyor. The four major types of detectors are optical, X-ray, single wavelength **infrared (IR)**, and multiple wavelength IR.

Optical systems rely on vision systems that determine the color of a container; X-ray sensors can distinguish PET from PVC by sensing the presence of chlorine atoms in the PVC. Chemical detection can occur rapidly—with some systems requiring less than 20 milliseconds. Single wavelength IR systems can determine opacity and, based on the results, sort containers into clear, translucent, and opaque streams. Multiple wavelength IR systems can determine the chemical constitution of a container by comparing its results to a known standard. Compared to the single wavelength IR systems, the multiple wavelength systems require more time for identification.

Automated sorting systems can be modest, with equipment to recognize only a few materials. A basic system can distinguish three main classes: natural HDPE; PP, PET, and PVC; and mixed-color HDPE. A slightly more powerful system would distinguish PET from PVC.

Some color systems claim the ability to distinguish millions of shades of color. IR systems extend the capabilities further. After identification is complete, the selected containers are blown by air jets onto appropriate conveyors or hoppers. These automated systems can process containers at a rate of two to three containers per second or about 1500 lb per hour. To improve on that rate, multiple lines are needed. However, the costs of such systems can reach $1 million.

Chopped commingled materials. Elimination of all sorting can simplify the systems in MRFs. However, the chopping of commingled plastics results in mixed chopped flakes. Sorting the flakes into appropriate material streams can be done in various ways.

Flotation systems can distinguish materials based on differences in density. Froth flotation separates plastics by differing surface-wetting potentials.

Systems based on an optical sorting technology bring a stream of chopped flakes past detectors. If the detectors indicate the presence of an unwanted flake, air blasts remove it from the stream. The efficiency and speed of these systems is still under development. Currently, one pass through the system can remove about 98% of contaminates; however, to clean the stream to the level of 10 parts per million (ppm), several additional passes are required. Similar systems based on magnetic separation can distinguish PVC from PET.

Automotive Recycling

Approximately 10 million automobiles are discarded every year in the United States. They arrive first at automotive dismantlers. After removing parts useful for resale, the dismantlers hand the remains over to shredders. There are approximately 180 shredders in the United States. After turning a car into pieces, the facilities sort ferrous from nonferrous metals and feed these materials to foundries and steel mills for reprocessing. About 75% of the materials in automobiles are recycled. The shredder residue, sometimes called shredder fluff, contains plastics, glass, fabrics, adhesives, paint, and rubber. The **automotive shredder residue (ASR)** accounts for 3 to 4 million metric tons per year. Between 20 and 30% of the ASR is plastics materials, most of which goes into landfills.

In an effort to reduce the shredder residue, the major automobile companies have established procedures and guidelines for recycling. To make recycling work throughout the automotive industry, several major automobile companies have created the **Vehicle Recycling Partnership (VRP)**. This partnership is currently attached to the United States Council for Automotive Research (USCAR). As part of the efforts, they established a code for making plastics—**SAE code J1344**—to aid in identification during disassembly. This code utilizes the ISO (International Organization for Standardization) designations for plastics. (For information on ISO tests, see Chapter 6.)

In addition to efforts aimed at the entire automobile industry, major companies have established internal guidelines for recycling. For example, Ford Motor Company established

recycling guidelines in 1993. These guidelines promote the use of recycled materials and encourage the reduction of painted plastics. Molded-in color reduces volatile emissions from painting operations and makes recycling easier. The guidelines also recommend the use of a limited number of plastics and suggest the use of polypropylene (PP), acrylonitrile-butadiene-styrene (ABS), polyethylene (PE), polyamide (PA), polymethyl methacrylate (PMMA), and polylcarbonate (PC). PVC should be used only where separation and recycling techniques are established. In addition, suppliers were urged to recover and recycle materials at the end of the useful life of vehicles. In 2003, Ford started a recycling program called Core Recovery Program. By 2013, the company estimated that it had diverted 120 million pounds, including plastic bumpers, from landfills.

Chemical Recycling

Chemical recycling involves two levels of depolymerization. The original polymerization of some plastics is reversible. Depolymerization yields monomers, which can be used to make new polymers. Other plastics do not depolymerize to immediately useful monomers.

The type of depolymerization that produces useful monomers is called **hydrolysis**. It is beyond the scope of this discussion to thoroughly explain hydrolysis and the chemical reactions it utilizes. It is, however, a technique that is feasible for polyesters, polyamides, and polyurethanes. The chemical techniques vary depending on the type of plastics. For years, companies making PET have used a form of hydrolysis to convert manufacturing waste PET to monomer.

Some plastics can be converted to monomers with thermal depolymerization. This process involves heating the plastics in the absence of oxygen. This process is also labeled **pyrolysis**. Acrylic, polystyrene, and some grades of acetal yield monomers under these conditions.

Other plastics arose through irreversible reactions and consequently cannot be depolymerized into monomers. They can be depolymerized into useful petrochemical materials by pyrolytic liquefaction. Materials appropriate for this treatment are HDPE, PP, and PVC.

In simple pyrolytic liquefaction, pieces of plastics enter a tube that is heated to about 1000°F (538°C). The plastics melt and decompose into vapors, and the vapors condense into liquids. Liquids are used as feed stocks in petrochemical plants. Some facilities hope to make gasoline from the plastics.

Recycling in Germany

In the United States, some packaging and container manufacturers now face various recycling laws and mandates. Such laws do not currently extend to producers of appliances, automobiles, and electronics. In contrast, Germany has placed full responsibility for recovering, reprocessing, or disposal of packaging on the manufacturers.

To meet this challenge, over 600 manufacturers and distributors combined their forces and created a system called Duales System Deutschland (DSD). DSD was founded in 1990 and functioned as a private company until 1997, when it was converted into a public company with about 600 shareholders. DSD collects, sorts, and arranges for reprocessing of all packaging materials. During 1993, DSD collected 360,000 metric tons of material. In the year 2000, it collected over 5.6 million metric tons of material. The materials recovered include glass, plastics, and metals. Before 2006, stores were required to take back only the containers they sold, but since May 2006, stores are required to take back any and all packages made from the same materials they sell. This has helped make the system more efficient. In 2006, DSD recovered 5.2 million metric tons of materials. Although that volume is about the same as in the year 2000, packaging companies have continuously optimized package designs. As a consequence, the annual consumption of sales packaging has been regularly reduced. In 2012, DSD received 100% of the packaging containers that participate in the system. That meant that none of those containers went to landfills.

DISPOSAL BY INCINERATION OR DEGRADATION

An alterantive to landfills has been to burn waste materials. Burning reduces the volume of the materials and yields considerable heat. Plastics in solid waste are an energy-rich fuel. However, incineration also generates emissions, sometime toxic. Degradable plastics, although still small in total volume, avoid these undesirable emissions.

History of Incineration in the United States

Burning of solid wastes in open dumping areas was common for centuries; however, the concerns for environmental protection closed open dumping and burning areas and replaced them with landfills. Some communities constructed special incinerators to dispose of the solid wastes. By 1960, approximately 30% of **municipal solid waste (MSW)** was handled in incinerators without any attempt to recover or use the heat. This method grew until the early 1970s. The Clean Air Act, which was passed in 1970, closed about half the incinerators because the retrofills for pollution control were considered too expensive. To make incineration viable, some method to pay for the cost of equipping a facility was required. One possible

solution was to use the solid waste as fuel in the generation of electrical energy or steam.

From the late 1970s through 1980, there was a tremendous increase in **waste-to-energy (WTE)** facilities. By 1990, about 15% of the MSW was incinerated. These waste-to-energy facilities were expensive; a well-equipped facility required at least $50 million to construct. In 1991, there were 168 active incinerators in the United States. In comparison, Japan had about 1900 and Western Europe had over 500 incinerators. Because of strict regulations on incineration, a number of US incinerators closed in the mid-1990s. In 1999, the United States had only 102 combustion facilities with a capacity to burn up to 87,000 metric tons per day. In 2010, the United States had 87 plants for its 300 million people, and Denmark had 29 plants for its 5.5 million.

In Japan, construction began on a unique WTE facility in 2001. The $81 million power plant was designed to generate 74,000 kW and to burn only plastic waste. The plant's capacity was 680 metric tons per day, and it should emit fewer pollutants than most oil-fired power stations.

Advantages of Incineration

One of the advantages of incineration is that it does not require sorting of the solid wastes. The entire collection of paper, plastics, and other materials can go into the incinerator. It provides an 80% to 90% reduction in the volume of the solid waste, turning many cubic yards of material into a few pounds of ash. WTE plants incur an operating cost of about $10 to $20 per ton. To offset the cost, the WTEs have two sources of revenue. They charge city solid-waste organizations to deliver truckloads of compacted MSW. Incinerator facilities receive approximately $50 per ton for accepting the MSW. In addition, the incinerators sell electricity. The cost of electricity from these facilities is comparable to those of other electric generating plants—generally not significantly lower.

For many cities, the alternative to incineration is landfilling. However, landfill costs are high in highly populated regions of the country. In New York and Massachusetts, landfill costs can exceed $50 to $60 per ton. In some areas of California, landfill costs have reached as much as $85 per ton.

Disadvantages of Incineration

When new incinerators are proposed, some citizen groups vehemently oppose them. The grounds for trying to stop new incinerators involve two factors: first, the incinerator ash, and second, the emissions from the incineration process.

Incinerators generate two types of ash: bottom ash and fly ash. **Bottom ash** comes from the bottom of the incineration chamber and contains noncombustible materials. Mass burn incinerators deliver the full contents of the compacted load of waste into the burning chamber. Bricks, rocks, steel, iron, and glass go into the bottom ash, along with the residues of combustion. The **fly ash** is material collected from the smokestack gases by pollution control equipment.

Fly ash often contains relatively high concentrations of heavy metals and some hazardous chemicals. In contrast, the bottom ash usually contains less toxic materials. Some incinerator facilities mix the fly ash and bottom ash together.

A point of conflict concerns the danger to citizens from the ashes and the proper disposal method for the ashes. If the ash is considered a toxic material, then it must be landfilled in a special landfill designed for toxic materials. That raises the cost tremendously compared to regular landfills.

The emissions from incinerators often contain various levels of furans, dioxins, arsenic, cadmium, and chromium. These are all very toxic materials, and many people fear potential adverse health effects. Proponents of incineration argue for comparisons between incinerators and power plants that burn pulverized coal. Environmentalists argue that the emissions are potentially carcinogenic and should be banned immediately.

A particular concern for the plastics industry is dioxin. When compounds that contain chlorine, such as PVC and paper whitened by chlorine bleaching, are incinerated at high temperatures, various chlorinated chemicals are produced. When the gases containing these chemicals cool to about 300°C (572°F), dioxin forms. The Environmental Protection Agency (EPA) views dioxin as a probable human carcinogen and a dangerous noncarcinogenic health threat.

An EPA report published in 1995 cites medical waste incinerators as the biggest source of dioxin in the United States. The second largest source is municipal solid-waste incinerators. Although the medical waste incinerators burn small volumes compared to MSW incinerators, the medical waste stream has a high PVC content. In addition, there are many more medical waste incinerators than MSW incineration facilities. In 1994, over 6700 medical waste incinerators were operational.

Two approaches have been proposed: first, the elimination of all chlorinated wastes from incinerators, and second, the improvement of emissions controls for incinerators. Reducing dioxin emissions will require significant investments in pollution-control equipment, perhaps involving at least 60% of existing incinerators. If the new air quality regulations are enforced, about 80% of the existing medical incinerators will probably cease operation. To handle medical waste, a small number of extremely well-controlled incinerators may be able

to meet the standards. Hauling the waste to a few incinerators will also add to the cost of handling medical waste.

Another possibility is to deliver medical waste to huge autoclaves, which heat the materials to a temperature that kills biohazards. After autoclaving, the waste materials then go into a traditional landfill.

Degradable Plastics

Considerable controversy surrounds biodegradable plastics. A focus for the controversy was the rings or yokes used to hold six-packs and eight-packs of beer or soft drink cans or bottles together. It was proven by various environmental groups that some animals, particularly sea birds, were getting stuck or trapped in the rings. The response to this was legislation requiring that such rings, yokes, or other devices be degradable.

Raw material suppliers introduced **photodegradable** and **biodegradable** grades of material for these applications. The photodegradable materials contain chemicals that are sensitive to sunlight and cause the rings to disintegrate. Biodegradable grades often contain cornstarch or other starches, which are attacked by microorganisms in water or soil. The rings also disintegrate over time. In all cases, the thinner the packaging material, the quicker the physical deterioration.

Currently, 28 states have laws requiring degradable connecting devices. Michigan requires degradable within 360 days; Florida allows only 120 days. Other states do not specify the time lapse permitted.

This did not end the controversy—environmental groups attacked the degradable materials. They argued that bio- or photodegradable plastics can contaminate otherwise useful recycled plastics. They also view the degraded materials as a potential threat to water purity. After sufficient bio- or photodegradation, the rings break down into small pieces. However, these small chips are often rather chemically stable. For example, a grocery sack made of polyethylene with cornstarch as an additive will disintegrate into tiny particles of polyethylene. It will appear to be gone from the roadside, but the tiny pieces are still there. They are likely to remain intact for long periods of time.

Since 2000, a number of companies have begun selling bioplastics. Bioplastics and biopolymers are polymer materials that derive from renewable resources. In contrast to petroleum-based plastics, these materials begin as corn or other plants. Many bioplastics are also biodegradable, but some are not. In a major development, Braskem company, a Brazilian-based chemical company, started making conventional polyethylene using sugar instead of oil or gas as the raw material. In 2010, Braskem started a plant with an annual capacity of 200,00 metric tons. The company claims its polyethylene is a sustainable product, made with a lower carbon footprint than polyethylene from oil or gas. By 2011, the global production of bioplastics reached 1161 thousand metric tons, divided into nondegradable materials and degradable materials. The leaders among the nondegradable materials were PET and polytheylene. The leader in degradable materials was PLA. Although the usage of biopolymers is limited, they offer a potential to compete with conventional polymers if oil prices continue to rise and production of bioplastics becomes more cost-effective. Polyactic acid (PLA) usage represents about 40% of the total of nonpetroleum-based plastics.

The "green" plastic that has received the greatest attention is polyactic acid, which is based on starch from corn, wheat, and other grains. The chemical name for PLA is polyhydroxyalkanoate, a natural polyester that has been studied for many years. In the past, it was expensive and had very limited properties and processing ranges. The process involves fermentation of cornstarch to yield lactic acid. The lactic acid then goes through a catalytic ring-opening polymerization to generate PLA. Even before it was ready for the market, big agricultural companies were interested in the potential of PLA.

In the United States, both ADM (Archer Daniels Midlands) and Cargill have entered the market. During the 1990s, Metabolix, Inc., developed techniques to make PLA easier to process and at reduced costs. ADM and Metabolix established a joint venture and created a new company, Telles™. Cargill created a new unit, NatureWorks®. Telles™ offers three injection-molding grades of its PLA, named Mirel™. Telles™ also sells two grades of Mvrea, a compostable material intended for grocery bags and other film applications. The unit of Cargill now sells Natureworks polymer and Ingeo® extruded fibers for clothing. In 2012, Natureworks had a capacity of 140,000 tons (US) of Ingeo®. Because of 25% to 30% annual increases in the early 2010s, NatureWorks had instituted efforts to build a new processing plant in Thailand.

PLA continues to have various limitations. It is difficult to foam. It has relatively low thermal stability and needs careful drying to remove moisture. It is also prone to color change due to lower thermal resistance. Some applications also require special equipment.

A German company makes Bio-Flex® mulch, a biodegradable film for agricultural use. It is intended to replace traditional PE agricultural films. After use, it can be plowed under, eliminating the time and cost of removing traditional films. Some automobile companies are considering PLA for components in order to promote the claim of environmental concern. Toyota has established a pilot plant for making PLA. In 2009, Toyota announced that it had developed an alloy of PLA and PP that was intended for use in injection molded parts.

Some of the most visible applications of PLA have been in food and beverage packaging. BIOTA, a company based in Colorado, sells spring water in bottles made from PLA. They claim that the bottle will completely degrade in 80 days in commercial composting. Excellent Packaging and Supply (EPS) is a distributor for SpudWare™, a line of biodegradable cutlery and plates made in China from a bioplastic that is 80% vegetable starch and 20% vegetable oil. Some organic fruits and vegetables are packaged in biodegradable films.

A few organizations now claim the promotion of bioplastics as their mission. European Bioplastics, an association begun in 2006 to represent users of bioplastics and biodegradable polymers (BDP), states its mission is to support the use of renewable raw materials. It also encourages compliance with the provisions of EN 13432, a standard for compostable polymers that is valid in all European Union (EU) member states. International Biodegradable Polymers Association & Working Groups is an organization based in Germany. In addition to promoting biodegradable plastics, the organization has assisted in the development of a system for the certification and labeling of biodegradable materials and compostable plastics products. This system identifies biodegradable and compostable plastics so they will not enter the recycling stream with conventional plastics.

The concern with recycling may hinder the growth of PLA, because a small amount of PLA can contaminate the PET recycling stream, which is the largest of all recycling flows. Most bioplastics are labeled as "7," the recycling code for "other" materials, but beverage bottles such as the ones offered by BIOTA could easily end up in recycling bins.

ORGANIZATIONS IN THE PLASTICS INDUSTRY

The plastics industry supports a large number of organizations, ranging from international, all-encompassing societies to small, highly specific groups. Some of the larger groups will receive attention; many of the smaller organizations will receive mention only.

The Society of the Plastics Industry (SPI)

The SPI was established in 1937 to serve as "the voice of the plastics industry." According to its mission statement, the SPI seeks to "promote the development of the plastics industry and enhance public understanding of its contributions while meeting the needs of society." The Society has a structure composed of three major councils and one special interest group. The councils are Equipment, Material Suppliers, and Processors. The Equipment council concerns machine safety, standards, equipment statistics, and programs/conferences. The Material Suppliers council consists of fluoropolymer manufacturers, organic peroxide producers, vinyl producers, and programs/conferences. The Processors council includes film and bag manufacturers, thermoformers, medical products, emerging issues, statistics/benchmarks, and programs/conferences.

One of its most familiar activities is organizing the National Plastics Exposition (NPE) and International Plastics Exposition every three years. This exposition began in 1946 and now draws visitors from 75 countries. The exposition brings together equipment manufacturers, raw materials, suppliers, laminators, fabricators, mold makers, and manufacturers of plastics.

The SPI maintains a publications service. To locate the various publications, visit the Plastics E-Store on the SPI's website: **http://www.plasticsindustry.org**.

Society of Plastics Engineers (SPE)

In 1942, 60 salesmen and engineers met near Detroit, Michigan, and began the SPE "to promote scientific and engineering knowledge related to plastics." In 1993, its members numbered over 37,800—divided among 91 sections in 19 countries. Large local sections hold monthly meetings, which provide social as well as technical benefits to members. The SPE maintains its world headquarters in Brookfield, Connecticut, and recently opened a European office in Brussels, Belgium.

The SPE supports and promotes formal education related to plastics. It encourages students to engage in research projects on plastics materials and processes, and provides scholarships for both undergraduate and graduate study. Students can join SPE student chapters, which number 32 throughout the world.

The SPE provides continuing education for its members through a wide range of seminars and conferences. Regional and national technical conferences provide members with access to the most current research in the field. The largest conference is the Annual Technical Conference and Exhibition (ANTEC). In 1943, the SPE held its first Annual Technical Conference, which had 50 exhibitors and fewer than 2000 visitors. In 1993, ANTEC drew about 5000 members and hosted over 650 technical presentations. In 2001, ANTEC was held in Dallas, Texas, and featured over 700 technical papers, 20 seminars, and 130 exhibitors. The 2012 ANTEC was held in Orlando, Florida, in conjunction with the NPE. The advantage for the SPE members was the ability to visit the extensive

exhibitions, featuring equipment in 13 international pavilions, and over 400 domestic companies.

Every month, the SPE publishes *Plastics Engineering*, a magazine containing articles on current developments in plastics. In addition to *Plastics Engineering*, the Society also publishes three technical journals that include articles and papers of scientific and scholarly merit: *Journal of Vinyl Technology*, published four times a year; *Polymer Engineering & Science*, published 24 issues per year; and *Polymer Composites*, with six issues per year.

The SPE publishes a catalog annually, containing a variety of books from world-renowned publishers. The books cover two broad areas: one concerning engineering and processing of plastics materials, and the other on polymer science. The catalog also offers the proceedings of regional technical conferences and the ANTEC proceedings and subscriptions to the SPE journals.

The SPE holds the position as the world's largest technical organization for scientific and engineering knowledge relating to plastics. For further information or membership applications, visit the website or write to:

Society of Plastics Engineers
14 Fairfield Drive
Brookfield, CT 06804-0403
www.4spe.org

The Plastics Institute of America (PIA)

The PIA is now a not-for-profit educational and research group. Scholarships are offered to students seeking careers in the plastics industry, and employee training is provided in collaboration with the University of Massachusetts Lowell. To contact PIA, visit the website or write to:

The Plastics Institute of America, Inc.
UMass-Lowell Campus, Wannalancit Center
600 Suffolk Street
CVIP, 2nd Fl South
Lowell, MA 01854
www.plasticsinstitute.org

Society for the Advancement of Material and Process Engineering (SAMPE)

This society has members who are involved in the development of materials and process—chiefly materials and process engineers. It publishes the *SAMPE Journal* bimonthly and the *Journal of Advanced Materials*. To contact SAMPE, visit the website or write to:

SAMPE Headquarters
1161 Park View Drive, Suite 200
Covina, CA 91724-3751
www.sampe.org

Other Organizations

International Association of Plastics Distributors (IAPD)
www.iapd.org

The Association of Postconsumer Plastic Recyclers (APR)
www.plasticsrecycling.org

The National Association for PET Container Resources (NAPCOR)
www.napcor.com

Association of Rotational Molders International (ARM)
www.rotomolding.org

Plastic Lumber Trade Association
www.plasticlumber.org

Plastics Foodservice Packaging Group (PFPG), formerly Polystyrene Packaging Council
www.polystyrene.org

Polyurethane Foam Association
www.pfa.org

Polyurethane Manufacturers Association
www.pmahome.org

Publications for the Plastics Industry

Plastics Technology is published monthly by Bill Communications, Inc. It features articles for plastics processors and a pricing update. Plastics Technology also publishes *PLASPEC*, which provides information on various grades of materials. For more information:

Plastics Technology
www.ptonline.com

Trade Newspapers

Plastics News is a weekly publication from Crain Communications, Inc. It includes short articles on business topics and reports on sales and acquisitions of processing plants, new materials and designs, seminars, and resin prices. For subscription information:

www.plasticsnews.com

RELATED INTERNET SITES

- **www.braskem.com.** Braskem is a major, global chemical company. On the home page, select "Sustainable Chemistry" to access "Green Products." This section contains information on the production of "Green PE" from sugar.
- **www.cereplast.com.** Cereplast, Inc., sells biopolymers. Selecting "Products" on the home page leads to a discussion of compostable plastics, which will completely degrade, and sustainable materials, which replace up to 95% of the petroleum content with materials from renewable sources.
- **www.epa.gov.** The Environmental Protection Agency (EPA) has an extensive site. For a summary of facts about recycling of municipal waste, contact **www.epa.gov/wastes/nonhaz/municipal/**.
- **www.european-bioplastics.org.** This association began in 2006 to represent users of bioplastics and biodegradable polymers (BDP). Its mission is to support the use of renewable raw materials. Selecting "Standards" on the home page leads to choice of "Standardization." That section contains information about EN13432: 2000 Packaging, and EN14995: 2006 Plastics. These two standards define the specifications a bioplastic must meet to be considered compostable.
- **www.excellentpackaging.com.** Excellent Packaging and Supply (EPS) includes a division, BioMass Packaging. This division distributes a number of biobased packaging materials and features, SpudWare™, Biobag®, ECOSAFE®, and Greenware®.
- **www.natureworksllc.com.** NatureWorks LLC sells bioplastics that have gloss and clarity like polystyrene and strength like PET. The company claims that this material has a much lower adverse environmental impact than conventional packaging materials.

VOCABULARY

The following vocabulary words are found in this chapter. Use the glossary in Appendix A to look up the definitions of any of these words you do not understand as they apply to plastics.

automotive shredder residue (ASR)
biodegradable
bottom ash
elastomers
elutriation
flotation tank
fly ash
gaylords
hydrolysis
infrared (IR)
materials recovery facility (MRF)
municipal solid waste (MSW)
photodegradable
picking lines
plastic
plastics
polymers
pyrolysis
resins
Resource Conservation and Recovery Act (RCRA)
rubber
SAE code J1344
thermoplastic elastomer (TPE)
thermoplastic olefin elastomer (TPO)
Vehicle Recycling Partnership (VRP)
waste-to-energy (WTE)

QUESTIONS

2-1. Explain the difference between recycling and reprocessing.

2-2. What is pyrolysis?

2-3. How large is a gaylord?

2-4. How do plastics and elastomers differ?

2-5. How are resins different from plastics?

2-6. Approximately what percentage of the US workforce is directly involved in plastics manufacturing?

2-7. How effective are bottle deposit laws?

2-8. Containers marked with the number 5 contain what type of plastics?

2-9. What does the acronym MRF stand for?

2-10. What are the four major types of detectors used in automatic sorting systems for plastics?

2-11. Explain hydrolysis.

2-12. What conditions are required for the formation of dioxins during incineration?

ACTIVITIES

Recycling HDPE

Schools, businesses, and communities often have containers for the recycling of various bottles. Among bottles, one of the easiest material to recycle is high-density polyethylene.

Introduction. Recycling of postconsumer HDPE is one of the biggest and most successful plastics recycling efforts. The bulk of the recycled HDPE comes through curbside pickup of HDPE bottles and containers—particularly milk jugs. Some companies advertise their use of recycled materials to demonstrate their environmental concern. Figure 2-37 shows a tool for removing bicycle tires from rims.

Procedure

2-1. If a curbside recycling program exists nearby, determine which plastics are acceptable. If the program accepts both PET and PVC, how do they guarantee that the PVC does not contaminate the PET?

2-2. Does the program expect the participants to sort the materials? Is the collection put into a truck with specific compartments, or is the material comingled?

2-3. Is there an MRF nearby? If so, how does it sort the plastics? Does it have any automated sorting equipment?

2-4. Does the program distinguish between natural HDPE and colored HDPE? If yes, how does this sorting occur?

2-5. How are the sorted HDPE containers handled? Is a baler used? Is the material chopped into flakes?

2-6. Who buys the HDPE from the recycling organization? What is the current price for baled material, dirty chopped flakes, clean chopped flakes, and reprocessed pellets?

2-7. How much difference is there between the price of recycled materials and virgin materials?

2-8. Is there a mandate on the percentage of postconsumer recycled materials in packaging? If yes, what percentage must be PCR?

2-9. What technologies are required for a company to turn bales for crushed HDPE containers into clean pellets or flakes?

2-10. Write a report summarizing your findings.

Figure 2-37. The marketing of this bike tire removal tool appeals to the environmental concerns of customers.

Additional recycling activity. This activity is not feasible without adequate equipment. If processing equipment and choppers are available, try to determine the difference between recycled material and virgin material.

! CAUTION

Use processing equipment only under the guidance of trained supervisors.

Procedure

2-1. Acquire milk jugs from a local recycling company. Generally, such companies are pleased to donate some HDPE milk jugs for students learning about recycling.

2-2. List the decisions needed. For example, how should labels be treated? How should cleaning occur? If a chopper is small and cannot handle complete bottles, how should they be reduced in size? Figure 2-38 shows pieces of milk jugs cut into a size that fits into a small chopper, along with chopped flakes. Should contaminated bottles be rejected? What determines the difference between contaminated and not contaminated? What should be done with screw-on or pop-on closures?

2-3. Determine a procedure to follow, and process enough jugs to yield 3 to 5 lb of chopped flakes. Should the flakes be washed? If so, how will this occur? Figure 2-38 also shows flakes produced from the milk jug pieces.

2-4. Extrude the clean flakes to produce pellets. Is there any odor of sour milk attached to the pellets?

2-5. Is there a color difference between virgin pellets and recycled pellets?

2-6. One way to examine the recycled material for contaminants is to make it into film. If blown film equipment is available, try to process the recycled material. If not, squeeze out the thinnest film possible using a heated platen press. Are impurities visible in the recycled materials? A microscope or magnifying glass will help answer the question.

2-7. Stretch, tear, and bend film samples of virgin and recycled materials. Do they appear to possess differing physical properties?

2-8. Write a report summarizing the findings.

Figure 2-38. These milk jug pieces were an appropriate size for a small chopper. The fines were not removed from the flakes.

ELEMENTARY POLYMER CHEMISTRY

CHAPTER 3

INTRODUCTION

Many people have no difficulty recognizing common metals such as copper, aluminum, lead, iron, and steel. They also know the difference between oak, pine, walnut, and cherry. In addition to identifying several metals and woods, many people also understand some physical qualities of these materials. For example, they know that steel is harder and stronger than copper.

In contrast, significant characteristics and names of major types of plastics are often unknown. This chapter discusses several commercial plastics, acquainting the reader with polymer names and chemical structures. To do this, some knowledge of basic chemistry is required. This chapter assumes the reader has an understanding of basic chemistry, elements, the periodic table, and some chemical structures. In this and following chapters, every reference to an atom also includes its chemical symbol. The outline for this chapter follows:

REVIEW OF BASIC CHEMISTRY

Understanding basic chemistry is crucial to learning about plastics. Chemical terms are used to explain the names and properties of polymers. Chemical structures determine the unique characteristics of polymers as well as their limitations. It is convenient to begin this section with a review of molecules and chemical bonds.

Molecules

Molecules occur when two or more atoms combine. The properties of molecules stem from three major factors: the elements involved, the number of atoms joined together, and the type of chemical bonds present. The number of atoms joined determines the size of the molecule, and the bonds determine its strength.

For example, water (H_2O) is made up of hydrogen atoms chemically combined with oxygen. Water consists of two hydrogen atoms and one oxygen atom—three atoms in total. Because only three atoms are involved, water is a very small molecule. The **molecular mass** of water is 18 because the number of **atomic mass units (amus)** is 16 for oxygen and 1 for each hydrogen.

Chemical bonding concerns the ways atoms can attach to each other. There are three basic categories of **primary chemical bonds: metallic bonds, ionic bonds**, and **covalent bonds**. Of these three, covalent bonding is the most important for plastics. Usually, covalent chemical bonding involves the sharing of electrons between two atoms. The exact mechanism of this sharing is beyond the scope of this chapter. However, it is important to know that covalent bonds have known strengths and lengths that depend on the atoms combined. Covalent bonds can involve varying numbers of electrons, as shown in Figure 3-1. The bond

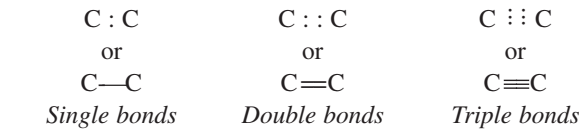


Figure 3-1. Types of covalent bonds.

that consists of the least number of electrons (2) is called a **single covalent bond**. If more electrons are involved (4 or 6), the bonds are called **double** or **triple covalent bonds**, respectively.

Unless otherwise specified, comments about covalent bonding will refer only to single covalent bonds.

HYDROCARBON MOLECULES

Hydrocarbons are materials that consist mainly of carbon and hydrogen. Pure hydrocarbons contain only carbon and hydrogen. When hydrocarbon molecules have only single covalent bonds, they are considered **saturated**. The word *saturated* implies that the bonding cites are fully "loaded up." In contrast, **unsaturated** molecules contain some double bonds. Because double bonds are more chemically reactive than single bonds, the saturated molecules tend to be more stable than unsaturated molecules. Table 3-1 lists saturated hydrocarbon molecules.

Table 3-1. Saturated Hydrocarbon Molecules with Melting and Boiling Points

Formula	Name	Melting Point, °C	Boiling Point, °C
CH_4	Methane	−182.5	−161.5
C_2H_6	Ethane	−183.3	−88.6
C_3H_8	Propane	−187.7	−42.1
C_4H_{10}	Butane	−138.4	−0.5
C_5H_{12}	Pentane	−129.7	+36.1
C_6H_{14}	Hexane	−95.3	68.7
C_7H_{16}	Heptane	−90.6	98.4
C_8H_{18}	Octane	−56.8	125.7
C_9H_{20}	Nonane	−53.5	150.8
$C_{10}H_{22}$	Decane	−30	174
$C_{11}H_{24}$	Undecane	−26	196
$C_{12}H_{26}$	Dodecane	−10	216
$C_{15}H_{32}$	Pentadecane	+10	270
$C_{20}H_{42}$	Eicosane	36	345
$C_{30}H_{62}$	Triacontane	66	distilled at reduced pressure to avoid decomposition
$C_{40}H_{82}$	Tetracontane	81	
$C_{50}H_{102}$	Pentacontane	92	
$C_{60}H_{122}$	Hexacontane	99	
$C_{70}H_{142}$	Heptacontane	105	

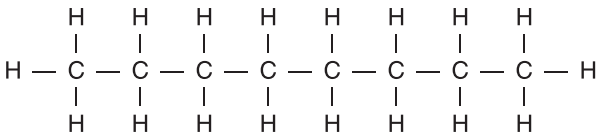


Figure 3-2. Chemical structure of octane.

As indicated in Table 3-1, molecules with one, two, three, or four carbon atoms have boiling points below 0°C (32°F). This means that they exist as gases at room temperature. Molecules from 5 to 10 carbons are rather volatile liquids at room temperature. When the number of carbons increases beyond 20, the materials become solid.

The hydrocarbon molecule with eight carbons is octane, which is familiar because of its use as automotive fuel (Figure 3-2). The molecular mass of octane is 114 amus, and here is its chemical structure:

Note: *Carbon has 12 amus and hydrogen 1.*

$$(8 \times 12) + (18 \times 1) = 114$$

Notice that the hydrogens are connected (with single covalent bonds) only to carbons. There are no bonds between the hydrogens. This means that the structural integrity of the molecule is proved by bonds between the carbons. If we imagine the hydrogen removed, what would remain is a row of eight carbon atoms. This line is called the **backbone** of the molecule. The strength of the molecule is substantially determined by the strength of the carbon-to-carbon single bonds.

As the number of carbons in the backbone increases, the molecules get longer and longer. Light liquids give way to viscous liquids or oils. Oils become greases. Greases turn to waxes, which are weak solids. Weak solids become flexible solids. Flexible solids turn to rigid solids. Eventually, the molecules get so long that they become rigid and strong at room temperature. Figure 3-3 graphically portrays this sequence of changes.

MACROMOLECULES

The simplest plastic structure is polyethylene, a saturated hydrocarbon with the abbreviation PE. A common PE molecule contains approximately 1000 carbon atoms in its backbone, also called a carbon chain. Molecules of plastics materials are often called **macromolecules** because of their large size.

Although these molecules are very large, they cannot easily be seen. A common PE molecule is approximately 0.0025 mm stretched out. The thickness of a sheet of typing paper is about 0.076 mm. It would require 30 stretched-out molecules placed end to end to reach from the top side to the bottom side of the paper sheet.