# Chapter 4

Conversion of Raw Materials to Package Components

Once raw materials are produced, they must be converted into a useable form in order to create the structures and devices required for finished packages and other uses. This chapter will examine many of the processes used to convert raw resources described in Chapter 3 into packaging materials such as paper and corrugated board, plastics, glass, and metals, as well as some of the ways they are converted into finished packages.

Paper

Paper manufacturing dates back to the time of the Egyptians' use of papyrus reeds to produce relatively sophisticated sheets of papyrus for the production of documents and records. However, the papyrus sheets that were produced were not paper in any sense of the current material, in that the reeds were cut open and laid at right angles in progressive layers to form a thin, writeable sheet. Paper constructed from slurries of fibrous material dates back to 2nd century BCE in China where vegetable matter and cloth fibers were used to produce finer sheets of paper with randomly oriented fibers. Paper manufacture continued with sheets of paper being formed by dipping fibrous pulp onto rectangular straining screens of either cloth or wire, and being dried as single, relatively small sheets.

Modern paper manufacture has evolved from hand-dipped paper made of cloth fibers to the use of digested wood products that are cast as a continuous sheet (or *web*) using either Fourdrinier or cylinder machines, each of which has traditionally had distinct characteristics and advantages, although these have converged and blended as the industry has matured. Paper can be produced in sheets ranging from very thin tissues and onionskin to thick sheets of chipboard that may approach the thickness of home construction materials. The most common uses of paper-based materials in the packaging industry are for pouches, cards, cartons, and shipping containers; the latter two of these are often made of thicker carton board and corrugated board, respectively. Modern papers and paper-based materials can be produced to very consistent standards of manufacture, but paper itself is fundamentally a natural material and is influenced significantly by fiber length and environmental factors such as humidity and oxidation, as well as being time- and rate-dependent in its structural characteristics (Figure 4.1). Because of this, developing precise engineering equations for the design of paper-based structures remains elusive, and the use of paper materials remains something of an art.
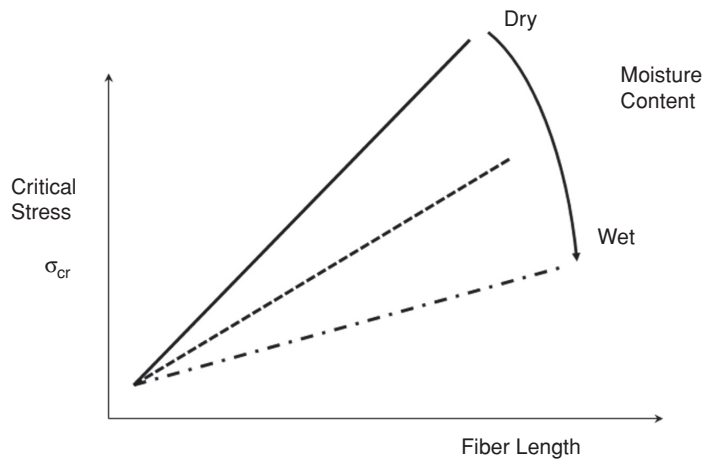
Figure 4.1. Relationship of Fiber Length, Moisture, and Strength in Paper

Cellulose Chemistry

The basic chemistry of the cellulosic plant materials, principally wood, that make up the raw material for paper manufacturing consists of three major components: cellulose, hemicelluloses, and lignin.

   Cellulose is a polysaccharide polymer of cellobiose that is produced from glucose by green plants, and will form itself into closely packed fibrils with a molecular length of 300–2,000 units (Figure 4.2). In plants, these are synthesized by *rosette terminal complexes*, structures containing the synthase enzymes that produce the cellulose chains. Cellulose provides a primary structural component of cell walls and as a strong, naturally occurring fiber is used both in nature and manufacturing for a wide variety of applications, from textiles to explosives. Because of the hydrogen bonding between adjacent chains in fibrils, it is also hygroscopic and susceptible to many water-dependent physical effects (Figure 4.3).

   Hemicelluloses are shorter-chain mixed polysaccharides that are usually somewhat alkali soluble and will assist bonding between cellulose fibers because of their ability to create water-based hydrogen bonding.
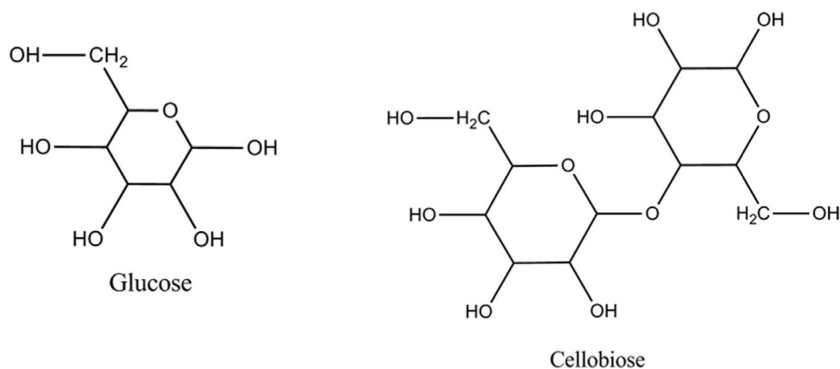
Figure 4.2. Glucose and Cellobiose, the Building Blocks of Cellulose
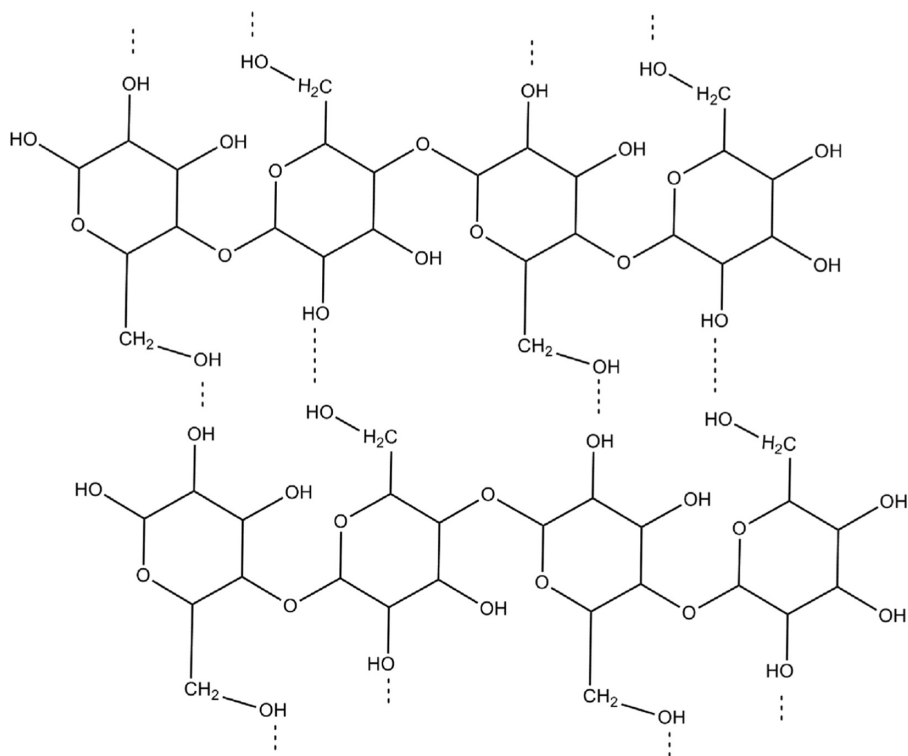
Figure 4.3. Interchain Hydrogen Bonding in Cellulose

Lignins are a class of heterogeneous biopolymers that constitute 25–35% of the mass of wood. These consist of a range of both compounds – typically, polymerized sugars and their derivatives – and polymer length. Because lignins, which are retained in mechanical pulp products like newsprint, can cause paper to yellow with age, their removal is important for the manufacture of high-quality paper. Lignins have a very high energy value and are often burned after extraction to power paper and pulp mills.

Chemical pulp manufacturing methods depend on the differential solubility of cellulose (which does not dissolve well in mild sodium hypochlorite or hydroxide solutions) and the lignin and some of the hemicelluloses that are dissolved in the chemical pulping process to disassociate the cellulose fibers for reforming into paper products.

Paper Manufacturing

The modern manufacture of paper in its most simplified form is simply the reduction of fibrous cellulosic materials, usually beginning as wood chips, to a water-based slurry of loose fiber by either mechanical or chemical methods, and then the reconstruction of the fibers into a dried, flattened mat of interwoven fibers, often several layers thick. The surface of the materials may be treated or coated to provide better printing surfaces, grease resistance, or *ovenability* (allowing it to be used for oven baking of foods at moderate temperatures).

The actual level of machinery implemented to economically mass-produce a consistent paper product may be enormous, requiring capital-intensive installations for production as well as the ability to handle large amounts of raw materials and to contend with wastewater treatment and other environmental issues.

Pulp Manufacturing

Pulp is produced in pulp mills that may be affiliated with a nearby paper manufacturing operation, although pulp can be shipped in bulk either by rail or ship to other manufacturing facilities depending on prevailing market conditions. This is done for many of the same reasons that iron ore is partially concentrated, then shipped to a fixed steel mill; it is less expensive to chip or pulp the product then ship that, than to construct a complete paper mill at each resource site. Because of this, an international trade in wood pulp has been created between timber-rich areas of the world and the processing plants of paper-consuming economies.

The first modern paper-manufacturing process was the mechanical grinding of wood fibers into a rough solution that could be cast into rough forms of paper. Modern manufacturing methods first automated this process, producing groundwood pulp (GW) with milling stones, and subsequently replacing it with thermomechanical pulp (TMP) processes that use heat and pressure to further soften the chips before the mechanically produced pulp is generated. This method has the advantage of using nearly all of the base fiber material in the paper pulp with a subsequent yield of 85–95% [1], and producing an absorbent paper well suited for printing because of the shredded cellulose fibers, but has the attendant disadvantage of having short fibers and not aging well due to the inclusion of lignins that are removed by chemical pulping methods. Chemical methods now produce the majority of paper fibers, but mechanical methods still produce roughly 10% of paper fiber. Other, less common types of pulp manufacturing that partially rely on mechanical pulping methods are refiner mechanical pulping (RMP) that is similar to simple GW except that rather than grinding logs or chips against a rotating stone, they are ground between a rotating stone and a fixed disk (stator), producing a stronger pulp from a wider variety of chipped fiber sources; and chemithermomechanical pulp (CTMP) systems that chemically pre-treat TMP source chips with various alkaline compounds as well as other agents at elevated temperatures to increase the fiber strength and bleach the fibers while retaining the lignins and keeping the process yield high.

Chemical methods rely primarily on the dissolution of the lignin and carbohydrate components that hold the desired cellulose fibers in place in order to free them into the slurry. The first of these dissolves hardwood fibers into an aqueous solution of sodium hydroxide and sodium carbonate to dissolve the lignins and related materials that hold cellulose fibers in place. This *soda* process is not commonly used, having been replaced by methods that can use softwoods and other less expensive sources of fiber, and produces a characteristically fine surface.

The *sulfate* process uses sodium hydroxide and sodium sulfide to produce a very strong mixture of hardwood and softwood fibers, commonly referred to as *kraft* paper, and in either natural or bleached-white form is the most commonly used sheet paper in the packaging industry. *Sulfite* processes use bisulfites and sulfuric acids in the same manner as the previous processes to produce an intermediate-strength paper that can be produced with a fine finish, although the residual acids cause it to degenerate over time. Archival papers are typically acid free for this reason, and are produced by other methods. Hybrid methods exist such as the semichemical pulps that rely on combinations of chemical, mechanical, and thermal treatments to produce

low-cost pulps that retain a great deal of lignin, and are therefore not as attractive as other applications.

An additional source of paper fibers is recycled materials that require much less effort to recover the fiber content, although the inclusion of non-paper materials (such as waxes, adhesives, and other contaminants) can be a problem in producing the final web of material. Additionally, several studies have shown that post-consumer materials such as carbonless paper chemicals and copy machine and laser printer toners will be retained in the pulp and may be transferred into food products [2]. Additionally, the increasing diversity of wood supplies has also introduced a concern with non-native wood sources introducing unknown microbial species, tastes, and odors to paper. Generally, a chemical de-inking process must be applied to remove inks that are then removed via air flocculation of the recycled fibers, and *sticky* contaminants that may clog subsequent equipment are removed via screening and centrifugation.

Once the basic slurry is formed, the fibers are beaten in an agitator to allow the cellulose fibers to be fully released, and to allow smaller fibrils to be liberated so that the final paper product has a high degree of fibril entanglement and the potential for hydrogen bonding in conjunction with water. At this point, several different pulps may be blended and other additives may be included to affect the strength and absorbency characteristics, optical properties, stiffness, and strength so that the final mixture, called furnish, has the proper qualities to produce the desired paper product.

Bleaching of the paper, to provide a bright surface, is typically done at this stage. Traditionally this had been done with chlorinated compounds, but concerns about residual organo-chlorine by-products, particularly polychlorinated biphenyls (PCBs), being released into the environment have caused the industry to adopt other methods such as hydrogen peroxide and ozone-based bleaching processes.

This mixture then is fed to forming machinery, all of which work on the basic principle of extracting the water from the furnish (pulp slurry) to form a finished product, although the means by which this is accomplished may vary.

Papermaking

Papermaking is based on pulp that is formed into a continuous thin sheet of interlocked cellulose fibers that can be further processed into a final paper product. The oldest continuous-production type of machinery is the Fourdrinier machine, which was supposed to have been invented by Louis Robert in France in 1798, but was introduced by the Fourdrinier brothers (for whom the machine is named) in England in the early 1800s, and was subsequently developed into a
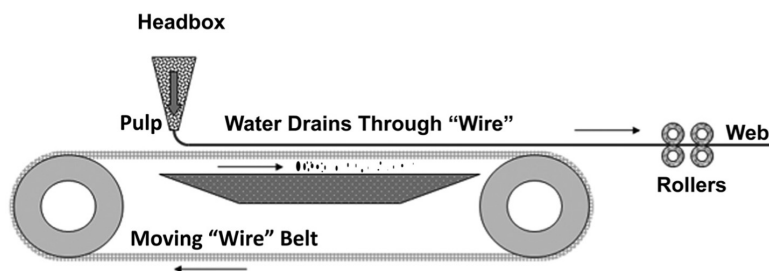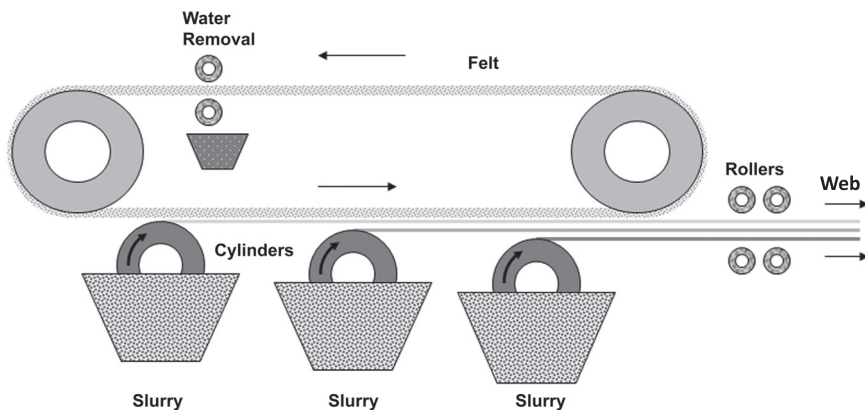

Figure 4.4. Schematic of Fourdrinier Papermaking Machine

large-scale production method. It is an automated extension of the old hand-dipped paper-making method in the sense that rather than dipping a mesh screen into a fiber slurry, the slurry is poured from a *headbox*, a reservoir with an adjustable slit allowing pulp to flow onto a continuously moving belt of metallic mesh (the *wire*), letting the water drain through the mesh (and through the fiber layer itself) to the point where it forms a continuous sheet that can be peeled from the belt and be further processed. Watermarks, if desired, are added by a dandy roll pressing the image into the paper web while it is still on or near the wire stage.

A modified version of this, the so-called *twin-wire* machine, has the slurry deposited at the convergence of two moving belts of wire mesh, which allows the web to be compressed between wires and dewatered more efficiently using gravity and suction. This method may be used for producing both paper and paperboard. To complicate things still further, multiply paper may be formed using a Fourdrinier-based machine that uses small Fourdrinier headbox and wire units to create individual plies that are then layered on a large wire to create thick-section papers and paperboard and avoid problems with the ability of the thick sections formed in a single machine to drain water properly.

The other major type of machine is the *cylinder machine* that was developed subsequent to Fourdrinier machine and relies on cylinders that pick up fibers from the slurry and deposit them in successive layers onto a *felt*, a moving belt of absorbent material, which is then covered with a second felt and pressed to remove the water. At that point, the web is sufficiently strong to be removed from the felt for further processing. Cylinder machines are constructed in one of several basic configurations, using either a cylinder mold former or rotary former to deposit paper fiber on the felt. The cylinder mold former lies in a flowing stream of slurry, and paper fibers are taken onto a rolling cylinder that has a slightly lower water level, creating a low-level suction to bond the fibers to the cylinder and then release them onto the felt. Rotary formers that were developed from the original cylinder designs have an inlet box on the surface of the roller before contact with the felt that allows drainage and suction to be used to dewater the pulp slurry more efficiently.

The significant difference between Fourdrinier machines and cylinder machines is the ease with which multiple layers may be added to provide thickness and specific properties to the finished material. Traditionally, Fourdrinier machines have only been able to provide a single layer of fibers, although the multiple-headbox machines have changed that somewhat. With

Figure 4.5. Schematic of Cylinder Papermaking Machine

each layer deposited by the Fourdrinier machine, drainage through the preceding layer becomes progressively more difficult, effectively limiting the number of layers that may be deposited. Similarly, cylinder machines were traditionally thought of as only being capable of producing thicker, coarse-grained papers, although subsequent developments have improved this as well. A cylinder machine can produce a paper or paperboard that has several layers of coarser or recycled materials sandwiched between outer layers of fine pulp to provide a strong, relatively inexpensive paper or board.

With either major type of process, once the web has been stripped from the wire or felt, it is fed through a succession of rollers in the press section to remove still more water and then to a dryer section that dries the stock using steam and hot air. At this point, the paper can be run through heated *calendaring* rolls that will form a glossy surface on the web by using slippage between a hot roller and the paper surface to iron a smooth surface into it before it is fed to a take-up reel. The surface finish can be tailored to the application by choosing whether to calendar a particular surface and the degree of slippage, heating, and pressure that are used if calendaring is chosen.

Paper Coatings and Additives

Paper may be coated, treated, or saturated with any number of materials depending on its final application. Sizing agents may be added to provide stiffness, strength, or resistance to absorption of inks, moisture, or oils and to add surface strength and resist fuzzing. Sizing is usually composed of rosin sizing or surface sizing. Rosin sizing, commonly used in most mass-produced paper, is an amphipathic (attracted to both fats and water) molecule that creates a hydrophobic surface by attaching its hydrophilic end to the paper structure. Surface or tub sizing is usually a glue or starch and is not common in mass-produced paper products.

Because many inks will wick along the fiber structures in paper and distort printed images, surface treatments of clay, chalk, or titanium dioxide can be added to fill pores and provide a non-directional, uniform printing surface for graphics reproduction. As a result, some glossy magazine papers have a substantial portion of their total weight from the clay coating needed for highly accurate graphics reproduction. Barrier coatings for resistance against moisture or gasses may be added if necessary, although truly gas-tight non-heat-sealed paper structures are rare because of gaps in their construction.

One of the most ubiquitous coatings of paper has historically been wax, to provide moisture and grease resistance, and although wax paper is still available for consumer use, it has been replaced in many applications by plastic film or plastic-coated paper. For extremely specialized use, coatings and additives to paper have been developed that involve microencapsulated inks for carbonless paper products, anti-counterfeiting features for currency, and even experimental uses of paper-based, printed flexible electronics. Printing processes and adhesives will both be discussed in more detail in Chapter 5.

Paper Properties

Commercial paper products are universally anisotropic (exhibiting different characteristics along different axes of reference) because of their methods of manufacture. The layering of fibers or straining of fibers through underlying materials dictates that, to some degree, there will be an increase of fiber length through the cross-section of the material, and the motion of the felt or wire will produce a predominant orientation of the cellulose fibers in that direction of travel.
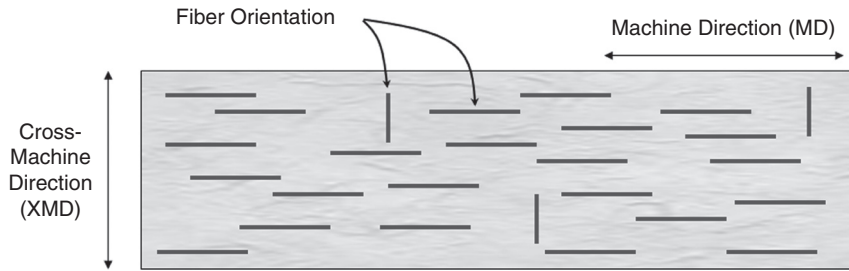
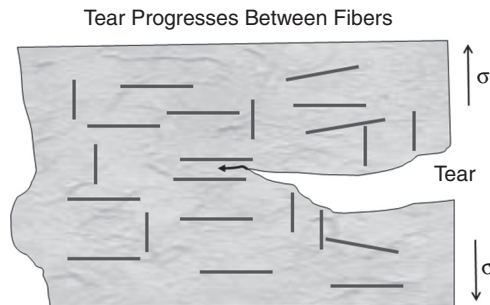**Figure 4.6.** Machine and Cross-Machine Directions in Paper

This orientation – the *machine direction* – is important because it dictates how the paper will behave when stressed and the mechanical changes that occur as a result of moisture (Figure 4.6).

Additionally, because the cellulose used in paper is a naturally occurring hygroscopic, viscoelastic material, the effects of stress and strain may be dependent on time, temperature, humidity, rate of loading, and the amount of time that a load is applied. This makes the mathematical prediction of properties beyond general estimations very difficult, particularly where extremes of humidity begin to radically affect the fundamental nature of the paper chemistry.
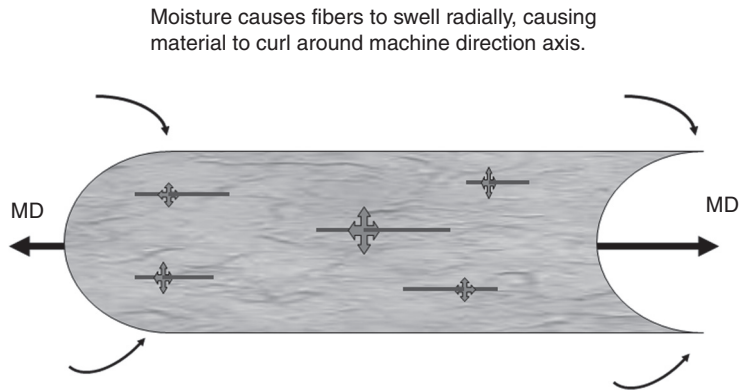
Machine Direction Effects

The orientation of paper fibers in the direction of wire or felt travel carries over into the finished material in that the paper will tear preferentially along the direction that the majority of fibers are laid down because a tear will require less energy to separate fibers from one another – in the machine direction – than it will to break the fibers off in the *cross-machine direction*. This has the effect of making highly oriented papers, such as those used in the printing of newspapers, easy to tear in one direction (usually from top to bottom) and nearly impossible to tear in a straight line at right angles to that direction (Figure 4.7).

The effects of moisture on the hygroscopic cellulose fibers will also reflect the orientation of the fibers. Cellulose fibers tend to swell or contract along their diameter rather than lengthwise in response to changes in moisture, and the predominance of machine direction fiber orientation can result in paper curling around or buckling along the axis of orientation as the fibers swell when one side is wetted, or when one side is constrained by being laminated to a non-paper material

Figure 4.7. Tearing and Machine Direction in Paper

Moisture causes fibers to swell radially, causing
material to curl around machine direction axis.

MD   MD

Figure 4.8. Moisture Effects and Machine Direction in Paper

(Figure 4.8). This may cause problems in high-speed packaging lines in wet environments such as food-processing plants and photography operations.

Specialty Papers

Glassine and Greaseproof Papers are produced by the extensive mechanical beating of the pulp, and are often not grease- or moisture-proof in and of themselves, but are used as a substrate that may be coated with water- or grease-proofing. Parchments are fully formed papers that have been re-digested by passing them through an acid bath that causes the surface cellulosic materials to fill the gaps in the paper, and provide a material that has a very smooth surface, is very strong when wet, and resists high temperatures well.

Synthetic "papers" such as Tyvek® and related materials are discussed more fully in the chapter on polymers, as they are compounded of polymeric fibers but are often used where extreme strength and durability are necessary. The most commonly visible use for synthetic papers is for express shipping envelopes, but they are often used to carry and ship sharp objects or to produce a reusable consumer package at low cost; they are also commonly used as a water-permeable draft barriers in home insulation systems.

Paperboard

Paperboard, defined as a paper material thicker than approximately 0.25-0.30 mm (0.010–0.012 in.), depending on local standards, is almost universally produced on cylinder-type machines or the multiple-pass Fourdrinier machines previously described. It may be produced in grades ranging from chipboard made of recycled and low-grade fibers and lined paperboard that may have one or two surfaces of high-grade paper fibers or clay coating to sulphate boards that are made completely of highly treated fibers. These provide good strength, excellent food contact surfaces, and, when bleached, a completely white structure that provides a high-quality appearance to the board. Because paperboard is constructed of several plies of material, the nature of the plies and their interlayer bonding will have an effect on the final mechanical properties of the finished board. Additionally, as the bending of board stresses the surface layers more than the interior, the surface plies of the paperboard should be made of a stronger pulp

to stiffen it. The compromise is that in the fabrication of finished packages, paperboard cartons often are required to fold without surface cracking that will reduce or destroy the strength of the carton. Backing cards, die-cut liners, and other structures that may form by interlocking or remaining rigid may be made of much more brittle material because these structures do not flex extensively in use.

Molded Pulp Packaging

Molded pulp is formed directly from pulp that is poured through a three-dimensional mold screen, leaving a paper-fiber-based molding that is increasingly used as a substitute for expanded foams and thermoformed sheets in many segments of packaging. Molded pulp is an extension of the paper-making process that can produce intricate moldings that range from rough carton fitments to thermoformed pulp structures that are somewhat similar to those produced by thermoforming sheet and foamed plastics and are becoming more competitive based on their recyclability and cost.

The most familiar molded pulp item for most consumers is the food tray that many fast-food and coffee shops use to carry several cups at once, although they are often used in the food industry as separators for fresh fruit and specialty display items (Figure 4.9). The consumer electronics and computer industries have led the development of even more complex molded pulp packing caps to replace those made of expanded polystyrene and other types of plastics, to permit easier recycling of materials and the use of recycled paper in the formation of the molding.

Molded pulp is formed by applying pulp in suspension, either by pouring or dipping, to a screen that carries a three-dimensional shape corresponding to the shape required in the final molding. Typically the *screen side*, with its smooth finish, is designed to be the side in contact with the product so that loose fibers from the non-screen side do not come loose onto the

Figure 4.9. Molded Pulp Bottle Holder
Source: Enviropak, with Permission

product. The pulp may be dyed to correspond with a particular design scheme or to mask the color variation that occurs with the use of recycled pulp in the molding.

Newer types of thermoformed pulp molding are available that rival thermoformed plastic sheet in appearance but offer easy recyclability for consumer items at the cost of low moisture resistance.
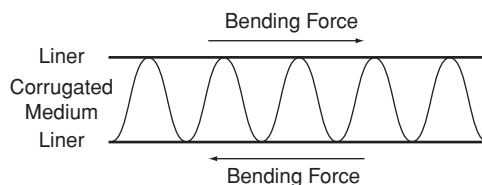
Corrugated Board

Corrugated board is commonly called *cardboard*, even though true cardboard, used for making display and playing cards, is actually a paperboard product. It is typically formed from three or more layers of either cylinder or Fourdrinier paper that form two *liners* and a crenulated *medium* layer that spaces the liners and makes the liner boards absorb bending stress in a manner similar to the web of an I-beam forcing the top and bottom plate to absorb a structural bending load (Figure 4.10).

Corrugated board can be produced in any number of thickness and layers of material ranging from the simple corrugated *medium* used as packing (and that was the hat band material that was the origin of corrugated board) and single-faced board often used as an underlayment for pastry and pizza to single and multiwall boards for more structurally demanding operations. Moreover, the thickness and spacing of the flutes can be configured for different applications ranging from the ubiquitous "C" flute to specialty grades. A common example of specialty corrugated board are the thin, very high flute count varieties that are used to form corrugated sandwich boxes for the fast-food industry, replacing difficult-to-recycle foam clamshell containers. Fine grades of corrugated board are often produced with printed copy as one of the outer liners, or laminated to the liner, producing a nearly flat surface for good graphics reproduction in the electronics and consumer appliance industry and for some types of higher-volume food containers.

Fabrication of Paper-Based Packages

Because of the incredible variety of paper containers, there is not enough space in this volume to describe the design and manufacture of all available types, but in general, paperboard containers are die-cut after printing (corrugated board may be cut and then printed, depending on the application) using either a rotary or platen-based cutting die; a factory seam is joined either with glue or, in the case of large corrugated cases, stitching – semi-automatic stapling – may be used to allow the carton to be erected into a rectangular shape on a packaging line, and it will typically have some type of end flaps that either interlock or are sealed to close the package. The specific parts of a paperboard folding carton are shown in Figure 4.11. These are typically shipped in stacks, ready to be used in the manufacturer's packaging line. Small folding cartons may be supplied in overwrapped stacks to ease placement in cartoning machine's feed magazines.

Figure 4.10. Corrugated Construction and Reaction to Bending
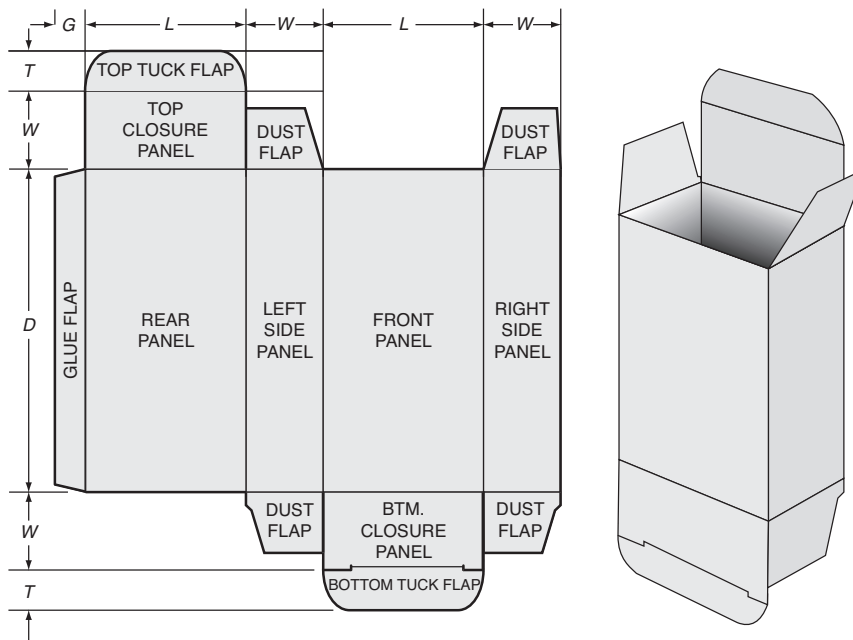
Figure 4.11. Parts of a Folding Carton
Source: Paperboard Packaging Council, with Permission

Cylindrical and rounded paper containers such as tubs and cups are typically wound on a shaped mandrel from tapered blanks, with a bottom seamed in during manufacturing, whereas paper-based cans are manufactured by producing a continuous winding on a mandrel, sectioning it, and seaming on the ends. In many cases where these are obtained from outside suppliers, these are tapered slightly so that they will nest, conserving shipping space while empty.

Paper sacks, as distinct from pouches, which are typically formed in form-fill-seal machinery described elsewhere, are still used as multiwall structures for large-scale shipping of materials such as grains, pet foods, food ingredients, and building materials, as well as for some types of food products in smaller quantities. These are described in more detail in Chapter 9.

Paper cartons for liquid products are similar in design to folding cartons used in other applications, but are sealed to prevent leakage. Although these were originally manufactured from waxed paperboard, this has almost universally been replaced by polymer coatings. Additionally, multilayer cartons and carton-like structures are laminated for use with extended shelf-life products ranging from refrigerated fruit juices to aseptically packaged foods.

In general, the design requirements for the physical structure of a paper-based package are straightforward. The package must be appealing to the consumer and be strong enough for use; it must protect the product (usually contained in a primary package inside the container) and must be easily handled and erected during production.

Strength of Cartons and Containers

The strength considerations for cartons and containers are almost always related to stacking strength. Folding cartons typically do not support enormous layers of product stacked

on top of them, but corrugated shipping containers must often support many times their own filled weight during shipping and handling. The stacking strength of corrugated containers may be predicted by one of several means. Historically, the McKee formula – a semi-empirical formula developed at the Institute for Paper Science and Technology in 1963 and subsequently modified to improve accuracy – uses the edge-crush strength of the corrugated board as well as the buckling mechanics of plates to estimate the final strength of the board (Equation 4.1) [3]:

$$P = 1.014(P_m)^{0.746}(D_x \cdot D_y)^{0.127} \left(\Sigma \, (W)^{0.492} \right) \left(1.593 \, (d)^{-0.236} \right) \tag{4.1}$$

P: Box Compression, lb_f
P_m: Edge Crush Test Strength, lb_f/in
D_x: Machine Direction Flexural Stiffness, $in - lb_f$
D_y: Cross-Machine Direction Flexural Stiffness, $in - lb_f$
W: Width of each panel, in
d: box depth, in

Other methods, based on finite element simulations, have been implemented, but they all depend on a large number of parameter inputs from the base material. These are all estimates at best, given that paper is a somewhat variable material that will change properties with age, temperature, and humidity, among other factors. Additionally, the effects of box additions such as handholds and internal dividers are not considered in this model, nor were a large variety of box types used for the experimental work. Whereas a robust shipping carton may perform well when first filled, the time-dependent properties of paper may cause a carton stack to deform or collapse. This can be aggravated by high humidity conditions and cyclic loading during use, which argues for a substantial *safety factor* in design, often several hundred percent [4]. ASTM D5639/D5639M–09 lists safety factors between 150% and 800% for stacks of single-product items depending on their weight, whereas the amount of load supported by the product and environmental factors while single-package shipments in the mixed-shipment express delivery environment have been shown to require safety factors of up to 370% [5, 6]. Because stronger boxes use more material and are more expensive, the final design is always a balance between strength and cost, with better solutions sometimes evolving out of structural design or the ability to pass some of the stacking load onto secondary containers in the package when possible. For example, glass jars or steel cans do not require a shipping carton at all and are often shrink-wrapped in unitizing trays, because the high stacking loads will be borne by the primary containers themselves. Fresh fruit, by contrast, cannot bear any of the load, and most fruit-shipping containers are extremely robust for this reason. Given the severe environmental variation and mechanical input experienced during shipping, it is prudent to follow up shipping container designs with damage assessments to determine the optimal level of strength and cost for a particular application.

Glass

Glasses are a class of material formed by the fusion of materials, usually silicate minerals, and having little or no discernable grain structure. Naturally occurring glass, Lechatelierite (obsidian) and Fulgurite, are formed by volcanoes or lightning strikes in sand, respectively, but

the most common connotation of glass is the hard, artificially formed material that is molded into objects or cast into sheets for windows. Glass is one of the oldest synthetic materials known, after fired pottery (which is seldom used for commercially processed food). Phoenician merchants transporting stone in the region that is now Syria in approximately 5000 BCE were reported to have discovered glass. Pliny, the Elder wrote of merchants who rested cooking pots on blocks of nitrate placed by fires. The intense heat of the fire eventually melted the blocks and mixed with the sand of the beach to form an opaque liquid glass. As glassmaking progressed over the next 7,000 years, the items that were manufactured went from simple opaque beads to exquisite pieces of art glass from the renaissance and on to the durable and attractive implements and packages that we use every day.

Glass beads and glassy glazes on potshards date back to approximately 3500 BCE, and the first pieces of glass containers date back to approximately 1600 BCE. The Egyptians were credited with the first large-scale craft glass production, with little changing until the development of glass blowing in Syria around 20 BCE. Industrial glass manufacturing remains dating from the 4th century BCE have been found in Beth She'Arim near Galilee and indicate that glass was made in large slabs, broken up, and shipped for reworking by artisans, simplifying the manufacturing process for local markets. From this, glassworking showed a slow progression of technical knowledge in formulation, kiln design, and production methods until the mid-1800s when glass was hand-blown into closed metal molds.

An American engineer, Michael Owens, developed the first practical automatic bottle-blowing machine in 1903. By the year 1920, there were around 200 automatic Owens Libby Suction Blow machines in operation in the United States. Adoption in Europe was somewhat slower, but soon displaced manual labor in all but crafts production.

Today, modern bottle-making machinery is accurately producing glassware that is thinner and lighter than in previous years, and is aimed at preserving a market that is increasingly being taken over by lighter, more durable, and less dangerous plastic containers. The conversion from press-and-blow to blow-and-blow technology, as well as multiple station blowers, is making glass a continuing competitor for upscale products and specialty items such as alcoholic beverages, cosmetics, sauces, and oils, particularly where glass's perceived quality adds marketing leverage.

Better understanding of the structural and thermal nature of glass itself, combined with the ability to do advanced computational structural modeling relatively inexpensively, and highly automated production facilities have combined to pare production costs of glass to an absolute minimum. Although glass excels in clarity, strength (though not toughness), recyclability, and dimensional stability, it suffers from problems with high energy cost, high weight, extreme impact fragility, and the attendant injury liability. Most glass-manufacturing facilities use natural gas to provide heat both to the glass kiln and to ancillary heating operations such as the annealing lehr and various heat-treatment stations. This puts the glassmaking industry directly at risk from fluctuating prices and supplies of natural gas, with the attendant marketing uncertainties that can result from this.

One of the greatest non-energy factors that affects the glass industry is the initiation of container return policies – a reusable glass bottle can replace approximately 12 disposable ones during its service life – so the increased number of bottle bills in the United States has caused a reduction in the number of glass-producing facilities. This has political consequences since the loss of jobs has to be considered against the environmental benefits. As a result, the glass container industry is a large contributor to efforts to lobby against bottle return legislation as discussed in Chapter 11.
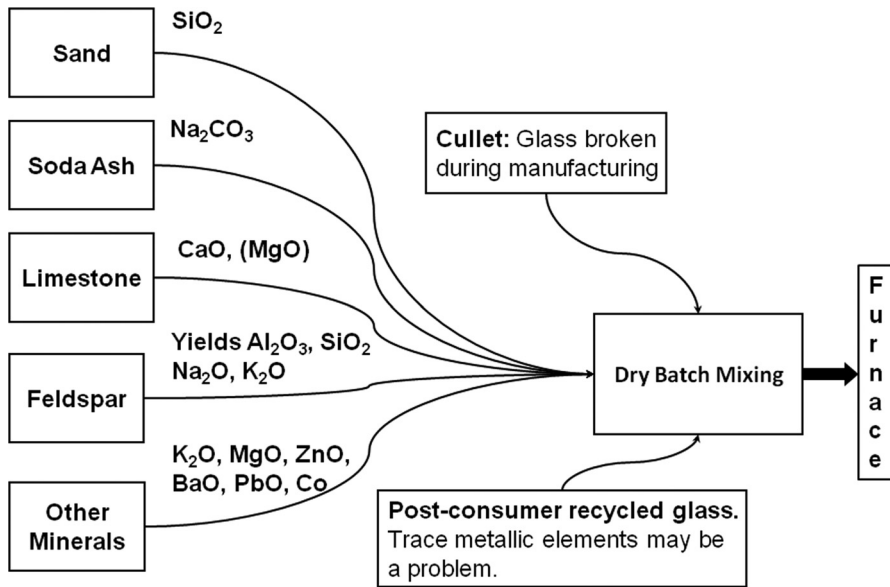
Figure 4.12. Glass Compounding

Glass Formulation

Glass at its most simple is a mixture of silicate sand, usually from beaches, lime rendered from limestone and soda ash, that is heated above the melting point of silica (ca. 1,610°C) to produce *Soda-Lime* glass. This is typically mixed with *cullet* – broken glass either from recycling operations or from within the production line – and then melted with other trace elements to affect the clarity, color, refractive index, or strength of glass (Figure 4.12).

Types of glass sand are usually classified according to purity and trace mineral content. Glass sands that have a mineral composition close to that needed to produce a particular color of glass are highly prized by the glass industry provided it can be transported economically. There has been some debate over the mining of glass sand from beaches and desert environments, although there is no known incident of glass plant closure from these concerns. Mineral additives are included, usually in small quantities, to change the color or strength characteristics of the glass melt as shown in Table 4.1.

Manufacturing Methods

Modern manufacturing methods create a nonstop stream of materials from a raw mineral and energy feedstock to finished containers, making glass unique in that the materials are not held at an intermediate state as with plastic resins, metal sheets and foils, and paper rolls and sheets. The capital costs of production and the specialized nature of the materials makes a modern glass plant an almost completely automated, non-stop production process that handles thousands of pounds of glass per day, as shown in Figure 4.13.

The first step in producing glass is to melt the components of the glass that have been added to charge the glass furnace, and to heat them to approximately 1,500°C. This produces a homogenous melt that is allowed to degas and for impurities to stratify in the mix. The melt then

Table 4.1. Chemical Ingredients Used in Glassmaking

Type of Component	Chemical Composition	Purpose
Antimony oxide	Sb_2O_3	Yellow colorant
Aragonite	$CaCO_3$	Calcium source
Boron	Bo	Produces high-strength borosilicate glass (Pyrex®)
Cadmium sulfide	CdS	Red colorant
Calcium fluoride	CaF_2	Produces opalescent glass
Carbon/Sulfur	C, S	Grey and amber colorants
Chromic oxide	CrO_2	Yellowish-green colorant
Chromic oxide	CrO_2	Green colorant
Cobalt oxide	CoO	Deep-blue colorant
Copper oxides	CuO_2, Cu_2O_3,	Red colorant
Cullet	Broken/recycled glass	Recycled component
Feldspar	$KAlSi_3O_8$ - $CaAlSi_3O_8$	Sodium, potassium source
Ferrous sulphate	FeS_2	Green colorant
Iron oxide	FeO_2	Yellow colorant. Will produce opaque black glass when used in large amounts.
Lead	Pb	Changes refractive index for crystal manufacture
Manganese	Mn	Violet colorant
Silica	SiO_2	Major constituent
Soda ash	Na_2CO_3	Sodium source

travels through an arched *throat* that allows only the molten glass to pass underneath, and then through a refiner and a forehearth stage to cool the melt from a fully liquid melt to a plastic state (ca. $1,000°C$–$1,200°C$) where it can be molded. A *gob* – a small cylinder of hot, pliable glass – is extruded from the bottom of the glass kiln, picked up by automated handling equipment and delivered to a molding system.
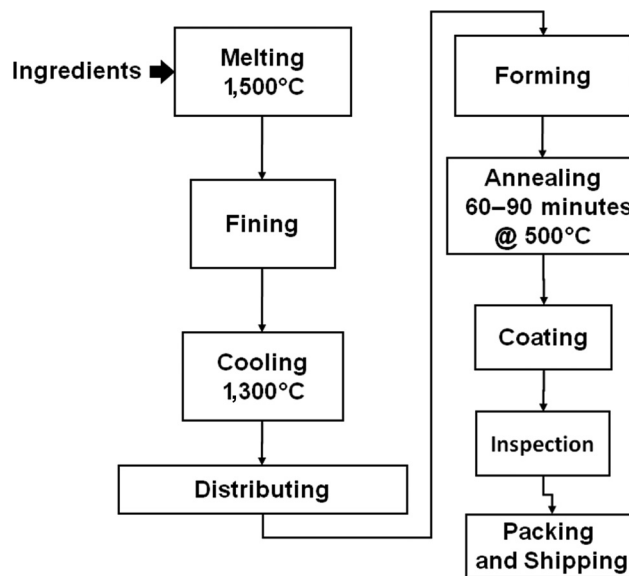
Figure 4.13. Glass Manufacturing

Types of Molding Systems

Glass molding of containers operate by a very similar method. The molten glass gob is initially molded into a *parison*, an intermediate molding that includes a precision mold of the finish to ensure proper closing, and a *transfer bead*, a small ring just under the finish on the bottle to facilitate handling of the container. The parison is then usually inflated with compressed air inside a second mold to form the body of the container. The exception is the *press molding*, which uses simple mechanical pressure to form glass items such as lens blanks, and is seldom used in package manufacturing. Molds are usually coated with high-temperature release agents to help prevent the molded piece from adhering to the hot mold surface. This basic blow-molding method has subsequently been carried over into the manufacture of plastic containers with few changes other than the method of parison formation and the much lower temperatures needed to operate the machinery.

The two principal types of glass molding systems are *press-and-blow* systems, which use mechanical compression in an inverted mold to force the molten gob into a parison mold before blowing into a finished container, and a *blow-and-blow* method, which uses compressed air to form the preliminary parison molding in an inverted mold before it is transferred to the final blowing stage. In the final blowing stage, compressed air forces the walls of the formed parison outward so that it conforms to the inner walls of the mold surface. Because of the highly viscous nature of glass, even the most carefully controlled processes may show some thickness variation, though this has been controlled much more effectively using newer manufacturing techniques.

Bottles are removed from the mold using the transfer bead with a fork-shaped handling device to move the still-hot container, and then the finished moldings are transferred to an annealing belt.

Once the container is blow-molded, it must be *annealed* – allowed to cool slowly so that residual stress will not cause the bottle to shatter. Before this process was understood, production facilities would simply allow containers and moldings to cool and ship the ones that did not break – hardly an efficient method. This involved a huge loss of product, as well as danger to workers and customers, that have been reduced since the annealing processes have been implemented. Currently, glass bottles are allowed to cool on a slow, continuously moving belt in a zone-controlled oven that moves the containers through a hot zone, heating them to approximately 1,300°C, to lower the viscosity to approximately 10^{13} Poise, and holding them at that temperature for several minutes, cooling the containers slowly to approximately 1,000°C over several minutes, and then rapidly cooling them to room temperature. The whole annealing and cooling process will usually take a total of 30 to 60-plus minutes for mass-produced moldings.

Surface Treatment of Glass Containers

Glass containers are usually treated with an exterior surface coating of material to reduce friction and scratching during handling, so that stress concentration areas are not formed on the bottle. Typically, there are two sets of coatings that are applied. The first, a *hot end* coating, is a coating of tin or titanium that condenses into a monomolecular layer on the surface of the glass and improves the adhesion of the second coating. The second, *cold end* (a relative term considering that the containers are still between 70°C and 170°C) coating, is usually a fine coat of oil and/or polymer applied at the "cool" end of the annealing lehr and provides a lubricating action between the bottles as they are handled in production lines. Historically, these coatings included soaps, waxes, stearates, silicones, glycerides, oleic acid, and polyethylene compounds. Few of

these are still in use because of restrictions on amounts that may be contained in foods as noted below, and silicones were eliminated because of their effect on label adhesives. Polyethylene and oleic acid, both relatively inert and often present in food from other sources, have remained as coatings applied as an emulsion and vapor, respectively. Oleic acid has the advantage of being easily removed in washing and being able to label with dextrin glues, whereas polyethylene is more durable [7]. Because these coatings are sprayed on open containers, it is inevitable that some of the coating gets into the container, and thus into the product contained inside. Thus, there are strict limits to the amount of certain types of bottle lubricants that may be contained in the product as indirect food additives:

> (1) From a coating intended for or employed as a component of a container not to exceed 1 gallon and intended for one-time use, not to exceed 0.5 milligram per square inch nor to exceed that amount as milligrams per square inch that would equal 0.005 percent of the water capacity of the container, in milligrams, divided by the area of the food-contact surface of the container in square inches. From a fabricated container conforming with the description in this paragraph (c)(1), the extractives shall not exceed 0.5 milligram per square inch of food-contact surface nor exceed 50 parts per million of the water capacity of the container as determined by the methods provided in paragraph (e) of this section.
>
>   (2) From a coating intended for or employed as a component of a container having a capacity in excess of 1 gallon and intended for one-time use, not to exceed 1.8 milligrams per square inch nor to exceed that amount as milligrams per square inch that would equal 0.005 percent of the water capacity of the container in milligrams, divided by the area of the food-contact surface of the container in square inches.
>
> <div align="right">(CFR21 § 175.300 (xxxvii)(c)(1,2)) [8]</div>

Increasingly, labels, sleeves, shrink-fit covers, and other bottle decorations are supplementing or replacing these exterior coatings, providing a contact slip material to reduce or eliminate scuffing from contact between containers.

Inspection and Cartoning

Inspection of finished glass containers was done entirely by human inspectors, but the problems of visual fatigue, increasing line speeds, and increasingly tight production tolerances drove the glass industry to be one of the pioneers in automatic visual and acoustic inspection of containers. Containers now travel through light boxes that provide the containers with a diffuse light source that highlights defects for inspection cameras that use computers to highlight defective containers and remove them from the production line. Acoustic testing uses an acoustic transducer to inject specific frequencies of acoustic vibration into the finished container and then sense if frequencies characteristic of mechanical flaws are present in the finished container. This is combined with data taken from the raised-bump heel codes on the bottom of the containers to correlate defect data during production. Even with all of the careful control of the manufacturing processes, 10–15% of glass containers may be recycled as cullet in any given production run.

Decoration, Labeling, and Shipping

Once past inspection, the finished containers may be pre-labeled for a particular customer, other decorations may be added, and the combination is usually packaged for shipment to filling lines in re-shipper cases that are pre-printed with the customer's product information, because it makes little sense to unpack them from one carton, fill them, and then pack them back into another. For this reason, filling lines that use glass containers handle both empty containers and

empty cases automatically, reinserting the filled containers into the re-shippers, so that there is little carton waste.

Failure in Glass Containers

Glass has many advantages, as previously described, but although an extremely strong material, it is also brittle in that it does not undergo plastic deformation before failure, and it is not a tough material that can absorb a great deal of energy before failure. The basic mechanics of glass failure are usually associated with various types of brittle fracture covered more extensively in Chapter 2. The material failure will begin at a stress concentration point, typically a material defect or a damaged area such as a surface scratch, or at an abrupt change in geometry of the molding. Once the failure point is established, the crack will focus the tensile force in the material and will continue to travel through the material – often at the speed of sound – until the stress is relieved or until the crack travels completely through the materials. Recent research has shown that although glass appears to fail in a manner different from other brittle materials, such as steel, the failure mechanism is very similar, with nanoscale voids opening in the material just ahead of the progressing crack tip, with effects accentuated in pressurized bottles [9].

The stress in a cylinder created by pressure can be estimated as shown in Equation 4.2:

$$\sigma_{\text{Circumferential}} = \frac{Pr}{t}$$
$$\sigma_{\text{Longitudinal}} = \frac{Pr}{2t} \tag{4.2}$$

P: Pressure differential across cylinder wall, Pa
r: radius of cylinder, m
t: wall thickness, m

Unfortunately, few glass containers are truly cylindrical in nature, particularly at the ends, which means that this estimation will not give accurate answers, particularly for complex configurations. Computer simulations have given better answers for complex molding using soda-lime glass and have shown that the maximum stress when highly pressurized is at the edge of the base of the bottle. Further tests showed that increasing internal pressure increased the crack density in failed containers, resulting in smaller fragmented pieces with the potential for wider distribution from hydraulic and pneumatic explosion during failure [10].

Thus, the stress concentration in a piece of glass can be increased many times by the addition of a single shallow, sharp scratch. This fact is exploited in the manufacture of sheet glass and in the making of art glass projects where the article is scored, then stressed to break off the required pieces. In glass containers, however, the effect may be quite destructive, causing breakage or explosion of pressurized containers. To prevent damage from occurring in glass containers, contact areas are often reinforced with extra material in *shock bands* and may be textured to avoid formation of stress concentration points.

General failure conditions in glass containers are usually a result of thermal, impact, or hydrodynamic (*water hammer*) stresses that provide enough energy to promote failure at defect

Figure 4.14.   Thermal Failure in Glass Bottle

sites and section thickness changes, and eventually to cause breakage in a well-formed and well-designed container.

Thermal Failure

Glass containers that are subjected to thermal stress in processing, distribution, or use may develop extreme stress areas due to the differential expansion and contraction. Because glass is both a poor heat conductor and a brittle material, moderate temperature changes, mild surface damage, included defects, or section thickness changes can cause an abrupt failure of the container. This may manifest itself, for example, as a container with a thick bottom section and a thin sidewall losing the bottom as an intact piece as the failure progresses circumferentially around the base's transition from thick to thin sections, as shown in Figures 4.14 and 4.15.

Significant advances have been made in the numerical modeling of glass containers to reduce or eliminate problems of post-manufacture thermal stress. Additionally, the trend toward thinner and lighter glass containers has been beneficial in that it promotes more uniform heat conduction throughout the container, reducing the failure rate.
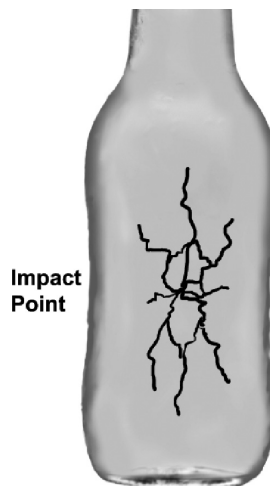
Impact Fracture

As anyone who's accidentally thrown a ball through a window knows, glass does not have the ability to deform extensively before exceeding the critical stress in the materials. In the case of glass packaging, the nature of the impact fracture is often critical both in understanding the failure mode of the materials and, all too often, in dealing with the legal disputes that may follow the actual damage caused by the fracture. Usually the pieces of a glass container can be carefully reassembled to discover the point of impact that caused the original fracture (Figure 4.16), and any subsequent factors such as internal pressurization that may have accelerated the failure.

It is often important to decide whether the container failed from impact or from internal pressure. A clue that may be useful in this is the nature of the fracture surface itself. When one

Figure 4.15. Thermal Failure at Section Thickness Changes

examines the edge of the fractured piece at the impact point (Figure 4.16), there will be surface features such as hackling that are indicative of the point of maximum stress at failure (on the inside for a pressure failure, and on the outside for an impact failure), and often can indicate its magnitude as well via measurement of the *mirror* and *mist* regions, as shown in Figure 4.17, and the application of fractographic analysis.

Figure 4.16. Bottle Impact Failure
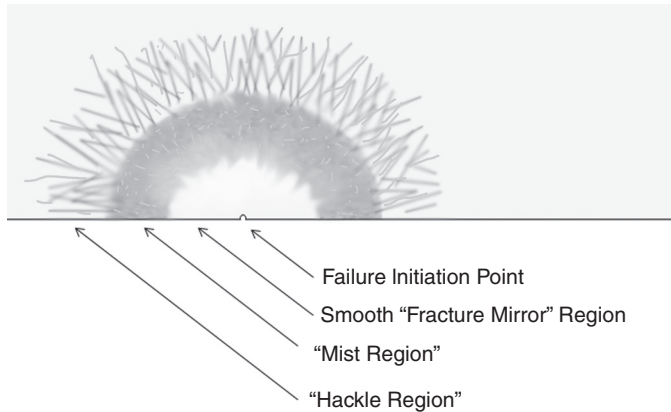
Figure 4.17. Fracture Features at Point of Failure in Brittle Materials

Water Hammer Effect

Sudden movement, particularly a small drop, of a container full of liquid or semiliquid materials can cause a catastrophic pressure failure in glass containers. This has been described as water hammer failure, which is usually the resultant inertial effect of suddenly stopping a flow of fluid, with its resulting shock. True water hammer failures involve fluids with a great deal of kinetic energy, whereas packaged fluids do not exhibit instantaneous flow when subjected to shock. Water hammer failures in packages are more likely hydrodynamic surge effects, occurring most usually around the bottom circumference of the container. These often have a distinctive appearance, as the pressure transient will "blow out" the sidewall of the container radially around the base, as shown in Figure 4.18, most likely from the pulse of hydrostatic pressure that travels through the fluid as the container is subjected to shock. Fluid viscosity will

Figure 4.18. Water Hammer Failure in Glass Bottle

affect the likelihood of failure, with less viscous fluids being more likely to contribute to failure, although the non-linear fluids that comprise many of the food products in glass containers may complicate this by sudden shifts in viscosity as shear-thinning or initial stress levels are overcome. This type of failure is distinctly different from failures due to thermal stress because thermal stress failures around the bottom of a container often will have only a single fracture line that propagates under internal stress rather than the distinctive shattering around the base.

Design Considerations for Glass Containers

Glass container structural design is an important consideration if glass is to be used in the production of a packaged product. Because of the enormous costs involved in producing glass molds and creating a glass production run, it is common to have a single type of glass container used with a broad variety of different labels to produce an entire product line packaged in the same container, thus reducing inventory costs. The basic considerations that one must incorporate into the structural design of a glass container – neglecting the esthetic considerations – are light weight, strength, and stability. A container whose shape causes it to tip over easily or wedge tightly in a production system will be difficult and expensive to produce, and may show the same faults when in use by the consumer.

Containers must be adapted to the type of product they contain. Liquid products may need smaller necks for dispensing than heavy, viscous, or semisolid materials, and the amount of headspace must be determined as well. Shape and color may be of critical importance to selling the product, but a particular shape may prove very difficult to produce because of the difficulty of molding glass in some configurations, and once produced may be difficult to integrate into a filling line. The design of the finish area of the container that accepts the closure that seals the container may be of critical importance in maintaining product integrity. Since glass is relatively impermeable to all gasses except hydrogen, it is an excellent barrier when hermetically sealed. Unfortunately, the production of high-accuracy moldings on the finish segment of the bottle is complicated by the viscous nature of glass (which impedes flow into fine mold cavities) and the very high mold temperature, which makes easily machined mold materials such as aluminum unusable and maintaining mold tolerances more difficult. This, in turn, leads to problems in producing a high-accuracy fit between the finish and the closure, requiring the use of flexible lid liner materials to seal the container. Compression force from the vacuum in thermally processed foods also increases the friction of these materials against the finish, contributing to difficulty in opening glass containers with large closures, such as jams and jellies.

Closures are discussed more fully in Chapter 5, but it is critical that the closure match both the dimensions and the thread type of the container's finished, as the shallow, easily molded threads on glass containers may be different than those on plastic containers of the same size, and mismatching can then cause jamming or leakage.

Metal Packaging Materials

Metal containers have nearly always been an integral part of mass-produced food packaging, and represent an improvement over the fragility of the glass wine bottles originally used for "canning" processes developed by the French. The lack of a substantial glass-blowing industry (vital to the French wine industry) in England left the British military looking for a suitably competitive container for the preservation of military rations after French demonstrations of

long-term food storage on Caribbean voyages in the early 1800s. The burgeoning industrial revolution in Britain, with its substantial iron and steel works, provided an answer in the form of thin steel plate, coated with Cornish tin, that could be used to form a sealed food container that would be quite durable. Initial products were hand-formed and soldered, filled, and then cooked, with production speeds being very slow (a good craftsman could produce 60 cans per day). The presence of lead-based solder, the absence of practical knowledge of the microbiology of spoilage, and the absence of regulations regarding food content led to some spectacular cases of food poisoning.

One of the substantial causes of non-battlefield death in the American Civil War, the Crimean War, and other conflicts of the era was poisoning from preservatives, such as formaldehyde, included in meat products by unscrupulous manufacturers. This level of poisoning continued until the effects of inadequate thermal processing and heavy metal toxicity were understood and inappropriate additives were banned many decades later.

Changes in fabrication techniques have replaced soldered seams with welded ones, processing conditions are now very well understood, and toxic additives have been largely eliminated (though bisphenol-A, a can-lining resin thought to be a teratogen, is currently the source of a good deal of debate), so that food in metal cans is currently both safe, durable, and very inexpensive.

Aluminum containers, primarily used for carbonated beverages because of the need for the supporting internal pressure in their soft structure, are a development of the latter half of the twentieth century and dominate the beverage can market in the United States, although British steel manufacturers produce a two-piece drawn can out of special low-carbon steel that is quite similar to the aluminum two-piece can. Steel and aluminum are both used for the construction of food and beverage containers, but steel foils are almost unknown in consumer food applications because of the ease of production and corrosion resistance of aluminum.

General Structural Consideration in Cans, Drums, and Pails

Cans most often fail because of applied stacking stress causing the sidewall of the can to buckle. Because of this, unpressurized cans are typically fabricated with flexible ends and *rings*, circumferential ridges around various parts of the central can body that prevent the initiation of buckling under vacuum, and therefore allow the use of lighter grades of steel in can fabrication. Although the buckling stress of a smooth cylinder can be estimated by Equation 4.3:

$$\sigma_{\text{critical}} \cong 0.605 \frac{E \cdot t}{r} \tag{4.3}$$

σ_{critical} : critical stress, Pa
E : elastic modulus, Pa
t : thickness, m
r : radius, m

in practical application, cans are rarely smooth cylinders because of end structures and design geometry. Can collapse without buckling usually involves the extensive deformation of the bottom of the can under excessive load or impact and will exhibit a characteristic bulging. Pressurized cans rely on the internal pressure of the contents, usually a carbonated beverage, which can be in the range of 60 kPa to 300 kPa. At this point, the thin-walled can acts as a

metallic balloon, and the amount of axial force it can withstand without buckling will be a direct function of internal pressure and the area of the can ends, because the ductile material of the can adds little strength.

$$F_{\text{pressure}} = p \cdot \frac{\pi d^2}{4} \tag{4.4}$$

F_{pressure}: force, N
$\qquad p$: internal pressure, pa
$\qquad d$: diameter of can end, m

Production of Steel

Steel is an alloy of iron and several common elements, principally carbon in varying quantities. For the manufacture of food containers, the need for ductility in the material demands that the steel used is *low carbon* steel, which typically has low tensile strength relative to many structural alloys, but is relatively easy to form and weld. Low carbon steel typically has less than 0.3% carbon content (0.3–0.6% is termed *medium carbon* steel, and over 0.6% is considered *high carbon* steel) and can contain other alloying elements such as sulfur, manganese, silicon, and phosphorus, as well as approximately 25% recycled steel (Table 4.2). Iron ore, often from domestic sources, is usually concentrated into pellet form and then shipped to refining mills. The concentrated ore is combined with a carbon source (most often the coke used by refining raw coal) using a basic oxygen furnace and heated along with alloying elements to form a final melt, which is then cast into slabs and ingots. If the steel is produced exclusively from scrap, it is most common to use an electric arc furnace to produce ingots, because these types of furnaces are well suited to recycling refined ferrous metals, and are common in small specialty steel mills. These ingots are then hot-rolled into *coil* – long rolls of strip steel – that is further reduced to its final thickness after cooling. It then may be electroplated with a very thin layer of tin (approximately 0.14 mm). Other coatings may include electroplated chromium or a polymer coating on unplated steel. It can then be cut and shaped into finished can bodies and ends.

Steel Cans

Steel cans are primarily manufactured as either deep-drawn two-piece cans or welded-seam three-piece cans. The traditional, soldered side seam three-piece can has given way to welded side seams because of the concerns with lead extraction into food products, although they are still produced in some countries and may be used for non-food products without problem. Additionally, competition from aluminum cans and plastic bottles has nearly completely usurped

Table 4.2. Composition of Common Can Steel Types

Classification	Maximum Composition (%)								
	C	Mn	P	S	Si	Cu	Ni	Cr	Mo
D Type	0.12	0.6	0.02	0.05	0.2	0.2	0.15	0.1	0.05
L Type	0.13	0.6	0.02	0.02	0.02	0.06	0.04	0.06	0.05
MR Type	0.13	0.6	0.02	0.05	0.02	0.2	0.15	0.1	0.05

the steel beverage container market – a multibillion dollar loss – so the steel container industry is continually searching for new market niches and competitive market positions.

Three-Piece Cans

As the name suggests, the three-piece can consists of two ends, one of which may have an easy-opening or other feature, and a body that is formed from sheet stock. The steel body is usually formed with a series of *rings* – circumferential corrugations that prevent denting and collapse under the vacuum that is often induced in packaged foods to reduce corrosion and product degradation. The body is then welded along its side seam by passing the blanks through a side seam welder that uses an electric current passed through contact wheels to resistance-weld the seam area. The weld fusion surface on both the interior and exterior is then usually coated to prevent corrosion in the area where the weld has oxidized away any protective coating or electroplating. At this point, the edges are flanged outward to accept the can ends, and then the can is usually shipped with the bottom edge flanged on.

Welding and Soldering Considerations

Welding is the fusing of two materials, often with the addition of additional material to replace that lost to oxidation in the heating process, and produces a joint that is as strong as the base materials. Although there are many types of welding, including solvent and friction welding for plastics, thermal welding of metals will be discussed in this section. Metal welding requires that the two materials are compatible and have similar melting points. For this reason, welding broadly dissimilar metals such as steel and copper is impractical, and so welding is typically done between very similar types of single materials, particularly steel. Additionally, welding metals will cause the surface to oxidize, which may require some adaptation of the methods and materials to compensate for this. An extreme example of this is the welding of aluminum, which must be done under an inert gas stream to prevent immediate and destructive oxidation during arc welding. Industrial welding of thick steels often uses a flux compound to clean oxidation from the surfaces to be joined and to protect the hot surfaces somewhat from subsequent oxidation as the molten metal cools. For sheet fabrication, and particularly for food-contact applications, flux would represent an unacceptable contaminant, so the welding process is carefully controlled and the weld surface is coated with an approved protective coating as soon as possible after the welding step.

By contrast, soldering is the use of a low melting point (usually below 400°C) filler metal to join two compatible metal surfaces by flowing filler into a heated joint by capillary action and cooling it to a solid. The resulting bond is not nearly as strong as the base materials, but the ease of bonding and simplicity of equipment makes soldering a very good method for permanent joints between metal components, particularly in electronic assembly. Most solders usually contains a percentage of lead to assist in lowering the melting point, which may then dissolve into food products and represent a health hazard, particularly for children, since lead may cause many types of neurologic and renal problems and is not readily excreted by the body. Brazing, not used in the packaging industry to any significant degree, is the higher-temperature version of soldering, with brazing fillers melting above 425–450°C and producing very strong bonds in metals. It is particularly useful where the excessive heat or difficulty of welding would be a problem, such as jewelry manufacturing and fabricating tempered-steel bicycle frames.

Although the interior surface of traditionally soldered can seams was coated, the lead content of the solder reduced, and the solder joint reduced in size to reduce the potential exposure, the food industry in the United States had stopped using soldered-seam cans by late 1991. The US Food and Drug Administration finally banned the manufacture of soldered side seam cans in 1995 and required that they be removed from commerce (along with lead foil capsules for wine) by June 1996. Although not legal in the United States, soldered-seam cans are still produced in some countries, and there is a great variety of restrictions on lead exposure worldwide.

Two-Piece Cans

Two-piece drawn cans are very commonly used for shallow-draft cans such as small fruit tins, and are rapidly replacing three-piece cans in many traditional applications such as vegetables and soups. These deep-drawn cans are fabricated in a manner similar to aluminum two-piece cans described in this chapter. A flat blank is deformed into a cup and then successively formed in separate *ironing* processes into a deep can that replaces the body and bottom assembly of a three-piece can. This body is then trimmed and both flanged and ringed as required. The advantages in two-piece cans are the potential for lower cost because of fewer components, better material use, and reduced potential for failure and corrosion because of the elimination of the bottom and side seams.

Corrosion in Steel Cans

Corrosion in steel cans throughout their service life follows a progression of processes that are somewhat predictable, as are some of the factors that can affect them. Although there is both a tin and often a polymeric coating to protect the steel, these coating will have microscopic defects that may allow corrosion to be initiated, and without the electrochemical protection of the tin layer, the container structure would soon have corrosive perforation. The general progression of corrosion in steel cans follows a three-step process (Figure 4.19).
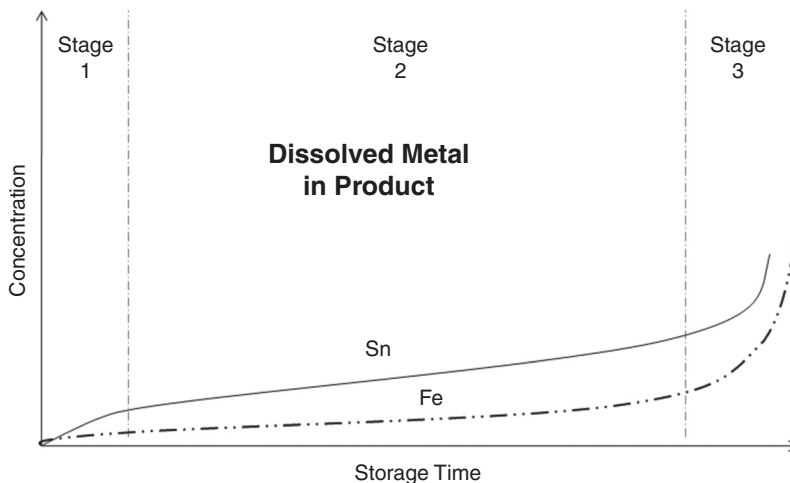
Figure 4.19. Dissolved Metal in Product Due to Can Corrosion
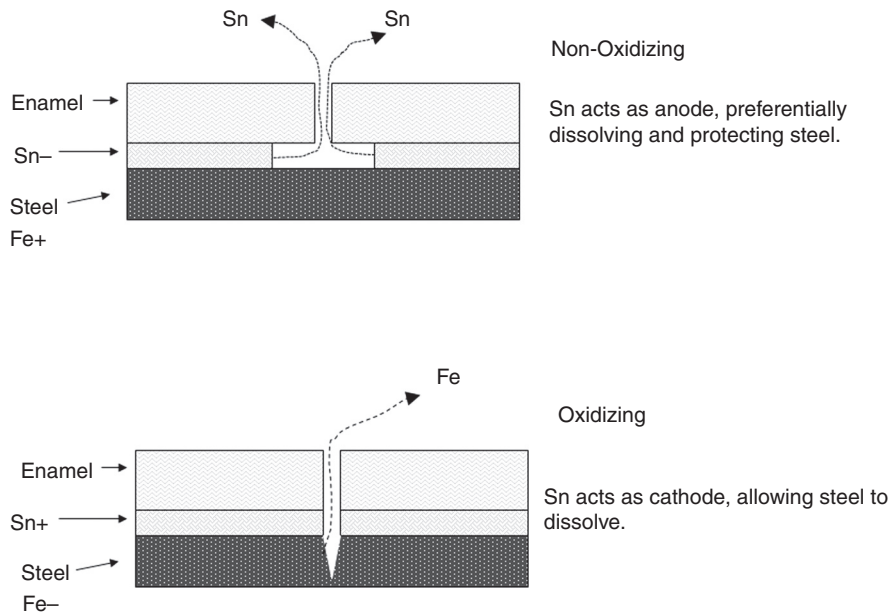
Figure 4.20. Oxidizing and Subsequent Non-Oxidizing Stages of Can Corrosion

Stage 1 (Oxidizing)

Immediately after closure, the interior of the can and the product will both contain some residual oxygen. In this oxidizing environment, the tin coating is cathodic and does not provide protection for the steel layer, as shown in Figure 4.20. After a brief interval, residual oxygen is bound up in oxidation products in the product and can material.

Stage 2 (Non-Oxidizing)

Once the oxygen in the system is bound up, the internal environment becomes non-oxidizing, and the tin, now acting as a sacrificial anode, protects the steel while slowly dissolving into the product. Depending on the various corrosion accelerants present, this may go for months or years until the tin coating becomes substantially depleted. Any additional source of oxygen will again allow the tin to become cathodic, accelerating corrosion of the underlying steel.

Stage 3 (Terminal)

As the tin is depleted in the non-oxidizing environment, the protection for the steel is removed, allowing corrosion and pitting of can, staining of product and can surface, and sulfide gas (H_2S) formation, as shown in Figure 4.21. This usually causes the can to build pressure and swell or burst, and the product will take on a rotten-egg smell even though it still may be microbially safe. If the can simply perforates, the product will become contaminated and will also swell – a primary indication of spoilage in either case.
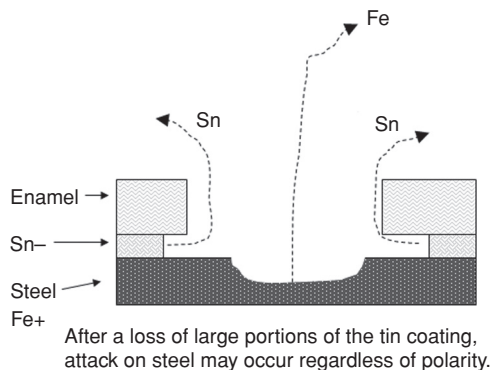
Figure 4.21. Terminal Stage of Can Corrosion

Corrosion Accelerators

Certain components in the product itself may enable or accelerate corrosion in the steel cans, as is illustrated in Table 4.3.

This illustrates the necessity of close monitoring of can performance, particularly when product formulations change as the shift in ingredients may have a secondary, unintended effect of changing the durability of the packaging. Sulfur and sulfide compounds may cause staining of cans as well as acting as a depolarizer; nitrates may reduce to NH_3 and act as corrosion accelerators; oxygen will act as a depolarizer as well as causing direct product decomposition; and thermal treatment and storage will affect the rate and nature of can corrosion.

Aluminum Production

Aluminum is produced very differently than steel, and has always had an extremely high incentive to include recycled metal due to the difficulty of producing metallic aluminum from aluminum oxides that are extracted from bauxite. The stability of aluminum oxide is both a blessing and a curse for aluminum, because it provides a corrosion-resistant coating on the metal's surface, but it also made the production of aluminum a difficult task until 1866, when Charles Martin Hall in the United States and Paul Héroult in France simultaneously and independently patented the process in which alumina (aluminum oxide) is refined electrolytically. The Hall-Héroult reduction process remains the only method to produce aluminum in commercial quantities, although continuous work on refractory cell design, electrode systems, and other components of the practical implementation of the process continue to yield steady gains in efficiency and purity of metals produced. Packaging currently accounts for approximately 21%

Table 4.3. Corrosion Changes Resulting from Different Acids Used in Canning

Acid	Oxalic	Citric	Malic	Tartaric
Dissolved Sn (ppm)	20.3	10.5	8.5	5.5
Rate nÅ/cm^2	26.8	13.9	11.2	7.2

of the aluminum used worldwide and is used as can blanks, a thin sheet for forming trays, foil for coverings and barrier applications, and laminated foils and vapor-deposited coatings that use the barrier properties of aluminum with the mechanical support of other materials.

Aluminum is cast into plates or ingots in a manner similar to steel ingots, and then may be rolled, re-tempered, and re-rolled into varying thicknesses of sheet or foil, depending on the application. Other mills will produce aluminum sheets and foils in a continuous process that starts with a continuous casting and progresses, being extruded through ever-narrower roller gaps until the final product is wound on a reel for shipment. Thicker sheets are often used to produce the stampings that aluminum cans are shaped from, whereas thinner foils, less than 0.15 mm (or 0.006 in), may be used to form trays and cups. Aluminum foil less than .025 mm (0.001 in) thick may be folded and rolled into very fine foils down to approximately 0.005 mm (0.00017 in) that are included in laminates as a barrier material. Finally aluminum may be evaporated as a coating on polymer films as a means of providing a good barrier or a reflective surface – this topic is considered as a surface coating of polymers later in this chapter.

Aluminum is a very ductile material and has less tensile strength than steel, though its final strength-to-weight ratio is higher, making it useful in aerospace applications. The high ductility allows the material to be shaped and formed with relative ease, and it may be easily embossed or textured for specific applications, but also makes it very fragile in thinner grades. Aluminum is resistant to attack by many food and beverage components, but is readily oxidized by materials containing organic acids and/or salts, so coatings may be necessary for some types of food products. For the relatively benign contents of beverage containers, often no coating beyond the naturally occurring oxide layer is necessary.

Typical alloys used in food packaging contain minute amounts of copper, zinc, manganese, chromium and magnesium, with 1xxx and particularly 3xxx series alloys being favored for foils and can bodies, and stiffer 5xxx series used for can ends. Specific choices are shown in Table 4.4.

The commonly-used "O" temper foil has been reheated above 340°C, which both softens and effectively sterilizes it. Partially annealed aluminum foil has temper H-25 and H-27 available, and is available in foils thicker than 0.05 mm. H-19 temper is the hardest temper available in thinner aluminum foils.

Table 4.4. Aluminum Alloy Compositions

Designation	AL	Fe + Si	Other*
1100 H-19 foil and O	0.99 – 0.993	0.009 – 0.006	Cu .00005 – 0.002
1145 H-19 foil and O	0.9945 – 0.9960	0.005 – 0.0035	
1235 H-19 foil and O	0.09935	0.0065	0.001 Zn
1350 H-19 foil and O	0.995	.005	
3003 H-19 foil and O	0.967 – .099	0.013	.01 – .015 Mn
3004 H-19 foil and O	0.955 – 0.982	0.01	0.0025 Cu, 0.008 – .013 Mg, 0.01 – .015 Mn, 0.0025 Zn
5052 H-19 Foil	0.957 – 0.977	.0065	0.022 – 0.028 Mg
5056 H-191, H-38 and O	0.957 – 0.977	.0065	0.022 – 0.028 Mg

*Other major alloying elements > 0.5% (.005). There are small amounts of other elements that are not listed in this chart and may distinguish similarly numbered alloys.

Aluminum Cans

Because of near-impossibility of efficiently welding paper-thin aluminum in a production situation, aluminum cans are formed as two-piece cans, having a body and an end, usually with an easy-open feature. The can bodies are formed by stamping flat sheet into *cups*, the sidewalls of which are progressively stretched by extrusion with successive dies until the desired height is achieved, and finally trimming and flanging it, and then the end features such as necking rings or other desired structures are added.

Because the bottom material is neither severely deformed nor stretched significantly in comparison to the sidewall, the resulting container usually has a relatively thick bottom structure and very thin sidewalls. To extensively deform the aluminum in this manner, a Mn-Al alloy such as Type 3004 may be used, and these have been specifically modified by adding more manganese to produce a finer, more ductile crystalline structure that does not score or tear during forming.

Can ends for beverages are formed separately from thinner stock than the can body, because the deformation required is less, but the alloy must be ductile enough to allow a rivet stud to be formed in the center (rather than as a separate, more costly separate piece), which allows the pull tab to be attached simply by flattening the protruding stud over a matching hole in the tab. The forming of the rivet from the can end was a necessary step in making the aluminum can cost-competitive with competing products at the time, and has been retained as an assembly feature. Additionally, the top stamping must tolerate being very accurately scored in the opening area so that leverage produced by the opening tab will be sufficient to tear the scored area and open the can.

The ductile nature of aluminum, which makes the two-piece can structure attractive in terms of manufacturing costs, works against using the cans for unpressurized products because there is little intrinsic container body strength in the material without supporting internal pressure. Although there has been some movement toward pressurizing aluminum cans with an inert gas to provide structural support so that the cans may be used for non-carbonated food, there has been a great deal of reluctance to implement this, particularly on the part of regulators. This is primarily due to the consumers' knowledge that gas pressure in a can is a primary indicator of spoilage or degradation. Artificial pressure would lead either to discarding safe products or learning to ignore pressure caused by dangerous spoilage. There has been some success in increasing pressure in carbonated containers by using low-solubility, inert gasses such as nitrogen to avoid over-foaming the beverage while still keeping the container rigid – a method that can be used in restaurant dispensers for low-carbonation beverages.

Aluminum cans with simple enamel coatings are stable at pH values above 5.0 with a simple enamel coating, but more acidic foods will show shelf lives and corrosion similar to steel (12–18 months), although aluminum cans do not produce blackening effects in sulfurous foods.

Bottle Cans

Newer developments have allowed the production of severely necked "bottle can" containers for use with aerosol products and potentially replacing some aluminum and plastic containers. Bottle cans are aluminum bottles formed to the approximate shape of glass bottles, most often, beer bottles, with fully formed closures capable of accepting a roll-on screw cap. These have also made considerable inroads on traditional designs for aerosol containers in cosmetic, household chemical, and lubrication and engineering compounds. They have the advantage of

being unbreakable, but to date have seen little success in unpressurized beverages because of the tendency of the soft aluminum sidewalls to dent badly and appear damaged on store shelves. The bottle can process depends on both the extreme ductility of aluminum and the lubrication and barrier properties of a PET lamination on the surfaces of the aluminum stock that is used to form the container.

The container begins as a flat sheet of laminated aluminum and is progressively formed in a draw-redraw process that requires no fewer than 15 steps to complete. A deep-draft thin-wall container is first formed, then domed inward in several stages, then a thread and curled bead finish is progressively formed, with final steps involving necking and flanging. The end result is a threaded-closure aluminum bottle with a fully curled opening that does not present sharp edges to the consumer. Work is being done on using pressure ram forming of aluminum sheet at elevated temperatures (approximately 250°C) to form aluminum bottles without the PET lamination. In this process, an annealed aluminum pre-form fabricated in a draw-redraw process is heated and pressurized in a closed mold in a manner very similar to the pre-form blowing operations described elsewhere in this chapter, with a result being an aluminum bottle that is produced with many fewer steps and good control over residual stresses in the material.

Aluminum Foils

Aluminum is a ductile enough material that foils can be readily produced by folding and rolling thicker sheets. Foil grades commonly used for packaging are shown in Table 4.5.

After forming, the foil may be embossed, coated, or printed to achieve a desired appearance. It is common to laminate thinner films to a substrate, most often plastic film or paper, before these treatments to provide strength. Thick aluminum foil is essentially impermeable to everything except hydrogen, but aluminum foil thinner than approximately 0.015mm will show small defects that will lead to permeation that increases as the foil becomes thinner. Other studies have shown that pinholes are formed by a variety of causes ranging from contamination in the rolling processes from a variety of sources to mechanical stress concentrating around metallic and non-metallic impurities, as well as the imprinting of defects in the rollers themselves.

Table 4.5. Aluminum Foil Types

Designation	Translation	Meaning
B1S, B2S	Bright, one or two sides	Specular, reflective finish on one or both sides. Matte finish on non-bright side, if any.
EB1S, EB2S	Extra bright, one or two sides	Brilliant reflective finish on one or both sides. Matte finish on non-bright side, if any.
M1S, M2S	Matte, one or two sides	Diffuse finish on one or both sides. Bright finish on non-matte side, if any.
MF	Mill finish	Non-uniform finish, seldom used except for internal laminations.
Foil, scratch brushed	Scratch brushed	Abraded surface to provide roughened or textured surface
Foil, annealed	Annealed	Foil fully softened using thermal treatment.
Hard foil	Hardened alloy	Foil work hardened by rolling
Intermediate foil		Foil hardness between annealed and hard
Embossed foil		Foil that has been textured or patterned using an engraved roller, plate, or other contact fixture

Aluminum foils are susceptible to crack formation from flexing and handling, and this and pinholing can lead to delamination as well as decreased barrier effectiveness. Very thin foils are almost always laminated to a substrate, and the barrier properties of these laminated materials are very similar to thicker grades of aluminum foil, presumably because the small defects in the foil are sealed by the laminate. A more extreme example of this is the tremendous increase in barrier properties of metallized plastic films, which have only the thinnest metallic layer (and similar problems with pinholing and scuffing of the coating) and are subsequently discussed in this chapter.

Other Metal Packaging

Although increasingly manufactured from non-metallic materials or metallic laminates, there are several types of traditionally metal packages that are still in substantial use. Steel drums, pails, and disposable tanks are more often used for construction and industrial chemicals than for domestic food items, but they still represent a significant component in the world's packaging industry.

Steel, Plastic, and Fiber Drums

Steel drums, first fabricated to replace wooden barrels in the early 1900s, are usually fabricated in a manner similar to the three-piece food can, with a welded side seam and several reinforcing rings pressed outward from the body to strengthen them and facilitate rolling, because their cylindrical shape was not as well suited to being rolled as the bulged wooden barrels they replaced. Plastic drums are usually fabricated using blow or rotational molding and are most often used for liquids and are fitted with a bung and/or threaded opening to allow the removal of product. Because of the relative ease of molding, plastic drums may be formed in unusual shapes for specific applications and may be specially formed to be included in industrial or dispensing equipment.

Drums range in size from approximately 19 liters (5 gallons) to 420 liters (110 gallons), although "a drum" is often used as a rough standard measure corresponding to 55 gallons (210 liters), as adapted from various common wooden barrel uses. One standard barrel of oil equals 159 liters (42 gallons), whereas a standard American barrel of beer is 117.3 liters (31 US gallons). In the UK, a standard barrel of beer will be 163.7 liters (36 Imperial gallons or 43.3 US gallons), and European beer barrels may range from approximately 34 liters to 110 liters, depending on the type of product, with no standard size at all.

Industrial barrels of different volumes are often fabricated to be a constant height, both for ease of manufacturing (since the width of the steel sheet used for the body will be the same) and because of the convenience of having mixed loads of barrels have a standard height for stacking palletloads. Drums can be lined with a variety of coatings or flexible bags, depending on the type of product to be contained, such as polyethylene and polyester bags or phenolic and epoxy coatings, and can be provided with sterile liners if necessary. Barrels for industrial use are typically fabricated as either an open-head or tight-head types. An open-head drum has a cover that fits into the end with a compressible seal and is retained either by a releasable ring that is bolted closed, held by a lever lock that can be opened without tools or by lugs that must be bent open, whereas a tight-head drum will have the cover permanently seamed on, but will be traditionally fitted with standardized 51 mm and 19 mm fittings for emptying and venting the container, respectively. Other fittings may be incorporated into the drum as required,

depending on the application. Drums may be tested for integrity using a helium leak detector or a similar method, and as barrels are often re-used, any re-conditioned barrels should be checked for damage and flex-cracking as well.

Open-head drums can be used to pack nearly anything that will fit into the container because the cover can be lifted and a liner or other packing material incorporated, and these types of barrels are occasionally used for machine parts and other unusual items because of their availability and sturdiness. Tight-head drums are limited to materials that can flow through the openings, and are almost always used for liquids.

Because of the durability of steel drums, they may be re-conditioned and re-used. This typically involves the minimum of cleaning and testing for leaks, but may be more extensive depending on the type of product involved and the condition of the barrels. Systems that can restore physical dimensions, re-coat the drum, burn them clean of contaminants, and perform other re-conditioning are available.

Fiber Drums

Fiber drums, although considered a paper product, are included in this section because they complement the steel drum applications and market. They are essentially enormous, spiral-wound cans manufactured as described in this chapter and fitted with ends held in place by a seamed-on end in a manner similar to metal drums. They represent a low-cost, low-weight solution for containing many types of products and can be fitted with liners or sterile bags to transport moist or perishable items. These are typically available in sizes approximating standard drums (55 gal/210 liters) and smaller, and are very often fitted with a lock-ring cover that is easy to remove in order to access the contents.

Beer and Syrup Kegs

Beer kegs are specialty items that are used for the relatively small-quantity bulk distribution of beer to bars and restaurants, and are almost always re-used. They are constructed of either aluminum or stainless steel, with the manufacturing method being similar for both materials. The body is deep-drawn into shape and has a skirt that is inert-gas-welded to the top and bottom ends to accommodate both standing upright and being lifted by the handles incorporated into the skirts. Kegs are either the Hoff-Stevens type, which has a bung in the side, or the more common SVK/Sankey® type that is equipped with a concentrically vented center fitting that allows automated cleaning and filling equipment to handle them efficiently. Smaller "pony", "log," and similar kegs may have synthetic rubber skirts bonded to the top and bottom to reduce cost, weight, and handling noise, and decorative outer barrels can be molded on to resemble wooden barrels. Similar small containers have been used for soft drink syrups for years but are rapidly being replaced by bag-in-box systems that are less expensive and do not require return, cleaning, and re-filling.

Metal Pails

Metal pails are formed in a similar manner to steel drums, with a side-seamed cylindrical body flanged to a bottom. The tops may be attached by any number of methods, though simple pull-off tops and flanged tops are most common. Because of problems with interaction with products, very few food ingredients are shipped in metal pails rather than molded plastic containers.

More common uses are for materials such as cleaners, roofing compounds, and chemicals, with molded plastic pails making steady inroads into traditional markets. The additional feature of child-resistant tops has given molded plastic pails the edge in markets such as pool chemicals and bulk cleaners.

Metal Tubes

Metal tubes bear the distinction of being one of the few commonplace items that was started by artists and is arguably one of the first packages that became popular because it added convenience to an already common product. Metal tubes were first developed as a means of reducing the annoyance of having to grind and mix pigments by the American artist, John Rand, during his apprenticeship, and were patented by him in 1841. These first tubes were similar to fast-food condiment packets or sample tubes in that they had to be torn or punctured open and could not be re-sealed. In 1842, Rand developed the production system for extruding tubes from soft metal, originally tin or lead, since aluminum cost approximately the same amount as silver at this time. These included a threaded neck and nozzle, and the design remains largely unchanged. Tubes were immensely popular in Europe, and their implementation allowed the beginnings of pre-fabricated art supplies.* Tubes remained as a niche market for paints and were originally manufactured in Britain and imported into the less industrialized United States, but were immediately successful in Europe where they were adapted for a variety of uses, from food to ointments.

A druggist, Dr. Washington Wentworth Sheffield, had invented a type of toothpaste in 1850, and his son, Dr. Lucius Tracey Sheffield, who had studied in Paris and had seen metal tubes used by artists, began selling toothpaste in collapsible metal tubes that customers immediately found more convenient than jars. Tubes were increasingly adopted by other cosmetic and dentifrice
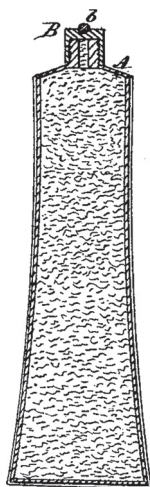
Figure 4.22. Early Toothpaste Tube
Source: USPTO Patent 125,098

companies throughout the late 1800s, and improvements such as embossing and printing were incorporated.

Metal tubes are now formed from aluminum and occasionally tin (lead may also be used, but not for food or pharmaceutical use) in an impact extrusion press that pushes the ductile material into a neck die and simultaneously extrudes it up the sides of the press to form the tube body. The extrusion is trimmed and at this point, aluminum tubes must be softened by annealing them so they will collapse properly without cracking, as the forming process work-hardens the aluminum and makes it brittle. Tin tubes, although more expensive, are still used as very small containers because of tin's ductility after being worked, and are typically used for medical compounds and other specialty applications. Tubes may be internally coated to help prevent product interaction with the material, but in most instances, reactive products have been given over to plastic or plastic laminate tubes discussed at the end of the chapter. Printing can be done before filling and requires the use of very flexible coatings, and labeling can be done either before or after filling, though proper label application is more challenging after filling. After filling the tube, the end is rolled over and crimped, often with a die that will include a date or product code. Screw caps, dispensers, or other fittings may be added before filling for tubes that are formed with an open neck, and afterward for products that must be opened by puncturing a seal in the neck.

Plastics and Synthetic Polymers

Polymers – organic and inorganic – are a natural constituent of most materials and all organisms. The materials that are commonly referred to as polymers, however, usually are man-made materials, and are usually organic polymers (although synthetic inorganic polymers – ceramics – are finding increased use in aerospace and specialty consumer applications). Development work using macrodefect-free cement and other inorganic compounds have been used to make packaging components such as formed cans, but there is no current industrial implementation.

The earliest synthetic polymers were a result of the booming industrial development of the chemical industry in the 1800s, when chemists found that they could dissolve cellulose using nitric acid and remold the resulting materials into nitrocellulosic materials – often referred to as collodion materials. The first uses for these materials were in early photographic processes, and in the manufacture of billiard balls as the cost of ivory from ever-scarcer elephants rose. These materials, whose use continued well into the 20th century, were notoriously flammable and volatile, and did not withstand the test of time well. The addition of camphor to nitrocellulose produced celluloid, which proved more stable and was used as one of the first truly useful thermoplastics – materials that can be melted and reformed many times under heat and pressure. The first completely synthetic man-made polymer, a thermoset named Bakelite, was developed in 1907 by Leo Baekeland. Bakelite was a phenolic-formaldehyde resin that was impervious to most conditions of heat and aggressive chemicals; once molded, the shape would never change, and it would chemically decompose before it was substantially altered by heat, pressure, or solvent attack.

The booming market for plastic materials in the 1920s and 1930s resulted in materials such as nylon, PVC, and the disruption of supply of natural raw materials for the war efforts of both the Allied and Axis armies in World War II caused a flurry of research on both sides intended to find suitable replacements for scarce natural rubbers and rope fibers that had been cut off by war in the Pacific region. The incorporation of new materials into aerospace structures, as well

as use in consumer goods such as radio parts, lamp components, and related high-durability applications, pushed the chemistry and manufacturing technologies of synthetic polymers into its current state as the predominant source of structural materials for most consumer goods and many types of packaging applications.

The relative ease of forming simple organic gasses – most often derived from petrochemicals or coal – into long chains has seen a steady progression of control and sophistication from the initial days of producing relatively soft and fragile moldings that did not stand up to use to the current wide range of inexpensive materials that have very specific properties. These can be tailored to suit a particular application either by initial compound formation or by subsequent modification of structure by mechanical or other means.

Unfortunately, the inherent source of plastics production in the petrochemical industry has put resin availability and prices at the mercy of the unstable world oil and natural gas market. However, considering that this is a direct use of petrochemicals rather than using them as a heat source for the conversion of other materials, it represents a relatively efficient use of resources to produce synthetic materials. In times of oil and natural gas market upheaval, resin price and availability may fluctuate wildly, although this will in all likelihood be a smaller variation than with materials that have very high basic energy content, such as glass.

Basic Polymer Synthesis

Although polymer synthesis is a broad field of basic research and industrial production, the relatively simple types of plastics used in many packaging materials can provide a clear illustration of the simple types of manufacturing processes that are used to produce them. Although the reactions that are shown here are quite simple to describe, the actual processing conditions and degree of control of the processing variables involved have required many years of work on process design to allow polymer synthesis operations to accurately and predictably control the formation of reliable polymer structures.

Most polymers are synthesized from *monomers* – small, simple units that are typically linked into long chains or networks, forming *polymers*. For the simplest types of polymers that are used for the majority of applications in packaging, the structure of the polymer is simply an endless repetition of a small sequence of chemical compounds, so for the sake of convenience, these are often given as *repeat units*, the smallest repeating structure in the finished polymer, usually with any end structures indicated, as shown in Figure 4.23 for many common polyolefins used in packaging.

Additive Synthesis

Additive synthesis is, as its name implies, a process of adding compounds together to produce a synthetic result. The most common are single-monomer syntheses, although, as will be discussed later, multicomponent syntheses, producing *copolymers*, are also commonly used to produce high-durability polymers for use in the manufacture of tires and high-impact plastics. There are additional polymers that will be discussed, but most of the polyolefins result from the polymerization of alkenes.

Although there are many types and variants of additive synthesis, in its simplest form, additive synthesis polymerization has three major steps: initiation, propagation, and termination.
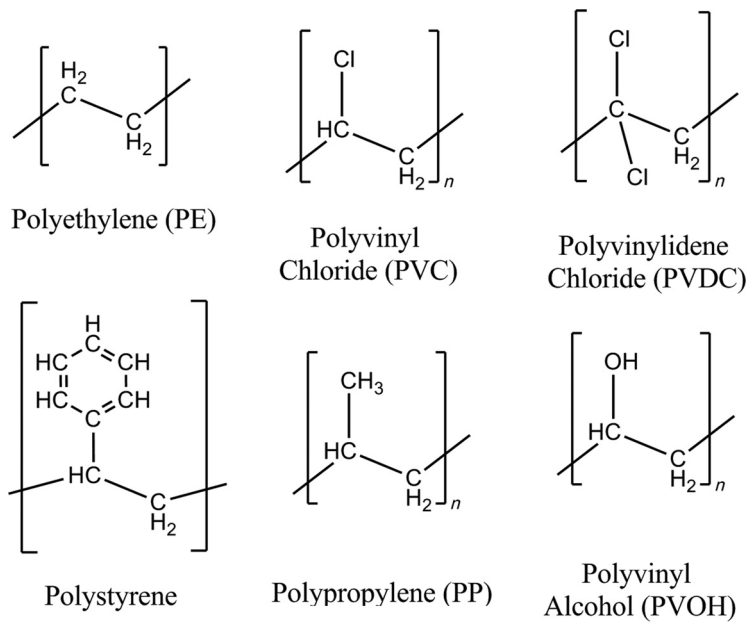
Figure 4.23. Repeat Units of Common Polyolefins

Initiation

Initiation is usually caused by a combination of heat, pressure, and the addition of a catalyst, and causes the relatively stable monomer structures – in this case, ethane – to shed a hydrogen atom and provide an *active site* to which other such molecules can bind.

Propagation

During the propagation step, the molecules with available sites bond ends to form longer and longer chains that are led by the progressively catalyzed site. Random attachment of side-chains may cause branching in the structure as well.

Termination

At some point, the chains will have grown until they either encounter an impurity or the end of another growing chain that blocks the ongoing addition reaction; run out of molecules to add to the grown chain; or until the reaction is quenched by the manipulation of external variables such as heat and pressure, as shown in Figure 4.24.

   The conditions under which the polymerization reactions are stopped will have a great effect on the final material qualities of the polymer. Very rapid termination will result in very short chains, providing thin synthetic oil, whereas long reactions will result in very high molecular weight polyethylene (UHMW) that is used as a solid and very strong engineering material. Thus, by controlling the polymerization conditions, the chain length, and thus the molecular weight of the polymer chains, can be controlled.
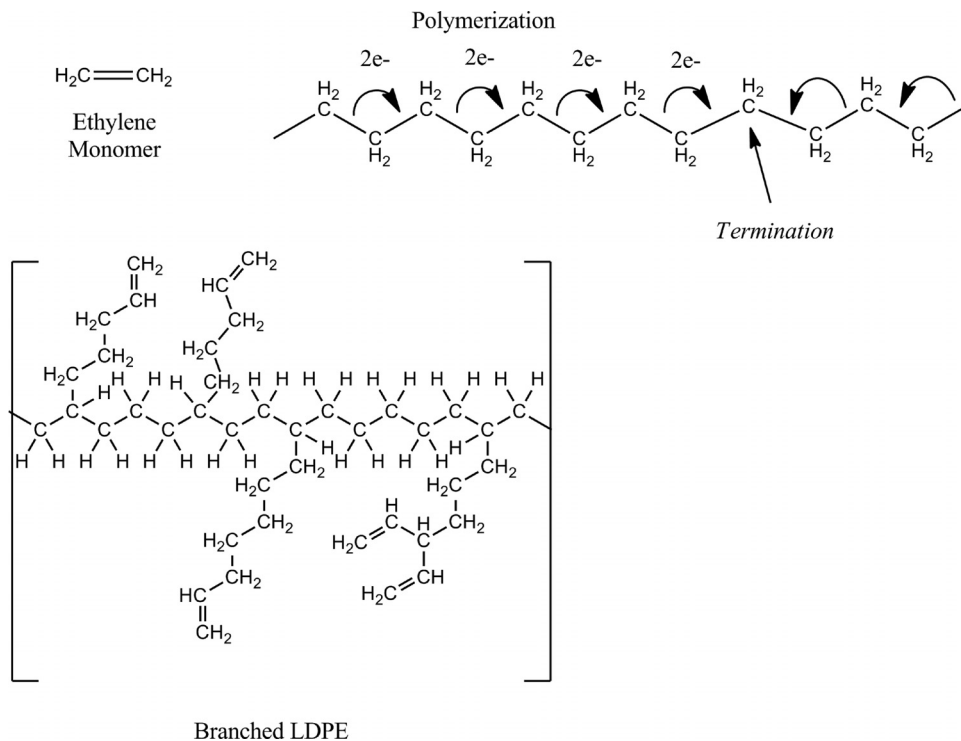
Figure 4.24. Monomer, Polymerization, and Branching in Polyethylene

Other Common Types of Chain-Addition Thermoplastics
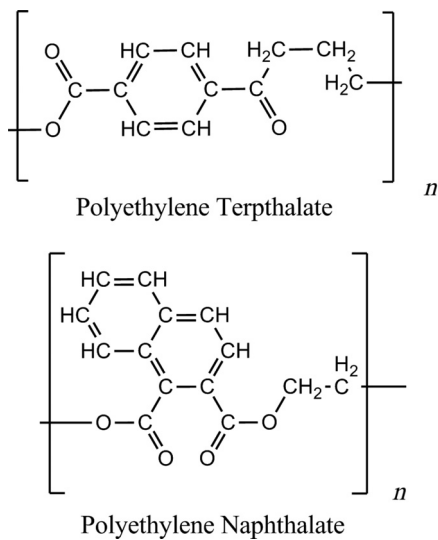
Figure 4.25. Common Packaging Polyesters

In a manner similar to the polyethylene described earlier, other common types of chain-addition thermoplastics can be constructed by the linking of suitable repeat units, as shown for packaging polyesters and nylon in Figures 4.25–4.27.
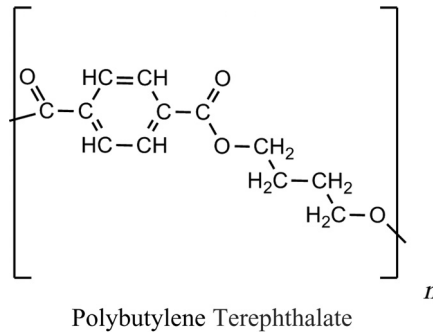

Polybutylene Terephthalate

Figure 4.26. Polybutylene Terephthalate
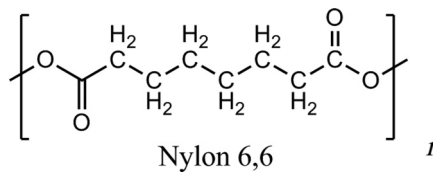

Nylon 6,6

Figure 4.27. Nylon 6,6

Biopolymer-Based Resins

To explore non-petrochemical feedstocks for commercial resins as well as develop biodegradable polymers for packaging, a good deal of research is being done on biopolymers, chiefly based and funded in several general commodity groups. Although there is a wide range of biopolymer sources under investigation, several have proven commercially viable in niche markets and others are actively being investigated.

Fermentation Biopolymers

Polyhydroxyalcanoate (PHA)

PHA is the intracellular energy source for microorganisms, and is extracted by enzyme cell wall degradation, lyophilization, and chloroform extraction. Currently, the process uses a detergent breakdown of cell structure, but research has indicated that it is possible to engineer *E. coli* to respond to a signal so that it lyses, spilling the PHA inclusions into the culture medium.

Polyhydroxybutyrates (PHB, PHBV)

PHB, a similar cellular product, is water-insoluble and a good barrier. Originally produced by Monsanto, it is currently commercially produced as Biopol by Metabolix. It can be used for packaging applications and as a light engineering plastic for medical devices and consumer

goods. It is currently used as internal suturing thread because it biodegrades over time. A PHB copolymer, PHBV–Poly(3-hydroxybutyrate-co-hydroxyvalerate), is also under development.

Polylactic Acid (PLA)

PLA is produced from microbial fermentation of plant polysaccharides (chiefly dextrose) into lactic acid, and is polymerized using either of two methods: high vacuum and temperatures and solvent water removal, or lower-temperature water extraction and vacuum distillation of intermediate products, then polymerization using heat.

PLA can be used as a moderate engineering plastic as well as for packaging materials, and is currently sold as Cargill-Dow's NatureWorks® polymer. Its chief market is disposable food service tableware and snack food containers, but it has been used for some time in surgical implants and single-use medical equipment that degrades if autoclaving is attempted for reuse.

Plant-Based Biopolymers

Starch-Based Plastics

Starch is a naturally occurring polymer consisting of various levels of amylose and amylopectin depending on the species from which it is derived (unmodified cornstarch is approximately 25% amylose and 75% amylopectin). Low starch content plastics have up to 20% starch content in petrochemical polymers, and will enhance the disintegration of the structure but do not add to biodegradability. Medium starch content plastics (approximately 50% starch by weight) are considered a plastified starch material and can be processed with many types of existing commercial plastic-processing equipment. These will biodegrade but leave substantial petrochemical residue. High starch content plastics are 90% or more starch and can be difficult to form. Injection molding in particular can be very difficult because starch does not melt and flow readily with heat. This high modulus behavior is exploited in the production of stiff starch foams, used as packing pellets for padding shipping containers, and which is the bulk of the current bioplastics market.

Soy Protein-Based Plastics

Soy-formaldehyde composites have been made since the 1920s. Cross-linking made them non-biodegradable, as previously described, but current efforts are aimed at creating a commercially viable molding resin that approximates commercial thermoplastics with soy protein isolate as the usual starting point. The polymers are approximately 90% protein, extracted from protein concentrate with alkali leaching and re-acidification. These can be molded using injection or compression molding, extrusion blow molding, or casting.

Other Naturally Derived Polymers

Chitin 2-acetamido-2-deoxy-β-D-glucopyranose

This is typically extracted from shellfish and fungi walls and can be formed into fibers and films. Its deacetylated form, Chitosan 2-amino-2-deoxy-β-D-glucopyranose, has antibacterial properties and is formed into medical films and fibers.

Factors That Affect the Behavior of Polymers

Copolymerization and Blending

In some instances, it may be desirable to combine several monomers at the molecular level to provide a proper mix of material's properties. The two most common examples are Styrene-Butadiene-Rubber (SBR) used in car tires, and Acrylic-Butadiene-Styrene (ABS) used in many high-impact molding for sporting goods and vehicle construction. These individual-component polymers are combined during chain formation and should be distinguished from blends, which are simple mixes of the finished resins usually done at the molding or formation stage. Although each has its benefits, the former allows very specific and predictable product properties to be produced during resin formation, whereas blending is usually done at the final production step and may be subject to a degree of variability, particularly in the case of forming equipment that does not mix the resins thoroughly. The advantage that blending offers is simplicity – simply a matter of stirring together resins and colorants and fillers as required during the production step to produce very specific properties on demand.

Branching and Cross-linking

As might be expected in a polymerization reaction, more than one active site may be made available on a particular backbone molecule as it grows. When this occurs, polymerization proceeds in more than one direction creating a *branching* phenomenon, as a predominant backbone molecule has long secondary chains propagating outward from a point on the main backbone chain. Control of branching has been an ongoing subject of applied polymer research for many years and has resulted in several specific types of polymers that are commonly used in packaging.

Low Density Polyethylene (LDPE) has a high degree of branching, as previously shown in Figure 4.24, where there are a large number of side chains that provide a large amount of interstitial space in the polymer structure, giving it its characteristic of low density and, unfortunately, a low modulus and failure strength.

High Density Polyethylene (HDPE) has had the degrees of branching severely controlled, resulting in a chain morphology that packs tightly and provides a high level of strength. The drawback to this particular variant of polyethylene is that the costs of controlling the branching during polymerization are quite high, which makes this particular material somewhat unappealing from a cost perspective.

Linear Low Density Polyethylene (LLDPE) has evolved as a compromise between these two materials. It is produced with a number of side branches similar to that of LDPE, but the length of the side branches is controlled so that the ability of the side branches to affect the strength of the material is minimized. The costs of production are significantly lower than with HDPE, and the material has found widespread uses in packaging materials, grocery bags, and similar applications.

Role of Catalysts in Polymerization and Branching Behavior

The type of catalyst used in producing polyolefins has had a central role in producing more accurately controlled chain lengths and degrees of branching. The first industrial catalysts were so-called Zeigler-Natta catalysts (named for the discoverers of the general class of reactions

that they promoted) that used to polymerize olefins and were revolutionary in that they allowed the production of a variety of polymers with a high degree of stereospecificity. Typical Zeigler-Natta catalysts were originally titanium and aluminum compounds, and had the disadvantage of providing too many active sites during active polymerization. This had the result of producing a broad and poorly controlled range of molecular weights and branching. To better control the catalysis, *metallocene* catalysts have replaced the original Zeigler-Natta catalysts, although the reaction follows the same pathway discovered by Zeigler and Natta. Metallocene catalysts based on positively charged titanium, zirconium or hafnium, which date to the original Zeigler-Natta catalyst era, were originally rejected because of their low activity, but were adopted to better control the catalysis reaction when it was found that a methyl aluminoxane co-catalyst would increase their activity and allow them to be economically viable. The metallocene catalysts have a single reaction site and result in a much more controllable polymerization reaction, but have the disadvantage of being unable to efficiently polymerize highly polar monomers such as vinyl and vinyldiene chloride as well as many acrylics. To overcome this, work is being done to produce catalysts from late transition metals, such as the Brookhart catalysts that are complexes from palladium or nickel. These offer the advantage of activity nearly as good as the metallocenes, but with the ability to polymerize polar molecules. Research and development of catalyst systems continues and is a continuingly competitive field in the polymer industry.

Cross-linking in Polymers

Cross-linking can be thought of as an extension of unintentional branching in some theoretical sense, but more often it is an intentional step in the manufacture of materials. One of the first artificially cross-linked material was vulcanized rubber, developed by Charles Goodyear and patented in 1844. The process used heat and sulfur as a cross-linking agent to produce a rubber material that was not sticky and would not soften in hot weather, allowing it to be used for a wide range of consumer and commercial goods. By extension, a high degree of cross-linking is associated with thermal stability to the point where a thermoset plastics are considered highly (and permanently) cross-linked and will break down and pyrolize before softening when heated.

Because cross-linked materials' structures are completely bonded into a huge network of linked polymer chains, thermoset and highly cross-linked thermoplastic materials are often considered to be a single molecule of material. Less complete cross-linking will have the effect of binding the polymer chains into a rigidly elastic network that is temperature-stable and has a high modulus of elasticity. Highly cross-linked materials such as natural rubber are often very elastic yet can be considered brittle in the true sense of the word because they break before undergoing large-scale plastic deformation. Lower levels of cross-linking will reduce this effect, providing a lower modulus, more ductile material that will usually be "tougher" – able to absorb more impact energy.

At some point, the interaction of highly branched materials and materials with a low degree of cross-linking becomes approximately similar, owing to the similar interactions of the three-dimensional structure of the polymer, although these will often be distinguished by different thermal and melt characteristics during analysis.
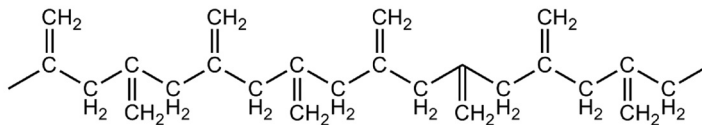
Tacticity and Conformation

When polymers have functional groups bonded to their backbone chain, the geometry of the distribution of these groups becomes an important factor in the determination of physical
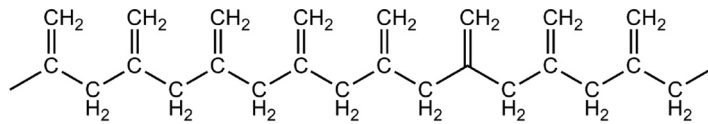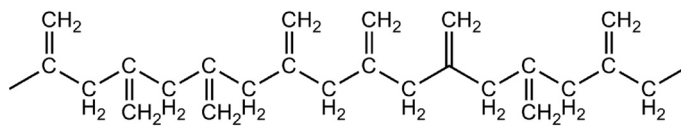
Atactic Polypropylene

Isotactic Polypropylene

Syndiotactic Polypropylene

Figure 4.28. Polypropylene Tacticity

and chemical properties, particularly barrier properties in packaging applications. A simple chain polymer such as polyethylene might be considered to have some degree of tacticity if the branching that occurs has any degree of regularity to it, but this is rare in any practical application. Co-polymers will have similar tacticity considerations if the co-polymer is compounded with a central chain of one polymer and the secondary polymers bonded as side groups. There are three predominant types of tacticity that are commonly referred to: isotactic, syndiotactic, and atactic, as shown in Figure 4.28.

Atactic

Atactic polymers have side groups that have a random arrangement on the chain; these may exhibit the least amount of interchain interaction because of the random nature of the distributions of high and low polarity on the chains.

Isotactic

Isotactic polymers have all of the relevant functional groups in the same position in the repeat units. Interchain interactions may be significant in this conformation because of stearic

interaction between the side of the group that has a large number of functional groups on it on one chain and the side that has relatively few on the chain adjacent to it.

Syndiotactic

Syndiotactic polymers have the relevant functional groups on alternating sides of the chain. This also effectively doubles the length of the repeat unit. This conformation may represent the lowest energy state due to the minimization of stearic interactions between side groups, but may also exhibit a great deal of interchain interaction because of the Velcro®-like nature of the interlocking of the chains that may occur.

Molecular Weight and Molecular Weight Distribution

As has been mentioned previously, the molecular weight is proportional to the chain length for a given monomer type, but because precise control of the molecular weight can be somewhat difficult, it has been the subject of ongoing polymer production engineering research. Because the chain length of a polymer, which is usually measured by size exclusion/gel permeation chromatography, can be described as a statistical function, there are several descriptors for the molecular weight distribution of a polymer. The most important of these is the average molecular weight because it quickly – albeit incompletely – describes the physical characteristics of the polymer. Most common usage truncates this to *molecular weight*, and this is usually incorrect. Molecular weight is actually a statistical function of the distribution population of chain lengths, and this misunderstanding has caused intermittent problems in the manufacture of goods from synthetic polymers when the polymers do not perform as anticipated.

If the statistical distribution of a polymer is centered around its average, it can be said to have a *normal* distribution, that is, the number of chains at some length shorter than average is roughly equal to the number of chains that are longer than average by the same length (Figure 4.29). If this happens, the mean (numerical average) and median (length that is halfway between the largest and smallest value) will coincide. Even within a normal distribution, however, the
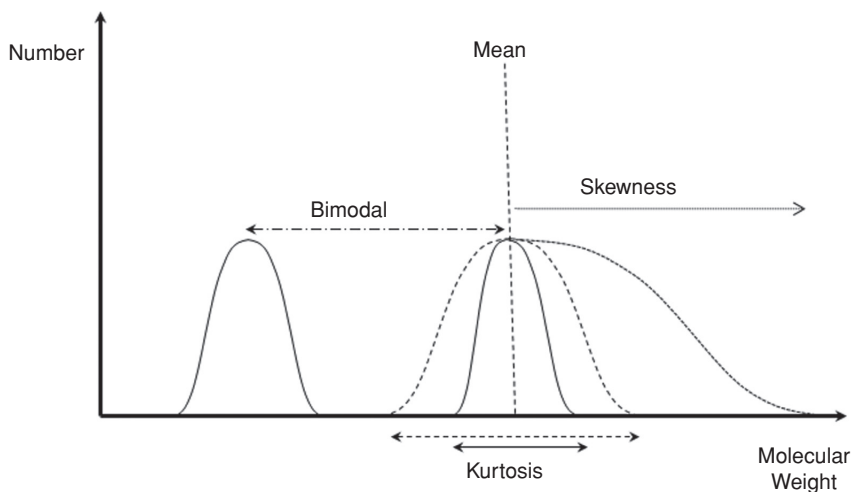
Figure 4.29. Molecular Weight Distribution Terminology

distribution's kurtosis may be considered *broad* or *narrow*. The narrow distribution of polymer chains and molecular weights will have a very tightly defined set of mechanical properties and will likely be suitable for precise applications, whereas the broader distribution will probably exhibit a broad range of strength and temperature stabilities.

If the polymerization process proceeds with the rapid formation of chains and the reaction is then allowed to continue for a long period of time, forming an ever smaller number of very long/high molecular weight chains, the chain length distribution will exhibit some degree of *skewness*, in which the mean and median chain lengths no longer coincide. This has significant implications for the properties of the polymers in that there may be a large number of chains some distance away from the average value that are dominating the polymer structure and defining its physical properties.

In an extreme example, the polymer may exhibit a bimodal distribution of chain lengths and could be considered to be an odd mix of light liquid and very dense solid, yet the simple value for the average molecular weight would not indicate that there is anything unusual at all about the material. The practical significance of this, particularly for packaging applications, is that the packaging engineer should be aware of the molecular weight distribution characterization as well as the simple molecular weight of the polymer resin to be used in production, because the difference between the two has occasionally resulted in production problems with moldings and extrusions that can be very hard to diagnose.

Crystallinity and Density

Crystallinity in the polymers used in packaging is not usually possible in the classic sense that is used for pure elements such as carbon, but refers to a high degree of three-dimensional order on a molecular level. By definition, then, some degree of disorder is considered acceptable, even with a high degree of crystallinity in a polymer. Remember that a high degree of crystallinity will result in a sharply defined melting point, glass transition temperature, or other thermal feature. More commonly, particularly in the polyolefins such as polyethylene and polypropylene used in packaging plastics, the polymer chains will have regions of high crystallinity (high degree of chain order) and regions of amorphous morphology (random orientation of chains). These can be directly observed using a high-power microscope and polarized light, or by indirect observation with coherent light sources, but each of the two types of regions will have different mechanical and thermal properties (Figure 4.30).

Highly crystalline materials are typically denser for a given material, owing to the close-order packing that occurs between chains, and they tend to have a higher modulus of elasticity, will soften abruptly at a reasonably well-defined temperature, and will be more brittle. The correlation between molecular weight, crystallinity, and many other properties is shown in Figure 4.31. Because there is little space between the adjacent chains, the polymers will often have a much lower ability to diffuse materials through their structure, resulting in a lower permeation rate – a feature that is exploited as a barrier in many modern plastic containers for carbonated beverages and oxygen-susceptible foods.

Amorphous materials will be less dense because the chains are randomly scattered and have a good deal of space between them. They have a broadly distributed melt temperature – that is, they will soften gradually as heat is applied – and tend to be mechanically tougher, more able to absorb energy by deformation before failure. Because there is a large interstitial space between the chains for compounds to diffuse through, the permeation rate of an amorphous polymer will be higher for a given amount of material.
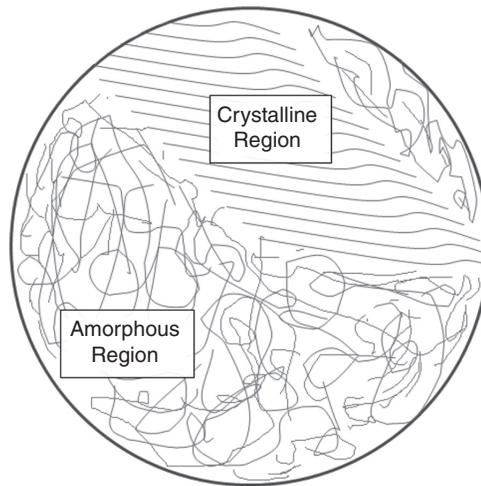
Figure 4.30. Crystalline and Amorphous Regions in a Polymer

As will be discussed later in the chapter, it is possible to convert a highly amorphous material to a highly ordered material by mechanically orienting it in one or more directions and pulling the polymer chains into the direction that the materials are stretched. This operation, if done correctly, has been shown to convert amorphous regions into crystalline ones, resulting in a nearly complete high-crystallinity material with the attendant low permeation – a feature that is exploited in the mass production of soft-drink bottles.
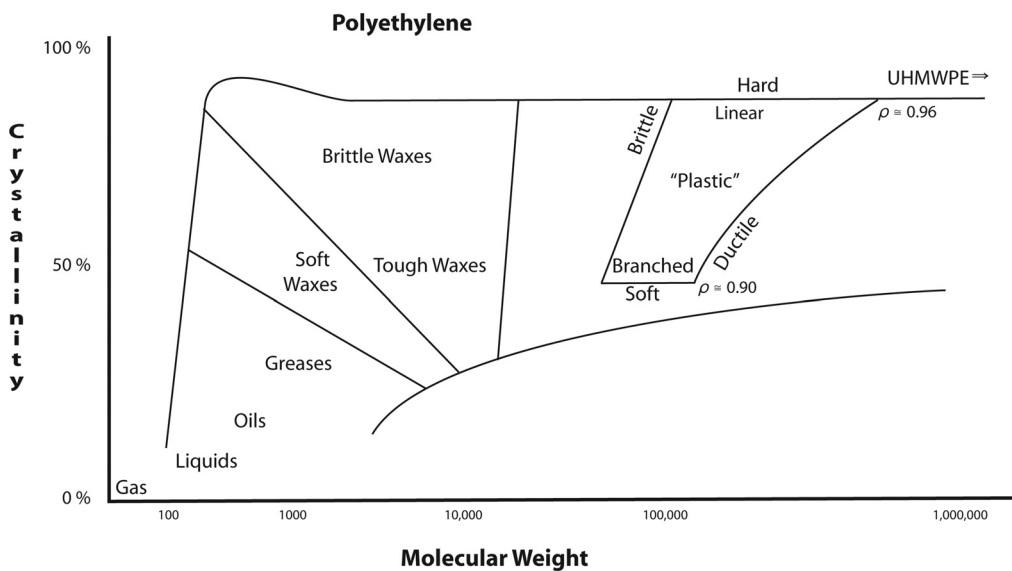

Figure 4.31. Density, Molecular Weight, and Physical Properties of Polyethylene

Thermal Characteristics of Polymers

Because thermoplastics are a statistical distribution of molecular chains of varying length, and because they are not completely cross-linked into a crystalline structure the way a crystal of salt might be, the melt characteristics of most thermoplastics are somewhat different than the classically sharp melting points of crystalline materials. In most cases, and particularly for the low-complexity polyolefins used in the packaging industry, the polymers will go through three distinct phases with increasing application of thermal energy.

Glassy: Polymer chains are not free to bend or rotate to any significant degree, and will not flow past one another. This state often represents the highest-modulus, lowest-permeation state of the polymer, but – as the name implies – may also be the most brittle because the polymer chains have very little latitude for movement when subjected to impact or excessive force.
Rubbery: The chains are free to bend and rotate, but will not flow past one another readily. This may represent a more durable state of the material, because the polymer can readily absorb impact energy in bond deformation and flexing, but is still dimensionally stable.
Melt: Chains are free to bend, rotate, and flow past one another. Obviously, this is usually not a useful state for a material expected to maintain its dimensional stability in a packaging application, but melt temperatures and melt-flow behavior while heated are of great interest to the fabricators of packages and packaging materials.

One of the distinctive measures of polymers is the *Glass Transition Temperature* (T_g) – the temperature at which the polymer makes the change from a glassy to a rubbery state. This is usually a well-defined temperature and is dependent on the polymer type, molecular weight distribution, and composition of any additives to the polymer matrix (particularly plasticizers). Glass transition temperatures are usually determined by calorimetric scanning methods, because the actual transition is endothermic and creates a distinctive signature in the calorimeter data.

For some types of polymers, the glass transition temperature can be a critical factor in design, because a glassy polymer may be very brittle at freezer temperatures, and the packaging material may fracture in use. In more practical terms, whether a polymer is above or below the glass transition temperature will have profound effects on the mechanical and chemical properties, particularly permeation that increases markedly above T_g, and may have critical impact on the final success or failure of the application.

Thermosetting Plastics

Thermosetting plastics are defined as being those that cannot be re-softened by the application of heat, and although they will have a thermal breakdown temperature that provides a practical limit of use, they do not have a useful melting point once they have been polymerized. In the packaging industry, one of the few remaining applications of thermosetting plastics is the manufacture of threaded caps for chemical containers or containers of extremely volatile materials, due to their chemical stability, but nearly all other applications have been replaced by thermoplastic resins because of the relative ease of molding, lower cost, and recyclability.

That the lack of a useful capacity for material reuse limits the recyclability of thermoplastics is of little concern to the packaging industry that no longer uses them, but if one considers the number of discarded tires that have to be disposed of, one can see that there would be a great deal of interest in finding ways to break these types of materials down to some useful set of

components so that they may be re-used. Some types of packages that use large quantities of thermosetting components must be disposed of rather than recycled.

Orientation

Once the basic resins are produced, the materials are usually molded in a series of steps to produce a stock material such as a film, sheet, or a finished package. The direction of strain in the formation process causes a resulting realignment of the polymer chains in a manner very similar to the alignment of paper fibers during paper manufacture. This effect may be simply a by-product of the manufacturing process, or it may be specifically engineered into the production method to allow the oriented material to perform a specific task.

Linear Orientation

Linear orientation is the result of deformation of the polymer in a single direction during manufacture. This will result in the statistical majority of the polymer chains lying along the direction of stress, with a result of a higher degree of tensile strength in that direction, as well as a reduction of permeability and an increase in density as the chains are reoriented from random orientations to a general orientation along the major axis of strain. This may be achieved in a number of ways, but the most common is the orientation of films and sheets during production by stretching the film after it is extruded.

Biaxial Orientation

As the name implies, biaxial orientation of materials occurs on two major axes. This changes the material from a more or less random orientation to one that can be visualized as a tight mesh of polymer chains, with the attendant increase in strength and decrease in permeability. Actually producing films and sheets that have a biaxial orientation is a challenge owing to the difficulty of adding the second direction of orientation during manufacture. The most common ways of providing a biaxial orientation for a polymer film are to either use a film-blowing tower or an orienting device that progressively pulls the film sideways using tenter grips, as well as orienting it along its major *machine direction* using increased take-up speed. The latter is a slow and somewhat expensive method, but can be used for many different types of materials.

For polymer films that are produced using a film-blowing tower, the orientation of the materials can be controlled somewhat by controlling the inflation regime and the take-up speed from the top of the tower, providing a radial and longitudinal orientation, respectively. This provides a low-cost, high-speed method of producing oriented tubular films that can either be slit along one side to provide flat stock or end-sealed and cut to produce bags.

Biaxial Orientation in Molded Bottles

The technology of orienting molded polymer packages has been the cornerstone of the production of high-barrier plastic bottles and jars to replace glass and metal containers for foods. The basic production steps strongly resemble the blow-and-blow processes that are used in the glass industry in that a *preform* (a parison-like structure) is molded, then allowed to cool below the glass transition temperature, and then blown into its final shape at a carefully controlled temperature and rate. Because the final blowing step is done at a cool temperature, a process

roughly analogous to cold drawing occurs in the polymer structure, with the end result being a container that is highly oriented, with very good clarity (if desired) and good resistance to attack by food components and oils.

General Orientation Effects

In general, orientation of polymer films may affect many properties of polymeric materials, particularly in thin-wall plastic films and moldings. In general, the transition of the polymer structure from one containing significant volumes of randomly oriented polymer chains to one that is highly ordered (crystalline) causes the structure to exhibit a higher degree of close-order packing and a higher density. A simplified demonstration of this would be to grab a double handful of randomly oriented string and pull it in opposite directions. The strings would orient themselves in the direction of pull and would most likely be packed much more tightly. The polymer morphology changes that accompany this can include changes in light transmission characteristics (such as a change in clarity), as well as changes in the optical birefringence characteristics, changes in tensile strength as the chains orient themselves in the direction of tensile strain (similar to *work hardening* in other materials), and changes in barrier characteristics as the degree of orientation progresses.

Studies have shown that permeation will actually increase slightly at low degrees of orientation change, possibly due to relaxation of the polymer structure, and then begin to decrease as the polymer chains begin to become more highly ordered and more densely packed. In the case of linear orientation, the overall permeation decrease is significant and is matched by the mechanical orientation of the plastic films, which can have secondary effects, particularly for consumers who find that their package splits open and spills its contents because the manufacturers are trying to increase barrier properties without considering other effects.

Biaxial orientation can have an even higher rate of barrier increase and will often have a balanced change in tear orientation to avoid problems with splitting. The orientation process may result in a stronger but more brittle structure – one that maintains a very high level of strength but will deform little before failing. This is ideal for a beverage bottle that must maintain its shape against high pressurization, but for a package that must be torn open, it often creates problems for the consumer unless a reliably produced tear-notch or other opening feature is provided.

Plasticizers and Additives

Plasticizers are materials that increase the ductility of polymeric materials, usually by allowing the polymer chains greater freedom to move with respect to one another and become an integral part of the overall material structure of the polymeric materials that are used in packaging materials. In the polymer industry, several types of plasticizers are available, though not all of them are suitable for food use. There are, among others, seven major types of plasticizers including: Phthalates, Aliphatics, Epoxidized Vegetable Oils (EPOs), Phosphates, Trimellitates, Citrates, and Polymerics. The simplest sort of plasticizer, and one that illustrates the mode of action (both intentional and unintentional) rather well are petrochemical or plant-based oils. When they are mixed into the polymer, the polymer becomes more ductile and susceptible to flow as well as more permeable, but as previously discussed, ductility produces flexibility as well. Polymers that are very brittle in their pure state, such as PVC, PVDC, and PS, would not be useful in most practical applications without a high level of plasticization to ensure that they do

not crack or shatter when used. Unintentional plasticization can occur when the package is made of a material that readily accepts food components that act as plasticizers, the most common being low-viscosity oils. This can have the unintended effect of "softening" the container and causing premature structural instability, in turn resulting in loss of stacking strength or warping or other deformation of the package, as well as increased permeability and decreased shelf life. Early types of plastic packaging for some materials such as motor oil, vegetable oil and products that have high concentrations of oils or volatile plasticizers had difficulty maintaining enough structural integrity to assure that the packages would remain upright in their displays and would not deform extensively, ruining their consumer appeal and delaying their introduction into the marketplace by many years.

Plasticizer extraction from the package into the product is an enormous concern for many types of food items and one that is often hotly debated both in the press and by researchers. From a regulatory perspective, these constitute an indirect food additive and are the subject of specific regulations regarding quantity and type of plasticizer (or other additive) that may be extracted. This is discussed in Chapter 10, but for food packaging applications it must be shown that the amount of plasticizer lost from the food packaging materials into a product simulant is below a specified level, or that a plasticizing material that is already on the FDA's GRAS (Generally Recognized As Safe) list is being used.

Other Additives

There is an enormous variety of components that are added to polymers for any number of different additional purposes. As with plasticizers, it must be shown that other additives are either acceptable as indirect food additives (GRAS substances, for example), do not migrate into the food, or migrate in sufficiently small quantities that their presence is not a matter of concern. Some of the common agents added to plastics used in packaging are colorants, fillers, antioxidants, odorants, stabilizers, and additives used to affect their properties during manufacture.

Colorants: Coloring of plastics usually occurs in one of two ways. It is possible to order plastic resins in specific colors other than those in stock production, but this often requires a very-high-volume order. Additionally, the plastic resin may be colored during manufacture using additives. These are typically inert pigments or dyes added to the polymer resin during manufacture by blending coloring agents with the plastic resin before melting.

Fillers: Fillers are materials that are used as *bulking agents* to reduce the cost of a large-volume molded piece. These are often simple inert materials; in large non-packaging structural moldings, talc or sand has been used. For more involved applications, fillers such as *microballoons* – hollow microscopic spheres – are used to provide a lightweight filler material. Fillers are used sparingly, if at all, in packaging applications due to the relatively low volume of material that is used in each component.

Antioxidants: These are materials that are intended to reduce the effects of exposure to oxygen or degradation during molding, and may be actual food-grade antioxidant additives (ascorbic acid, for example) to eliminate problems with indirect additives in the product.

UV Inhibitors: The "Sunscreen of Plastics," UV inhibitors will reduce the destructive effects of sunlight (or long-term exposure to some types of artificial light) in materials. Typically, these are materials that either convert ultraviolet light to lower-wavelength light, or are sacrificial in nature, degenerating preferentially to save the base materials. There are few applications

in the plastic packaging industry that require UV inhibitors for most consumer-grade food packaging, but large bulk containers, inks, paints, industrial coatings, and large structural moldings of materials like fiberglass often require some kind of UV-inhibiting coating to prevent degeneration in sunlight. UV inhibitors can be crucial in labeling applications where the product will be exposed to UV-rich fluorescent light or sunlight, because a faded package can prove to be unsaleable.

Odorants: Although not common in the consumer food packaging industry, odorants are volatile chemicals that are added to the polymer to produce a specific odor (or to mask another). Particular types of plastics that may have a "burnt plastic" smell after manufacture are occasionally treated with odorants, but the large application for this type of additive is type-specific moldings such as those used in children's toys or housewares.

Stabilizers: A more general class of additives than the antioxidants (which are stabilizers), these are typically added to provide protection against attack by a specific agent, such as a solvent in a product or a particular environmental hazard.

Manufacturing Additives: Manufacturing additives are substances that are added to the plastic resin in the manufacturing process to provide the plastic with specific characteristics to aid in proper manufacture. These may include plasticizers, slip agents, and other types of polymers to adjust the melt-flow characteristics or dimensional stability of the final product.

Structural Additives: Although rare in the packaging industry, structural additives are common in other plastics applications. A good example of this type of additive is glass-reinforced nylon. Nylon is a very durable and tough material, particularly when properly hydrated, but lacks a high degree of dimensional stability and overall strength. Manufacturers of structural components may combine nylon with fine glass fibers during molding. The glass fibers contribute their enormous tensile strength and stability, and the nylon component contributes toughness and abrasion resistance, with the final result being a molded piece that is stable, tough, and very durable.

Mold Release Agents (*Parting Agents*) Although not an additive in the strict sense of the word, release agents are used in nearly all plastic-molding operations at some point, and are familiar to most people as the oil used to prevent food sticking to cookware. Release agents are typically organic or silicone pastes, waxes, or oils that prevent the plastic from adhering to the mold surface. This will ensure that the molding can be easily removed from the mold assembly, and may prolong the life of the mold. Release agents may be particularly important if using a polymeric mold to form plastic materials, to prevent bonding. Application of release agents is most often done by either spraying or wiping onto the surface and may be automated to ensure that the mold has a consistent layer of release agent.

Over-application may result in an irregular surface on the final molding, so for continuous products such as chill-roll casting, the casting roll may have a combination of atomized deposition coupled with a wiper assembly to keep the release agent's film thickness to the minimum necessary. Additionally, sprayed mold release agents may represent an inhalation hazard and may contaminate adhesion processes such as gluing or labeling in other parts of a process operation if not properly controlled.

Manufacturing Polymeric Packaging

Unlike nearly all other packaging materials, plastics and polymer-based packaging are relatively simple materials to manufacture once the raw materials have been converted into plastic resin

powder, flake, pellets, or beads. The low forming temperatures and durability of plastic packaging has prompted even modest dairy operations to install their own bottle-forming equipment in locations where a source of supply is not available or would be too distant to economically ship in empties. This type of operation, adopted by many producers of food, drug, and cosmetic products, may be owned by the producer company or contracted as a (sometimes literal) "through-the-wall" operation from a supplier situated nearby. It is not unusual to see very large food production facilities ringed with container-manufacturing operations.

Additionally, there is a plethora of intermediate converters of sheet, film, moldings, closures, fitments, and other packaging components that can produce packages at many intermediate stages of manufacture for further modification during manufacturing. For example, it is possible to contract for PET bottle preforms and do the final stretch blow molding in-house to maximize efficiency. The decision point for the "make, contract, or buy" decision is entirely dependent on the individual operation, but as production rates climb into the several million units per year, making or contracting through-the-wall begins to become more and more attractive.

Extrusion Processes

Extrusion processes are one of the simplest and most continuous methods of producing plastic items of somewhat uniform cross section, and nearly all mass production of plastic packaging components involves extrusion at some point. As will be seen later, the extruder has been adopted to more complex methods of manufacturing as well as *hybrid* types of manufacturing, but in its simplest form the extruder can be a simple, high-output means of forming sheet, film, and tubing of various cross sections, as shown in Figure 4.32.

The extruder is a conceptually simple device consisting of a means of melting plastic resin and ejecting it through an orifice or die, something that home hobbyists are capable of building, usually for injection molding. On an industrial scale, the operation becomes more and more complex as the demands for continuous operation, precision, efficiency, and safety increase. The simplest type of extruders are ram extruders that simply have a ram forcing resin through a heated barrel (and perhaps past an annular heater to increase heat penetration). Although these are the simplest and least expensive machines to manufacture, the low thermal conductivity of
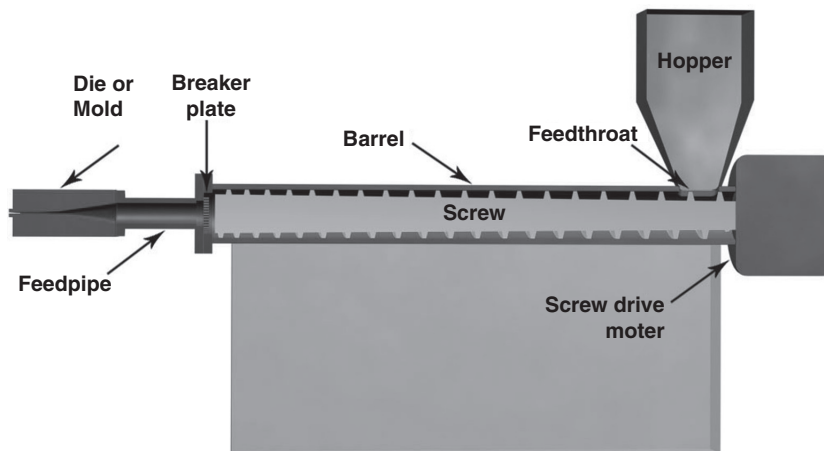
**Figure 4.32.** Cutaway View of Extruder

plastics, combined with the thick cross section of the resin charge and the lack of circulation of the cold resin, often renders this method inefficient when attempted on any scale.

To increase heat distribution in the resin, a screw-type extruder is used for most high-volume operations. This uses a rotating annular screw (or screws – dual-screw units are available) inside the extruder barrel to circulate the resin past the barrel's heater array and to allow control of temperature profiles in progressive zones as the resin progresses through the melting process from the intake hopper to discharge into a die or accumulator. For extruders that are coupled with large-volume injection-molding operations, the barrel may retract while rotating to provide an accumulated "shot" of resin for the mold, or it may feed an accumulation reservoir that is then discharged into a mold.

For sheet and film and tubing molding, the extruder will run more or less continuously to provide a constant production level, and the melted resin is usually discharged through one or more temperature-controlled dies. It is possible to gang multiple extruders into a single operation to produce co-extruded plastics, with the upper number of layers only limited by expense and the space available to feed the die. Sheet and film can be produced in a number of different methods depending on the characteristics required in the finished product. The most common methods are chill-roll, or water bath, casting and "blown" film.

Film Production

Chill-roll casting extrudes resin through a slit die onto the surface of a water-cooled die. The immediate quenching of the melt causes a very high rate of cooling and interrupts the coalescing of polymer chains into crystalline spherulitic regions, with the result being a less cloudy appearance and different strength characteristics. From there, the film may be taken through printing, coating, lamination, or other processes before final shipment, and may be oriented by stretching in the longitudinal direction by differential-speed take-up reels and laterally by the use of a tenter oven – a process that reheats the film and pulls it laterally using tenter clamps to orient it in the cross-machine direction. This is a complex and troublesome
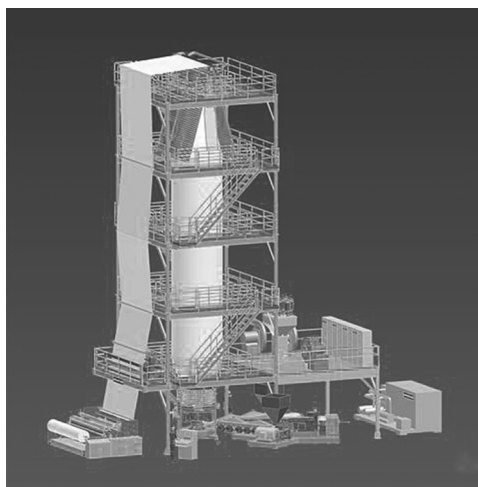
Figure 4.33. Film-Blowing Tower
Source: Alpha Marathon Company, Used with Permission
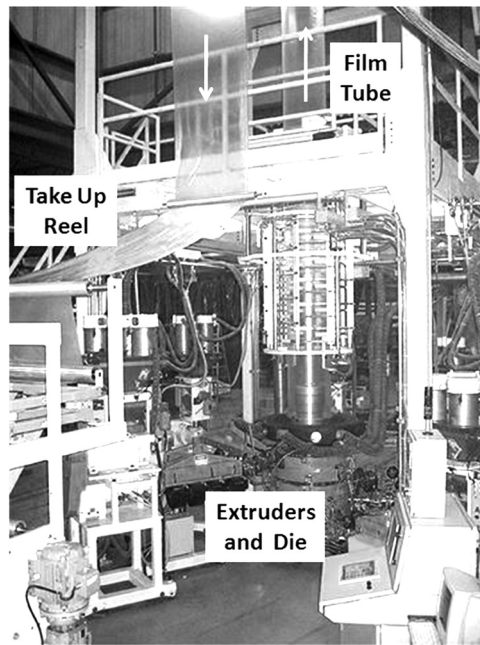
Figure 4.34. Detail of Extruders, Extrusion Die, and Film Bubble
*Source*: Alpha Marathon Company, Used with Permission

method, particularly for thin films, and has been superseded by blown tubular films in most applications.

Blown film, or tubular film production, is an extension of this process that offers an efficiency improvement for certain types of films because of its high rate of throughput. Blown film is manufactured by extruding film from a ring die that may have several stages to make multilayer films. The tube thus formed is drawn, usually upward into a multistory frame, and inflated with compressed air to form a large "bubble" of rapidly cooling plastic film that is subsequently taken up through a set of guide-frame rollers (Figure 4.34).

By controlling the rate of inflation and the rate of take-up speed, the circumferential and axial orientation may be controlled somewhat to produce a reasonably strong film or thin-wall tube, although the rate of cooling is not nearly as well controlled and so the film is often more cloudy than chill-roll cast films. By slitting one edge of the film as it is taken up, a flat film may be produced to be treated as previously described, or the tube may be left intact for use in bag or pouch making. Nearly all plastic grocery and garbage bags are manufactured in this fashion.

Film Metallization and Microperforation

Although the number and type of coatings and modifications that may be done to films used in packaging are extensive, two in particular should be mentioned here because they are a fundamental modification of the material structure and are quite common in food packaging.
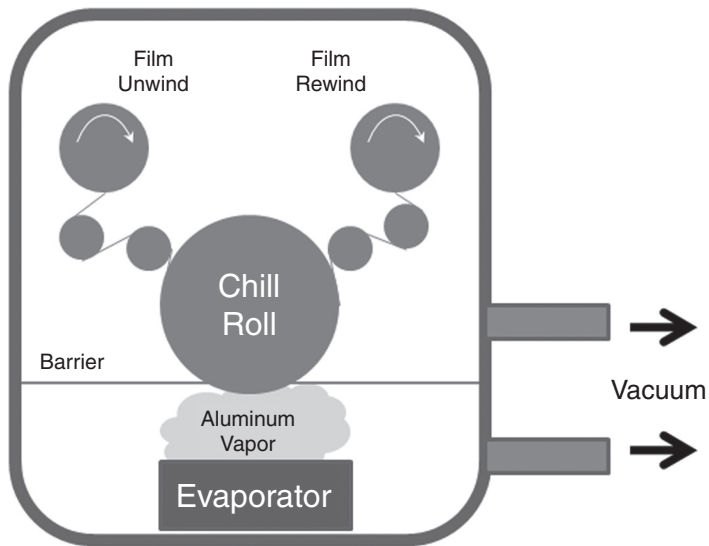
Figure 4.35. Vapor Deposition Metallization Process

Film Metallization

Metallization is the process of applying an extremely thin (ca. 3–10 nm) layer of aluminum in a vacuum evaporation process. The film is placed in a vacuum chamber and spooled through a cloud of electrically charged aluminum vapor that is attracted to and condenses on then bonds to the surface of the film as shown in Figure 4.35.

This process provides two benefits: increased barrier properties without using a laminated material, and an appealingly bright film surface that accentuates any graphics or printing. During metallization, the film may be pre-"printed" with an oil that resists adhesion of the aluminum layer to provide a pattern used in the thicker coatings in microwave susceptors. Problems with film metallization usually are a result of poor film surface condition or poor process control. Deposition may be uneven or have microscopic defects that can cause severe degradation of the barrier properties of the material. Additionally, although aluminum is a fairly stable material, it will oxidize and may change characteristics over time, particularly if there are corrosive elements in the product and if the metallization layer is not protected.

Microperforation

Microperforation causes films to become "breathable" for use with fresh and cut produce containers as well as bread bags and even some types of breathable rainwear. The perforations must be small enough to keep water droplets from penetrating via the droplets' surface tension but large enough so that gasses and water vapor may be exchanged. Hole sizes using mechanical puncturing systems, laser, or electrostatic discharge equipment may range from 2 to 150 μm (or larger). Gas exchange rates may increase in practical applications by at least an order of magnitude (to more than 1,000 cc/100 in^2-day) to that approximating porous materials such as paper, but retaining waterproof characteristics so that liquids in the product are not lost or

spilled. Additionally, some preferential gas transfer may be achieved with CO_2 being retained and oxygen transmission rates being much higher.

Extrusion Blow Molding

Extrusion blow molding of rigid and semi-rigid containers is an extension of tubing extrusion and resembles the manufacture of glass containers in several respects. Blow-molded containers begin as parisons that are extruded as molten tubing that is placed into a mold and inflated. Contact with the coolant chilled surfaces of the die cools the inflated parison and locks the plastic into shape. Extrusion blow-molded containers are common in food and household chemical products, and nearly all plastic dairy containers are manufactured in this manner. Size limitations on blow-molded structures have increased steadily, so it is currently possible to blow mold drums and tanks, as well as boats and vehicle parts. In practical terms, consumer-level packaging is most often limited to large containers of detergent and other household chemicals.

Because of advances in extrusion technology, it is possible to extrude a multilayer parison to incorporate recycled or filler materials, or to incorporate a barrier layer to extend shelf life. Blow-molded bottles, particularly those of polyesters such as PET, are very often layered with an oxygen barrier layer (often polyvinyl alcohol) to reduce discoloration of the surface layer of product that may make the container appear to have been spoiled. A variation on the co-extrusion strategy has allowed container manufacturers to *stripe* the parison – and thus the container – with a line of uncolored resin, producing a container with a visible fill-level indicator that is often used for household and automotive products.

Because of the extension of materials into the far crevices of a mold, it is often necessary to control the thickness of the parison tube via a variable extrusion die to produce a *programmed* parison. This allows the areas that require more resin to extend the molding farther into the mold to be sufficiently supplied.

Injection Blow Molding and Stretch Blow Molding

Injection blow molding resembles glass molding practices in that an injection-molded preform is produced and then inflated, often in a separate step that reheats the original molding as previously described. The advantage offered by this method is most apparent during *stretch blow* molding when the polymer structure is subjected to severe cold-drawing orientation by rapidly inflating the reheated preform. This produces a container that has both an accurately manufactured finish and is highly oriented, resulting in a very-high-barrier package with very good optical properties. It is possible to produce multilayer stretch blow molding using a carefully injection-molded preform, which allows the manufacture of highly accurate high-volume containers as well as those with non-spherical geometries while keeping wall thicknesses intact.

The ability to produce a practical and economical alternative to glass containers has driven both the food and soft-drink industry into using of these containers for their products, and has created the capacity for even small bottlers to manufacture oriented bottles from commercially produced preforms using specialized machinery. One of the hidden benefits of these types of containers is that when failure occurs, they do not disintegrate into a large number of dangerous splintered pieces, the way glass does. This not only provides a lighter and more economical container, but relieves concern (and costs) associated with consumer liability issues. Additionally, the recouped downtime on filling lines has proven to be a bonus. When filling lines are converted to plastic bottles and jars, the need to stop the line and clean a large

portion of it out of fear of glass fragment contaminants is eliminated, allowing more continuous production and higher plant efficiencies. This is particularly pressing in the food industry where fears of contamination from broken glass, and the downtime incurred from cleaning up on-line breakage, have driven a widespread industry movement toward plastic containers in many market segments, particularly baby foods.

Surface Treatments of Blow-Molded Containers

The continuing search for low-cost ways to produce a high-barrier container have led to several ways of surface treatment of containers that have shown sufficient commercial potential that their adoption has been growing. Fluorination is a process by which polyolefin containers are subjected to concentrated fluorine gas, which displaces the C-H bonds and generates a C-F structure that approximates polytetrafluoroethylene (Teflon®) at least at the surface level of the material. This in turn creates a high gas barrier layer that can extend the shelf life of products or reduce volatile losses. Because of the toxicity of fluorination, this process is usually contracted through dedicated providers.

Diamond and Silicone Microcoatings

Microcoatings of impermeable materials have been under investigation for some time and work well, but are limited by production speeds in some instances. Coating is done by Plasma Enhanced Chemical Vapor Deposition (PECVD) of oxidized silane or ethane compounds to provide a crystalline carbon or silicone coating. The prospect of a diamond-studded bottle may be appealing, but the layers are typically only a few μm thick and are transparent, although they provide substantially reduced gas and vapor transmission rates and reduced off-flavor and off-odor contamination when used inside the container.

Injection Molding

Injection molding is used to produce precise components that cannot be formed by thermoforming or blow molding. In injection molding, melted resin is forced from the melter/extruder into the mold through a *sprue* and then through runners into the individual mold cavities, as shown in Figure 4.36. Considering that production tooling for injection molding can be very expensive
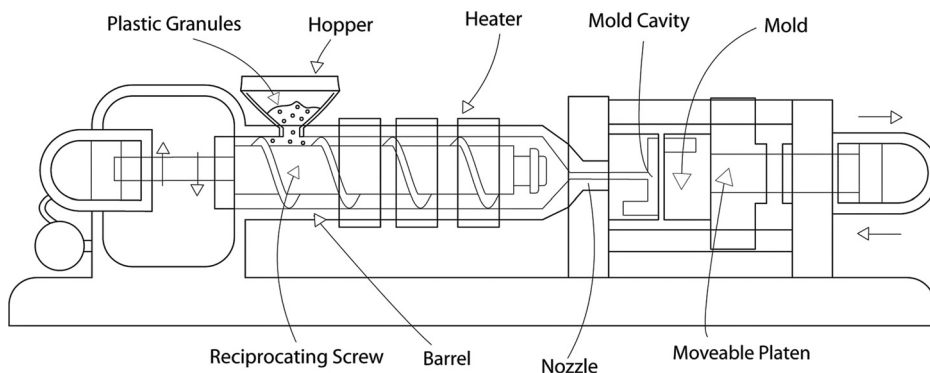
Figure 4.36. Extrusion Injection Molder

and cycle time is at a premium, the molds may be designed to do many simultaneous moldings at once. Dimensional tolerances as well as temperature control requirements are usually exacting in injection molding. For small moldings such as beverage bottle screw caps, a hundred or more caps may be produced in a single cycle, whereas for very large moldings such as tubs and pails, there may be only one molding per cycle, although the molds may be mounted on rotating fixtures to keep the injection equipment moving at full capacity. Very large moldings such as plastic furniture and vehicle parts may require specialized molding machinery and enormous resin reservoirs to manage each "shot."

Rotational Molding

Rotational molding is mostly used for very large and hollow or open structures and operates by tumbling the mold to distribute a thin layer of resin over the interior surface of the cavity. Because there is no interior male component to the molding process, the interior surface remains distinctively unfinished. A variation on the process uses centrifugal force to assist resin distribution during injection molding. Tooling is generally less expensive than for many other types of molding, but good resin distribution during the molding process can require some refinement. This method is also used for other types of specialized molding such as hollow chocolate figures.

Thermoforming

Thermoforming is often used to produce trays and bowls for the food packaging industry, as well as many types of blisters for card-backed packaging and many household and vehicular items. It has been used since the 1930s to form optically clear aircraft canopies from acrylic sheet, although these methods used heated fluid to soften and force acrylic against a mold. The current radiant heat and vacuum system did not appear until 1940 and has been adapted to manufacture many different types of thin-wall structures ever since.

Thermoforming processes, which are simple enough to be often used by hobbyists to form parts and by industrial designers to form prototypes, consists of heating plastic sheeting – most often with radiant heat from gas, infrared, or resistance heaters on one or both sides – draping a mold with the softened sheet, and using a combination of pressure, vacuum, and mechanical assist, as appropriate, to form the film to the contours of the mold. In all cases, the pressure differential – whether mechanical, pneumatic, or hydraulic – forces the sheet to form to the desired shape and with the desired wall thickness.

Packaging applications of thermoforming are typically used for trays, bowls, and blister covers that are used for display packaging, internal supports for consumer electronics, containers for frozen and shelf-stable foods, and as aftermarket food storage containers. Thermoforming containers for food items such as frozen dinners and dairy products are very often done in-house using externally supplied sheet and film stock. In many instances, food items are filled into trays that are formed on line from rolled sheet stock, and then are sealed with film or lidded with a similarly molded cover and trimmed in subsequent steps before retorting or freezing. This has the effect of efficiently compacting an entire forming, filling, and sealing line for relatively complex menu items into a small area, and minimizing the amount of packaging material stored by doing conversions in process. It is easily adapted to changes in tray design and product by changing the dies used in the molding step.
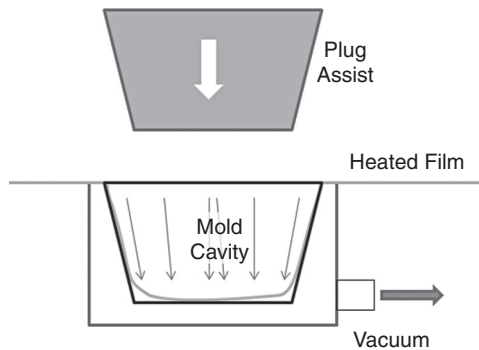
Figure 4.37. Simple Thermoforming Cavity with Plug Assist

Beyond this, there are several different types of thermoforming that are used for different types of plastics. Conventional thermoforming, previously described, forms materials in the melt phase at higher temperatures, but this type of forming makes materials such as polypropylene hard to manage because of the relatively small temperature window and a tendency for poor thickness distribution. In response to this, Solid Phase Pressure Forming was developed, which forces the molding into shape at a temperature below the melt phase but above temperatures approximating its glass transition point. This requires both good mechanical molds with smooth surfaces and careful control of the temperatures (154–158°C for solid-phase molding of a clarified polypropylene homopolymer, as compared to higher temperatures for melt-phase conventional thermoforming) in the molding machinery, as well as usually requiring plug-assist in making the final moldings. The result of this is to allow polypropylene and other materials to be accurately molded using thermoform equipment with good optical qualities and thickness distributions.

As shown in Figure 4.37, thermoforming is conceptually simple, and the molding forms can be built of low-temperature materials such as wood or plastic, if necessary. To control the wall thickness distribution, however, some care must be taken with the mold design to ensure that the plastic sheet or film is not overextended by drawing it too deeply for the method used. This may result in a molding that, although not torn, will be too weak to be useful. Additionally, as with nearly any non-sectional mold, there must be enough draft in the mold design that the finished piece can be easily extracted. Reversing the vacuum with a burst of air pressure may help extract the moldings.

Synthetic Papers

Synthetic papers generally fall into two classes: printing film and *tearproof paper*. Printing film is a thermally stable film that is coated with a stable surface that resembles paper and may be used in thermal printing systems such as laser printers without melting. These are typically used for weatherproof labels, documents, and maps and do not currently have many packaging applications, although they may be used for tagging and labeling machinery and electrical equipment.

Tearproof papers (such as Tyvek®, a high-density PE fiber structure) are actually a non-woven fabric and are typically manufactured from polyethylene, polypropylene, polystyrene, or polyester fibers, which provides the desired flexibility and strength, and that are then formed

into non-woven sheets. These provide a very strong, stable structure that resembles paper but is dimensionally stable, resists boiling water, and can be fabricated to be porous enough for gas sterilization while preventing microbial recontamination. Other forms are used as structural vapor barriers, shipping envelopes for overnight delivery services, containers for sharp objects, sailmaking, and other specialty applications that require a very strong, flexible material. Cost considerations are still preventing the use of many of these materials as a replacement for more traditional pouch papers, but the cost is often justified in specialty applications such as boil-in bags and single-pack coffee filters.

Multiple Material Packages

Laminates and Multiple Material Packages

Although the term "Composite Material" conjures up images of aerospace applications involving expensive high-tensile fiber laminations, composite materials have been used for many years in the packaging industry. Often, several materials will be combined to provide a mix of contributions that can be carefully fitted to the most optimal physical and economic properties to suit the particular product application.

There is a distinction between coatings and laminations, in that laminations usually involve the adhesive joining of several (often very different) materials ranging from metallic films to cloth. Although it may be possible to coat paper with a polymer film so that the net effect would be similar to laminating the two materials, it would be impossible to coat paper with aluminum and then with a layer of polymer film on top to protect the foil. Unfortunately, as recycling of materials becomes more and more of an issue, the multiple-material nature of composites may work to their disadvantage because they cannot readily be decomposed into their constituent parts for separate recycling.

Lamination Processes

The simplest lamination processes are those that simply glue two or more layers of material together using an adhesive. This may be done in several ways: either using a contact adhesive that is first applied to each of the layers then dried prior to lamination, or using a liquid adhesive that sets fully after the lamination process. Additionally, a polymer melt may be used as a lamination adhesive, with an extrusion device feeding molten adhesive between layers in the lamination process. Simple glue processes have the advantage of being able to use simple equipment for small runs of materials, but have the disadvantage of requiring water, organic solvent removal or glue polymerization at some point in the manufacture of the laminate. Contact adhesives often require solvent removal during coating, which adds to the complexity of the process, and glues that adhere by solvent removal or polymerization may require time for the proper bonding to be established.

Thermal lamination may rely on heat and pressure to laminate materials together, most often using a thermally activated adhesive *tie layer* to adhere the layers together. This has the advantage of not requiring solvent removal in the lamination step, and providing a nearly instant high-tack bond in the materials. It is not always necessary to have a tie layer if the final effect is to bond a layer of a low-melting-point polymer to the surface of a substrate, but most often, a tie layer has a lower melting point than the laminate materials to reduce thermal distortion in

the final materials. For materials such as foil, a bonding layer is necessary, and many foil types require a great deal of care in handling to reduce problems with holing and tearing.

Design Considerations for Laminates

Materials Structures

Laminates can be assembled from many types of materials depending on the requirements of the product. Most types of laminates used for pouches and bags are designed with five basic and somewhat subjective functions in mind: cost, strength, appearance, barrier, and sealability.

Cost optimization of materials is the broader intent of most packaging laminates, so careful attention must be paid to the overall costs of the materials and how well they can integrate into the overall packaging system. False economies occur when a lower-priced material is substituted for the originally specified one if it costs the packaging operation more in defective products, sales losses, or production downtime. Using a spreadsheet, one can construct a simple model for the initial optimization of laminates that considers both the costs of each material and the properties provided by each layer. The consideration of barrier will add to the complexity of this, and will demand a *Pareto optimal* solution – one that balances both strength and barrier when considering the final value of the material – but the solution methods are still quite simple. As with many types of composite materials, it will be necessary to evaluate prototypes of the materials to ensure that their values are as predicted, because the diverse mechanical and barrier characteristics can interact in unusual ways. Strength in simple food product packaging applications has traditionally come from a paper layer, most often a bleached kraft pouch paper, although the current trend in newer types of consumer products are to replace this with a high-strength materials such as polyester to improve the surface appearance when design copy is reverse-printed inside the lamination. It must be remembered that each of the layers in a laminate will contribute something to the overall mechanical strength of the material, so a packaging material that has a critical stress higher or lower than necessary can be modified to adapt to the requirements at hand, but this should be done as a last step when the other functions – particularly barrier properties – are satisfied.

Appearance can be a very subjective term. In the case of a dry-ingredients pouch that is included in a boxed dinner mix, the appearance requirements can be quite minimal, but for newer types of consumer products such as snack foods and retort pouches, it may be necessary to provide an appearance that not only distinguishes it from other similar products, but will overshadow the competition in more traditional types of packaging. Many new types of packages are being produced that take advantage of the bright appearance possible when laminates are printed on the reverse side of the outer layer of film (so that the copy shows through the clear layer), as well as metalized films that add a bright, reflective layer to the package. Other types of surface features such as a microembossed holographic image or clear window can be included in these types of packages, often to good effect.

Barrier characteristics depend on the type of materials used as well as their synergistic interactions. Aluminum foils below 0.001 in. thick with a simple polyethylene film will decrease permeability markedly. Thus, the addition of an extremely fine layer of foil will create an enormous increase in barrier characteristics. Similarly, the combination of several layers of polymer with or without other materials can be tailored to create barrier characteristics that are

specifically suited to an application, although this often requires that the prototype material is evaluated because the synergistic effects of lamination and the effect of the adhesive *tie layers* can be difficult to predict with a high degree of accuracy.

In addition to the traditional passive barriers afforded by more traditional materials, it is possible to include *active* materials in laminates, such as an oxygen-scavenging layer, to provide a proactive removal of harmful materials from the product. These types of materials are seeing more use in pouches, composite cans, and other laminate structures.

Sealability of laminates, in this case referring to heat sealing, can be a complex issue when the design requires very-high-speed manufacture or the inclusion of unusual materials. Because there is very little process optimization in sealing processes, with most adjustments being done on a guesswork basis, it can be difficult to predict exact sealing parameters for a single material that may come from several suppliers and be run on many different machines in diverse manufacturing locations. In most cases, an ad hoc knowledge of the sealing requirements is used to specify a layer of sealing material that is adequate, if not optimal. The thermal conductivity of the layers will play an important part in the sealability of the laminates as well, and if one of the internal laminates has a particularly low melting point, it may be problematic in that the pressure of the sealing jaws may cause partial delamination of the film due to melting and cohesive failure near the seal area. Sealability of laminates that use cold or contact adhesives is a much simpler issue provided that the adhesive does not interact with the polymer and has not caused changes in the film during application. Package sealing will be dealt with more comprehensively in Chapter 5.

Multiple Morphology Laminates

The problem with separation of multiple-material laminates for recycling has highlighted an intriguing possibility in laminated polymer films – that of multiple morphology laminates. It is possible to produce a film (polyethylene, for example) that is highly oriented for strength and barrier and another polyethylene film that is largely amorphous for sealability. Combining these materials will a structure that will yield a good mix of characteristics in a structure that can be considered as a single material, and is readily recycled, but that might previously have required effectively unrecyclable sets of different laminated materials.

Laminates for Aseptic Processing

Laminates that are used in aseptic processing operations must both maintain the microbial integrity of the package after formation and filling. These typically have separate layers for strength, barrier, and heat sealing, although it is possible to produce them with fewer. A typical juice box package is usually made of coated or laminated paper, foil, and a heat-sealable inner plastic layer. Many aseptic packages are supplied in ready-to-erect form and are assembled and sterilized as part of the aseptic processing. It is also possible to use simple laminates as part of a form-fill-seal system in the aseptic process, as has been done with many of the early aseptic packaging systems. Other laminates are used as tray and lidding stocks in aseptic filling operations and may be sterilized by radiation, hydrogen peroxide, or ultraviolet light prior to final sealing in an integrated filling-and-sealing line that operates under sterile conditions, as described in Chapter 6.

Laminate and Composite Cans

Composite cans have been a feature of food packaging almost from the beginning, used for dry goods as well as moist products in later years. The ubiquitous oatmeal package is a composite can that has been laminated from paper, although many different types of composites are possible. Multiple layers of paper, foil, plastic film, and even foam are possible, with the structure optimized for the properties required for the product. Composite cans are manufactured by spooling materials onto a cylindrical mandrel in a continuous spiral, so that the formed laminate tube is then cut and fed off the end of mandrel on a continuous basis, allowing for a relatively high-speed production and the absence of a distinct side seam. Convolute cans are formed in a similar manner, with the materials being wound perpendicular to a forming mandrel that rotates in alternating directions to form a layered, seamed can body – this type of equipment must stop forming long enough for the formed blanks to be removed from the mandrel before reforming the next set of materials, which results in lower production speeds.

Composite cans may be produced in any number of geometries ranging from cylindrical to nearly polygonal – slightly rounded corners are a necessary result of the fabrication process – and can be capped at either end with metal, plastic, or paper seals, dispensers, and other types of fitments used to dispense product.

Two-piece cans made from thin aluminum sheet laminated on both sides with PET film have emerged in Japan and Europe in recent years. These have been commercialized most widely in Japan under the names of HiRetoflex® and TULC®, for small trays and beverage cans, respectively. A similar material, Ferrolite®, developed jointly by Carnaud Metalbox and British Steel, is also used in Europe.

Rigid Composite Tubes

Rigid composite tubes are seldom used in the food industry but are quite common for use with construction adhesives and sealants, as well as many other industrial materials. These may be made of rolled paper with or without foil and paper layers in a manner similar to "paper" cans, and incorporate a piston on one end to mate with a dispensing gun that pushes the product out and a molded nozzle on the other. Traditional composite tubes have a membrane seal fitted behind the nozzle that must be punctured before use, whereas molded plastic tubes have sufficient integrity that they are well sealed until the tip of the nozzle is cut off. Current industry trends are toward single-piece tubes of molded plastic because of durability, simplicity, and cost.

Composite Squeeze Tubes

Because of the difficulty of labeling metal tubes, and their tendency to remain wrinkled and crack in everyday use, the development of molded composite tubes has resulted in tubes that are more durable and in many cases can have a great deal of graphic appeal. These are used for frostings, spices, and pastes in the United States, but their use is much larger in Europe and Asia and includes tomato products, chocolates, butter, and sour cream, among other applications. Two-piece plastic and composite tubes are produced by first making the tube that will become the tube body – for a plastic tube, this may be manufactured directly by single or multilayer extrusion. After this, the tube head and shoulder is molded to the body either by heat sealing a preformed molding to the body tube or by compression molding or extrusion molding to the tube. The head and shoulder molding will typically have the complete shoulder, the threaded

closure, and orifice. For single-piece tubes, such as those used for cake frosting and construction glues and sealants, the entire structure may be injection-molded in a single injection-molding step. After molding, the tube is printed, usually by offset printing, and has the cap applied before shipping to the filler. When plastic or composite squeeze tubes are filled, the ends are typically heat-sealed rather than being rolled and crimped as with metal tubes, and a date or production code may be incorporated into the sealing machinery.

Endnotes

* The portability and ease of use of paint in tubes also changed the face of art itself, allowing "plein air" (outdoor) painting to flourish among the impressionist and landscape painters of the late 1800s. Previous to this development, any outdoor paintings were typically painted from memory or sketches in part due to the difficulty of handling the pigments and oils and mixing them in the field.

** A Pareto optimal solution is, in the most general terms, a "best mix" solution that provides the most benefits at the lowest cost for all concerned, and cannot be improved in one measure without penalizing another. It is named for Vilfredo Pareto, the Italian economist who is responsible for the 80/20 Rule: that roughly 80% of the effects come from 20% of the causes.

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