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James L. Throne

Understanding Thermoforming

2nd Edition

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11 Polymers and Plastics

Thermoforming uses plastic sheet that is heated, stretched, cooled, and mechanically cut. For the most part, amorphous plastic sheet is manipulated as a rubbery solid. Crystalline plastic sheet is manipulated either as a rubbery solid or as an elastic liquid close to the polymer melting temperature. As a result, the solid or elastic liquid properties of polymers are more important than pure viscous properties. In this chapter, important polymer characteristics are examined. Then the characteristics of specific thermoformable polymers, including biopolymers are discussed. Filled, reinforced, multilayer, and foamed polymer characteristics are considered.

11.1 Polymer Characterization

Long chains of organic molecules

Polymers are pure organic molecules consisting of long chains of simple molecules. As an example, polyethylene, the polymer most widely used globally, is made by reacting ethylene gas at high temperature and pressure, in the presence of a catalyst. Ethylene has a chemical composition of $H_2C{=}CH_2$, where C is carbon, H is hydrogen, and the symbol "=" indicates a double bond or a reactive link between the carbons. The ethylene molecule is called a *monomer*. It has a melting temperature of –169 °C and a boiling temperature of –104 °C.

The structure of polymerized ethylene or polyethylene (PE) is often written as $H_2C{-}(CH_2{-}CH_2)_x{-}CH_2$, where x represents the number of ethylenic segments or *mers* in the polymer. If the value of x is relatively small, say on the order of 100, the polymer is a high-temperature wax. If the value of x is relatively high, say on the order of 15,000, the polymer has a melting temperature of approx. 130 °C. It degrades before it boils. This polymer is generally processed by one of the standard plastics processing methods such as injection molding, blow molding, rotational molding, extrusion, or thermoforming. If the value of x is very high, say on the order of 300,000, the polymer, called ultrahigh molecular weight polyethylene (UHMWPE), is usually intractable in normal processing equipment. Techniques such as compression molding or compaction-sinter-fusion of powder may be required.

11.1.1 Plastic vs. Polymer

Polymer + additives = plastic

Most plastics practitioners generally consider the words *plastic* and *polymer* to be interchangeable. Technically, they are not. Polymers are by definition the result of chemical reaction of organic monomers. Nearly all polymers are mixed or compounded with additives such as thermal stabilizers, antioxidants, color correcting dyes, internal and external processing aids, and product-specific additives such as fire retardants, colorants, UV stabilizers, fillers, reinforcing agents, and others. The term *plastic* refers to the polymer and its additives, delivered to the

processing equipment as resin pellets, powders, or sheet. As noted earlier, the terms *plastic* and *polymer* are used interchangeably here.

11.1.2 Thermoset and Thermoplastic Definitions

Definitions

There are two general categories of polymers – thermoplastic and thermosetting. When the polymer can be heated and shaped many times without substantial change in its physical characteristics, it is a *thermoplastic*. Polyethylene (PE), polystyrene (PS), and polycarbonate (PC) are examples of thermoplastics. When the polymer cannot be reshaped after being heated and shaped for the first time, it is a *thermoset*. Epoxies and phenol-formaldehyde or phenolic are examples of thermosetting polymers. Thermoforming is primarily concerned with conversion of thermoplastics.

11.1.3 Crystalline and Amorphous Definitions

There are two general categories of thermoplastics – *amorphous* and *crystalline* or semi-crystalline. When any thermoplastic polymer is heated from a very low temperature, it undergoes a physical transition from its low-temperature glassy state to a rubbery state. Although this transition occurs over a temperature range of several degrees, usually only one temperature is

Table 11.1: Transition Temperatures of Some Thermoformable Polymers

Polymer	Glass transition temperature [°F (°C)]	Melting temperature [°F (°C)]	Heat distortion temperature 66 psi (0.46 N/mm^2) [°F (°C)]
Polystyrene	200 (94)	– (–)	155–204 (68–96)
PMMA	212 (100)	– (–)	165–235 (74–113)
PMMA/PVC	221 (105)	– (–)	177 (81)
ABS	190–248 (88–120)	– (–)	170–235 (77–113)
Polycarbonate	300 (150)	– (–)	280 (138)
Rigid PVC	170 (77)	– (–)	135–180 (57–82)
PETG	180 (82)	– (–)	158 (70)
LDPE	–13 (–25)	239 (115)	104–112 (40–44)
HDPE	–148 (–100)	273 (134)	175–196 (79–91)
Cellulose acetate	158,212 (70,100)	445 (230)	125–200 (52–93)
Polypropylene	41 (5)	334 (168)	225–250 (107–121)
Copolymer polypropylene	–4 (–20)	302–347 (150–175)	185–220 (85–104)
PET	158 (70)	490 (255)	120 (49)

Glass transition temperature

reported as the *glass transition temperature*. Polymers that only have glass transition temperatures are called *amorphous* polymers. Polystyrene (PS), polyvinyl chloride (PVC), and polycarbonate (PC) are examples of amorphous polymers. Amorphous polymers constitute about 80% of all polymers that are thermoformed. Furthermore, about 70% of all amorphous polymers that are thermoformed are styrenic in nature – polystyrene (PS), impact polystyrene (HIPS), ABS, styrene-acrylonitrile (SAN), and others.

Melting temperature

When polymers exhibit a second physical transition, from a rubbery state to a fluid, molten or melt state, they are called *crystalline* or *semi-crystalline* polymers. This second transition usually occurs over a temperature range of several degrees, although usually only one temperature is reported as the *melting temperature*. Polyethylene (PE) and polypropylene (PP) are crystalline polymers. Generic transition temperature values for several thermoformable polymers are presented in Table 11.1.

All polymers have glass transition temperatures. Only crystalline polymers have melt temperatures.

11.1.4 Homopolymers, Copolymers, Terpolymers, and Blends

Homopolymers

If only one polymer specie or *moiety* is used in a given plastic recipe, the polymer is called a *homopolymer*. Low-density polyethylene (LDPE) and general purpose polystyrene (GPPS) are examples of homopolymers. Polyethylene terephthalate (PET) is made by reacting two moieties, ethylene glycol and terephthalic acid, but only one type of repeat unit or *mer* – ethylene terephthalate – is produced. Therefore, PET is a homopolymer. Polycarbonate (PC) is another homopolymer, made by reacting two moieties, bisphenol A and phosgene, to produce a polymer with only one repeat unit.

Copolymers

If one polymer is reacted with another, the polymer is called a *copolymer*. Impact polystyrene (HIPS) is an example, where styrene monomer is reacted with butadiene monomer. Many copolymers are used in thermoforming. Other examples include polypropylene-polyethylene (coPP), polyvinyl chloride-polymethyl methacrylate (PVC-PMMA), and styrene-acrylonitrile (SAN). If three polymers are reacted together, the polymer is called a *terpolymer*. The classic terpolymer is ABS, which is a reacted product of acrylonitrile, butadiene, and styrene.

Terpolymers

Occasionally, two polymers are extrusion or melt blended together to produce a specific plastic recipe. The classic blended polymer is modified polyphenylene oxide (mPPO). It is a near-equal blend of polystyrene and polyphenylene oxide, with good impact resistance and fire retardancy properties. Because these polymers are miscible, the blend is often called an alloy or an interpenetrating network polymer. A blend version of ABS is also produced by compounding SAN and HIPS.

11.1.5 Additives, Fillers and Reinforcements

PVC additives

Additives are used with most polymers. Some of these additives are required to make the polymer processible. Polyvinyl chloride (PVC) must be compounded with many additives to make it processible and useful for many applications. Octylphthalates are plasticizers that lower

PVC flexural modulus and glass transition temperature, producing flexible vinyl (FPVC) sheet that is thermoformed into interior automotive door panel and instrument panel skins.

Anti-block agents

Other additives, called anti-block agents and slip agents, are needed to prevent rolled sheet from sticking together. Additives such as antimony oxide are added when fire retardancy is needed. Odor suppressants are used with most polypropylenes, particularly when the product is to be used for rigid food containers. Anti-static agents are used to minimize static discharge when the product is to be used in electronic packaging. Additives are often used in concentrations of 1% (wt) or less.

A list of common additives is given in Table 11.2.

Fillers

Even though there is growing interest in forming filled and reinforced plastic sheet, nearly all thermoplastics that are thermoformed are neat, meaning that they contain no fillers or reinforcing elements. However, many types of fillers can be compounded into polymers, as noted in Table 11.2. Most fillers are inexpensive inorganic minerals such as calcium carbonate and talc. In general, fillers increase polymer stiffness and decrease polymer impact strength. Fillers do not appreciably alter transition temperatures. As a result, increased filler loading implies increased applied forming forces at conventional forming temperatures. Because fillers cannot be deformed, the degree of drawdown is restricted when forming relatively high filler-loaded sheet.

Fibers

Glass is the predominant fiber used with thermoplastics. Mineral, metal, and carbon fibers are also used, as noted in Table 11.2. Organic fibers such as sisal and cotton lintel are difficult to compound into thermoplastics and so are not often used. Short-length reinforcing fibers behave somewhat like fillers, increasing polymer stiffness and decreasing polymer impact strength.

Table 11.2: Fillers, Fibers, and Additives to Thermoformable Polymers

Additives	Fillers	Fibers
• Antioxidants – Lubricants – Internal • Viscosity suppressants • Antiblocking agents • Plasticizers • Antistatic agents • Pigments • Heat stabilizers • Ultraviolet stabilizers • Nucleating agents for crystallization • Nucleating agents for foam • Antimicrobials • Flame retardants • Fragrance enhancers • Foaming agents	• Silica and silicate minerals • Glass • Calcium carbonate • Metallic oxides • Other inorganics such as barium sulfate, silicon carbide • Metal powders • Carbon • Cellulosics such as wood and shell flour	• Cellulosics such as cotton, jute, sisal • Synthetic fibers such as nylon • Carbon fibers • Fiberglass • Glass yarn • Whiskers • Metallic fibers

However, when short-fiber filled sheet is formed, the fibers locally orient in the local direction of stretch. As a result, the mechanical performance – stiffness, impact strength, elongation to break – of the formed part may vary greatly across the part.

Long-length reinforcing fibers greatly inhibit the extensibility of the sheet. Typical problems include fiber prominence and resin-rich/resin-poor regions, particularly in small radii regions. As a result, high fiber-loaded sheet often requires special forming equipment such as heated, matched steel molds and high pressure forming presses. Autoclaves similar to those used for glass- and carbon-fiber thermoset composite forming have been used with high fiber-loaded engineering plastics.

Nanoparticles

Nanoparticles are extremely fine inorganics such as intercalated clay or kaolin that are compounded into polymers to improve stiffness without dramatically affecting impact strength or transparency. Typically, the compounding level is less than about 3% (wt). Nanoparticles should have at least one dimension that is less than 100 nanometers or 0.1 μm. By comparison, human hair is on the order of 20 to 100 μm in diameter[22]. The keys to successful nanocomposite compounding are the additives that minimize particle agglomeration. Commercial experience with thermoforming nanocomposite sheet is very limited. Because of this, little is known about formability of polymers containing appreciable amounts of nanoparticles. It is anticipated, however, that nanocomposite sheets, like filled plastic sheets, will be stiffer at plastic forming temperature and, as a result, pressure forming will be preferred over simple vacuum forming.

11.2 The Thermoforming Window

The thermoforming molding diagram or the interaction of sheet extensibility, sheet temperature, and applied force was discussed in some detail in Chapter 9.

Material specific characteristic

The thermoforming window is a plastic-specific criterion. It is considered to be the temperature range over which the polymer is sufficiently supple or deformable for stretching and shaping into the desired shape at a given applied force. Typically, amorphous polymers have broader thermoforming windows than crystalline polymers. Polystyrene, for example, can be formed at temperatures as low as 260 °F (127 °C) or about 50 °F (30 °C) above its glass transition temperature. It can be formed at temperatures as high as 360 °F (180 °C) or only a few degrees below the temperature at which it is injection-moldable. On the other hand, homopolymer polypropylene (homoPP) is so fluid above its melting temperature of 330 °F (165 °C) that its thermoforming window may be no more than one degree wide. Because thermoforming equipment is not designed to control plastic sheet temperature this accurately, homoPP is frequently formed at temperatures just below its melting temperature[23]. Even then, the forming window range may be only two or three degrees.

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22 "Human hair", Wikipedia, May 2007.

23 When homopolymer polypropylene (homoPP) is formed below its melting temperature, the process is sometimes called Solid Phase Pressure Forming (SPPF), to contrast melt phase forming or forming crystalline polymers above their melting temperatures.

11.3 Thermoformable Polymers

As stated earlier, the majority of thermoformable polymers are amorphous, and the majority of amorphous polymers that are thermoformed are styrenics. Other amorphous polymers include vinyls, acrylics, cellulosics, polycarbonate, certain polyesters, and many biopolymers.

11.3.1 Polystyrene and Other Styrenics

Typical physical properties for styrenics are given in Table 11.3. About twenty years ago, polystyrene (PS) and the family of styrenics such as HIPS, ABS, SAN, ABA, and OPS, dominated the thermoforming industry. For example, in 1983–1984, nearly 80% of all thermoformed products were styrenics.

PS properties

Unmodified PS is characterized as having a high modulus, a low room temperature elongation at break, excellent clarity, superior hot strength drawability, and a very broad thermoforming window. Although PS is easy to thermoform, its trim dust is tenacious and improper trimming can cause edge microcracks that ultimately lead to cracking and part failure. Highly stretched regions in formed parts tend to be very brittle.

Imroving properties

To improve PS impact resistance, it is either melt-blended or co-reacted with butadiene, a synthetic rubber, to form impact polystyrene (HIPS). The rubber forms a second phase, rendering the polymer hazy to translucent to opaque, depending on the size of the rubber moiety and the level of rubber, which typically ranges from 2–10% (wt). Rubber-modified polystyrene has improved impact strength but reduced modulus, tensile strength, and formability.

Acrylonitrile is co-reacted with polystyrene to produce styrene-acrylonitrile (SAN), a tough, transparent polymer that finds extensive use in appliance manufacture. Acrylonitrile-butadiene-styrene (ABS) is a tough, high-impact terpolymer that is used in electronic and medical cabinetry, appliances, and interior and exterior truck cab components.

Because rubber-modified styrenics yellow when overheated, care must be taken to avoid excessive heating during thermoforming. ABS is prone to moisture absorption. As a result,

Table 11.3: Physical Properties for Styrenic Family of Polymers

Property	PS	HIPS	ABS	SAN	35% GR SAN
Density [kg/m^3]	1050	1040	1050	1080	1360
Elongation at break [%]	3	40	15	5	2.7
Glass transition [°C[	105	100	105	106	106
Processing temp [°C]	160	155	165	165	200
HDT at 1.82 MPa [°C]	100	90	95	102	105
COE [10^{-6}/°C]	60	60	65	60	3
Tensile strength [MPa]	40	30	50	75	110
Flex strength [MPa]	80	80	75	135	150

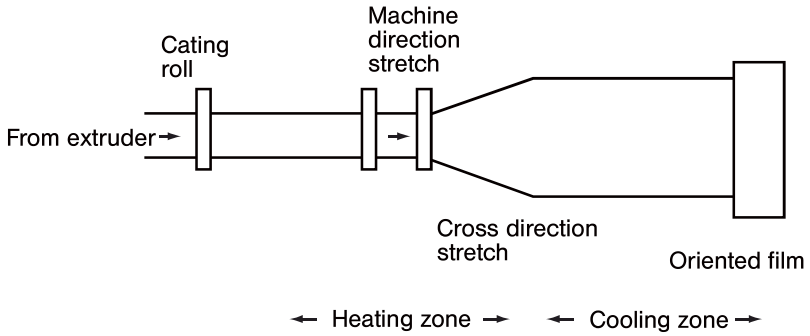


Figure 11.1: Sequential biaxial orientation of light-gauge sheet, using a tenter to achieve cross-machine orientation

ABS sheet must be kept dry prior to thermoforming to minimize moisture bubbles and surface defects in finished parts.

UV sensitive

All styrenics are ultraviolet (UV)-sensitive. As a result, styrenic sheet is usually laminated with acrylic (PMMA) or fluoropolymer (FEP) film prior to forming products for exterior applications. Solvent-based paints and certain acrylic paints adhere very well to styrenics. As a result, finished parts are often painted for exterior applications. Nearly all styrenics are solvent-weldable.

Orientation

Oriented polystyrene (OPS) finds extensive application in quality bakery containers such as cake covers. OPS is made by stretching hot light-gauge polystyrene sheet in both the machine direction and the cross-machine or transverse direction in a post-extrusion step. Orientation in the machine direction is achieved by differentially changing the speeds of the take-off rolls. Orientation in the transverse direction is achieved by reheating the sheet, gripping the sheet edges and pulling it at right angles to the machine direction in a technique known as *tentering*. This is shown schematically in Fig. 11.1. The sheet can be oriented up to a four-fold factor in each direction. Oriented polystyrene sheet is quite expensive to produce but is very tough and has exceptional clarity. The sheet must be heated very carefully to minimize loss of this orientation. Contact heat thermoformers are usually used.

11.3.2 Polyvinyl Chloride and Other Vinyls

Rigid and tough to flexible

Vinyl chloride was polymerized in the 1800s. The resulting polymer was intractable, degrading before it could be melted and molded. In the 1930s, polyvinyl chloride (PVC) was masticated with processing aids such as dioctylphthalate (DOP) on conventional two-roll rubber mills. Depending on the types and concentrations of processing aids, the final product properties could be changed from rigid and tough (rigid PVC or RPVC) to extremely flexible and transparent (flexible PVC or FPVC). The first sheet used in thermoforming was calendered from the rubber mills. Further additive development produced recipes that could be extruded in near-conventional equipment without serious degradation or property loss. The production of extruded sheet for thermoforming followed the extensive development of PVC in wire and cable applications.

Sensitive to heat

PVC is very sensitive to overheating. Early PVC was stabilized with lead. The toxicity of lead eventually led to its replacement, first with other heavy metals, and now with tin, zinc, and organic stabilizers.

Fire-retardant

PVC is inherently fire-retardant with a limiting oxygen index (LOI) greater than 30. As a result, it finds heavy-gauge thermoformed applications in equipment cabinetry. It has excellent UV stability and so it is used for exterior products such as siding, window fascia, and shutters. Semi-rigid, light-gauge sheet is thermoformed into containers in the packaging industry. Flexible, light-gauge sheet is thermoformed into interior automotive components such as door panel skins, arm and head rests, air bag covers, and instrument panel skins.

Degradation hazards

As noted, care must be taken when processing PVC. The first indication of excessive heat is color shift or discoloration. Ultimately, PVC degrades to a dark brown color and generates hydrogen chloride (HCl) gas. HCl is a corrosive acid, particularly in combination with moisture. It is a mucus membrane irritant. Because HCl is so corrosive, processing equipment in contact with PVC melt is usually stainless steel or chrome-plated steel. Although thermoforming equipment is less susceptible to corrosion than is extrusion equipment, heaters and electrical connections should be protected from potential damage when processing PVC. In light-gauge thermoforming, where a substantial portion of the sheet is trim, reprocessability must be carefully monitored and restricted to minimize contamination, usually in the form of black specks and gels, sometimes called *fish-eyes*. Although nearly all PVCs have some level of crystallinity, the crystalline level is quite low and the crystalline structure does not interfere with the formability of PVC. PVC thermoforms as if it is completely amorphous.

PVC is incompatible with many polymers. It is compatible with acrylates, however. Melt blends of PVC and polymethyl methacrylate (PMMA) are thermoformable into heavy-gauge products having good thermal stability, excellent weatherability, good scratch resistance, and fire retardancy. PVC is solvent-weldable.

11.3.3 Acrylics

Transparent and translucent

Polymethyl methacrylate (PMMA) is often the polymer of choice for transparent and translucent sky domes and outdoor signs. It can be drawn better and more consistently than any other polymer. In general, acrylics have superior UV resistance and high modulus but tend to be brittle. Rubber-modified acrylics have improved toughness but are often hazy to translucent to opaque. Acrylics are amorphous and are solvent-weldable.

There are two primary methods for making PMMA sheet. Cell-cast PMMA is made by pouring reactive resin syrup into a frame, surfacing the frame with floating plates of highly polished metal or glass, and warming the assembly to allow the resin to react. Extruded PMMA sheet is produced by the conventional extrusion of acrylic pellets.

Cell-cast PMMA has a greater molecular weight than extruded PMMA. It is tougher, more scratch-resistant, and more difficult to thermoform. Unlike extruded PMMA, it cannot be reground and recycled.

Care must be taken to ensure that the PMMA sheet is hot enough when forming it into three-dimensional corners. Cold-formed corners can be brittle and can exhibit severe stress-cracking. This is more critical with cell-cast PMMA than with extruded PMMA.

PMMA will absorb moisture. It is recommended that heavy-gauge sheet be protected from atmospheric moisture when produced. Sheet that has been exposed to the atmosphere for some time should be thoroughly oven-dried before forming. Absorbed moisture can result in haze formation during heating in the thermoforming process. Microbubbles act as stress concentration points during product use.

Moisture absorbent

11.3.4 Cellulosics

Cellulosics are often called the earliest synthetic polymers. In actuality, they are semi-synthetic in that the primary building block, cellulose, is a natural polymer. Cellulose nitrate or nitrocellulose (CN) was developed in the mid-1800s in England and the United States by reacting cotton with nitric acid. In the US, John Wesley Hyatt found that a moldable plastic was formed when cellulose nitrate was reacted with camphor. Sheets skived from camphorated nitrocellulose blocks, trademarked celluloid, were heated with steam and formed against steel molds to produce hollow products such as mirror cases and baby rattles [32]. The standard recipe for celluloid is 80 parts cellulose nitrate with at least 10% nitrogen, 30 parts of camphor, and 1 part ethanol [33].

Because cellulose nitrate (CN) is highly flammable, it was replaced in the early 20th century with cellulose acetate, being the reaction of cellulose with acetic acid. Cast cellulose acetate (CA) film is quite transparent and very tough. It was the first bread wrapper and was the inner layer between two sheets of glass to produce safety glass. It was also used extensively as thermoformed rigid packaging. Heavy-gauge cellulose acetate sheet was used to produce aircraft windscreens in World War II.

Highly flammable

Although cellulosics are nominally crystalline, they process as if they are amorphous. Cellulosics, in general, absorb water and transmit water vapor. Unless the cellulosic sheet is kept dry, the final product may contain microbubbles or pinholes. CA film, like CN film, is prone to splitting when bent sharply or creased.

Cellulose acetate has been replaced in many applications by cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP). These polymers are much tougher than either CA or CN, but they are also more expensive to manufacture. As a result, they are finding limited use, particularly as formable sheet and film. However, with growing emphasis on renewable resources for polymers, this may change.

11.3.5 Polycarbonate

Polycarbonate (PC) is a very tough, high-temperature, amorphous transparent plastic. PC, like PMMA, finds extensive use in heavy-gauge signage and skylights. It is more UV-sensitive than acrylic and tends to yellow with extended outdoor exposure. It is more difficult to thermoform, requiring long oven times to achieve uniform internal sheet temperature. Pressure forming yields the best products. Polycarbonate picks up substantial amounts of atmospheric moisture. Extensive moisture bubble fields develop at elevated forming temperatures. Microbubbles in finished parts act as stress concentrators that dramatically reduce impact strength. To minimize moisture pick-up, sheet should be kept wrapped in polyethylene film from the time of extrusion

Tough and transparent

to the time of forming. Sheet that has been exposed to atmospheric moisture for a few hours should be thoroughly oven-dried. Similarly, trim that is reground for recycle must be dried thoroughly before extrusion. Small amounts of absorbed moisture in the recycle stream will react with and degrade the polycarbonate by cleaving the polymer backbone.

11.3.6 Polyesters

PET

Polyesters are formed by reacting difunctional alcohols with difunctional acids to form long-chain esters. Although many polyesters are manufactured, the dominant polymer is polyethylene terephthalate (PET), being the product of the reaction of diethylene glycol with terephthalic acid. Water is the dominant small molecule that is extracted from the PET reaction.

Intrinsic viscosity

The level of PET molecular weight is determined through wet chemistry. A measured amount of PET is dissolved in a measured amount of solvent. The viscosity of the solution is then determined. An additional measured amount of solvent is added to the solution and the viscosity is again determined. This dilution is repeated, the viscosities are plotted against the polymer concentration, and the curve is extrapolated to zero polymer concentration. The intercept value is then divided by the known viscosity of the solvent and the value is reported as the intrinsic viscosity (IV) of the polymer. The IV is directly related to the molecular weight of the polymer. PET molecular weight or IV affects many physical properties, which in turn affect PET processibility. As examples, for fiber forming, PET IV is around 0.7, in sheet production and thermoforming, it should be around 0.8, while for PET beverage bottle production, it is around 0.9. For low-density PET foam production, the IV should be greater than about 1.2. Traditional condensation reactor technology is normally used to achieve IVs of less than approx. 0.9. To achieve IVs in excess of approx. 0.9, solid-state reaction under very high vacuum can be used but more recently chain extenders such as pentaerythritol (PAE) and para-mellitic dianhydride (PMDA) are employed. As expected, the cost of PET production increases as the IV increases.

Rate of crystallization

PET is a relatively stiff molecule. PET has a glass transition temperature of around 160 °F (70 °C). Under ideal thermal conditions, however, PET will crystallize, albeit quite slowly, to a maximum of about 40% (wt) and a melting temperature of about 510 °F (265 °C). The rate of crystallization of PET is governed by IV and its instant temperature. A measure of the rate of crystallization is the *halftime of crystallization* or the time it takes for PET to reach half its final crystallinity. This is shown as a function of temperature in Fig. 11.2. As is apparent, the rate of crystallization is extremely slow at low temperatures, just above the glass transition temperature, and the rate of crystallization is extremely slow at high temperatures, just below the polymer melt temperature. The rate of crystallization is maximum in a temperature range of ~340 °F (~170 °C) or about halfway between the glass transition temperature and the melt temperature. If a polymer is cooled very rapidly through this region, few crystallites can form before the polymer is too cold to allow further chain mobility.

APET

Amorphous PET (APET) is formed by quickly cooling an extruded sheet from the melt to room temperature. APET has a reasonably high modulus, and is a tough, transparent to slightly hazy polymer.

Thin APET sheet is frequently thermoformed into rigid packages. Because PET is a commonly post-consumer recycled plastic, APET competes quite well with other light-gauge transparent

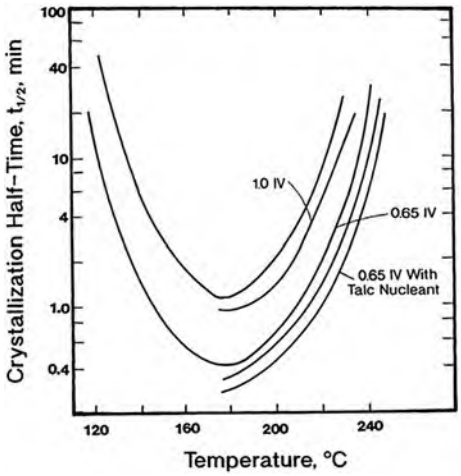


Figure 11.2: Temperature-dependent halftime of crystallization for PET. Parameters include IV and the effect of talc as a nucleant

package plastics such as polystyrene (PS) and PVC. Even though APET is not recommended for steam sterilization, it is used in medical packaging where gamma sterilization is used. In thermoforming, care must be taken to prevent overheating APET sheet as it will begin to crystallize in the oven. This will lead to poorly formed parts that may be hazy rather than water-white. APET regrind must be thoroughly dried and recrystallized before it can be mixed with virgin PET as feed to the extruder. APET cannot be heat-staked and is difficult to solvent weld. Pressure-sensitive adhesives (PSAs) have been developed that work well with APET.

Copolymer PET for heavy-gauge sheet

PET is not normally extruded in thick sheets, simply because the sheet cannot be cooled rapidly enough to prevent centerline crystallization. Copolymer PETs have been developed to meet the heavy-gauge sheet and thermoforming markets. Typically, a portion of the diethylene glycol is replaced with a longer-chain aliphatic glycol. One of the earliest was neopentyl glycol. The copolymer PET, generically called PETG, is amorphous as the longer-chain glycol prevents the PET from crystallizing. PETG is more expensive than PET, but its thermal stability is desired for thick sheets and applications such as medical packaging where processibility is more important than cost.

Moisture sensitive

In general, polyesters are quite moisture sensitive. Moisture does not normally manifest itself as moisture bubbles in the final part. Rather, at high temperature, water attacks the polymer backbone, degrading it. This results in excessive sag during heating in the thermoforming oven and in a difficult-to-detect loss in mechanical properties such as impact strength. PET polymer producers recommend moisture levels of no more than 50 parts per million (50 ppm) in the feed stream to processing equipment.

Light-gauge polyester tends to be very difficult to trim cleanly, necessitating very sharp, heated trim dies. Improper trimming can result in fuzz, angel hair, and substantial trim dust. Trim dust is the primary problem when trimming heavy-gauge polyester products.

Biaxially oriented polyethylene terephthalate (OPET) film is produced in blown film processes and match-metal formed into speaker cones and microphone diaphragms.

CPET

Beginning in the 1980s, the wide use of microwave ovens – both commercial and residential – led to the development of high-temperature food packaging that could be used in either microwave ovens or conventional hot air ovens. The first polymer to meet this criterion was crystallizable PET (CPET). CPET has essentially the same polymer base as APET but materials are added that accelerate the formation of crystallites. The additives are organics such as polypropylene or inorganics such as talc. CPET containers are formed by heating a light-gauge PET sheet rapidly enough to minimize crystallization, and forming the crystallizing sheet against a mold heated to about 340 °F (170 °C). In other words, the optimum cycle time occurs when the mold is about the temperature at which the maximum rate of crystallization occurs, see Fig. 11.2.

The formed part is held under pressure against the mold until the PET has a crystalline level of about 20% (wt). At this level of crystallinity, the formed container will not distort when placed in a 400 °F (200 °C) hot air convection oven for up to one hour. Because PET is transparent to microwave energy, the formed container can also be used in microwave ovens.

Warpage and distortion

Because PET density greatly increases as the polymer crystallizes, final part dimensions are dramatically altered as the part crystallizes. Because the wall thickness is not uniform across the part, differential crystallinity often leads to part warpage and distortion. To minimize these effects, the part is often fixtured after it exits the mold. As with other polyesters, the CPET recipe requires substantial drying to prevent moisture absorption that can ruin the formability and mechanical properties of the formed product. Pressure sensitive adhesives have been developed for lidding CPET containers.

11.3.7 Polyethylene

Amorphous polymers account for about 70% (wt) of all polymers thermoformed. Because crystalline polymer sheet must be heated above the polymer melt temperature to be formed, the polymer must have sufficient strength in the melt. Otherwise, the sheet will come apart and fall into the heater.

Most often used in heavy-gauge forming

Polyethylene (PE) is the crystalline polymer most often used in heavy-gauge thermoforming, primarily because of its very high melt strength or hot strength. PE melt strength is demonstrated in blow molding to produce a hollow container. A tube of PE, called a parison, is extruded and allowed to hang vertically as mold halves close around it. Parison blow molding of other crystalline polymers such as nylon (PA), polypropylene (PP), and PET, is impossible because of their poor melt strengths.

Density

High-density polyethylene (HDPE) has a density of about 960 kg/m^3. It has exceptional impact strength, chemical resistance, and excellent outdoor weatherability. As a result, it is thermoformed into pallets, dunnage, totes, marine applications, and many outdoor products. Low-density polyethylene (LDPE) has a density of about 920 kg/m^3, has a much lower modulus than HDPE, and competes with flexible PVC in soft packaging and other non-transportation applications. Care must be taken when heating LDPE to its forming temperature as it can sag very quickly in the forming oven.

Linear low-density polyethylene (LLDPE) is tougher than LDPE but softer than HDPE. It is far more difficult to thermoform than either of these. The reason for this will be discussed in the following when the problems with formability of homopolymer polypropylene (homoPP) are discussed.

11.3.8 Polypropylene

Properties

Polypropylene (PP) has a density of 910 kg/m^3. Until recently, it was the least expensive, in terms of cost per unit volume, of the four commodity polymers – Polystyrene (PS), PVC, polyethylene (PE), and PP. PP is sought for its high melting temperature, its excellent chemical and moisture resistance, high modulus, and good impact strength. Homopolymer PP (homoPP) is semi-crystalline with a glass transition temperature of around 32 °F (0 °C) and a melting temperature around 330 °F (165 °C). The crystallites in homoPP are quite large. As a result, light-gauge homoPP sheet is hazy to translucent. Furthermore, homoPP has very poor melt strength, meaning that it is not normally thermoformed in a melt state. Instead, it is carefully heated to within a few degrees below its stated melt temperature and pressure formed into the mold. Because the crystallites do not completely melt, the formed part retains much of the haze present in the sheet.

coPP

For years, PP polymer chemists strived to produce a PP that could be melt-phase formed in a fashion similar to HDPE. One early success involved copolymerization of around 10% (wt) PE with PP. Copolymer PP (coPP) has a glass transition temperature of around –5 °F (–20 °C) and a melting temperature around 310 °F (155 °C). It has lower modulus and lower crystallinity but improved melt strength. This allows it to be heated to forming temperatures a few degrees above its melt temperature. Formed parts have substantially less haze than those formed with homoPP. More importantly, heavy-gauge parts can now be formed from coPP.

HDPE has few side chain branches and so appears as a rather smooth molecule when compared with highly branched LDPE. However, the HDPE polymer chain is quite flexible. This allows for extensive entanglements that increase the polymer resistance to shearing force. This provides its great melt strength.

Strain rate hardening

Homopolymer PP is also a rather smooth molecule, with the backbone rotating to protect the pendant methyl group. The polymer chain is quite stiff when compared with HDPE and few entanglements occur. This implies that the polymer has little resistance to shearing force and therefore poor melt strength. Measurement of the time-dependent extensional viscosity of polyolefins reveals this. If the extensional viscosity increases with time, the polymer is considered to be *strain rate hardening*. This is seen in Fig. 11.3 for HDPE, where entanglements cause the time-dependent increase in viscosity and in Fig. 11.4 for LDPE, where long side chain branches cause the time-dependent increase in viscosity. On the other hand, as shown in Fig. 11.5, homopolymer PP shows a dramatic reduction in viscosity with increasing time under load [34].

Recent work has focused on developing short side chain branches on PP, as seen in Fig. 11.6 for high-melt strength PP (HMS-PP). Improved melt strength implies less sag while the sheet is in the oven, wider forming windows, and deeper draws and more uniform wall thickness in the forming station. Again, these improvements have spurred interest in thermoforming heavy-gauge parts of PP.

PP is a slowly crystallizing polymer. This is best demonstrated by examining its recrystallization temperature. Differential scanning calorimetry (DSC) is used to measure material transitions [35]. The technique involves side-by-side constant rate of heating (or cooling) of a small sample of polymer and a reference sample. If the polymer is not undergoing a transition, its rate of heating parallels that of the reference sample. As the polymer reaches a transition temperature

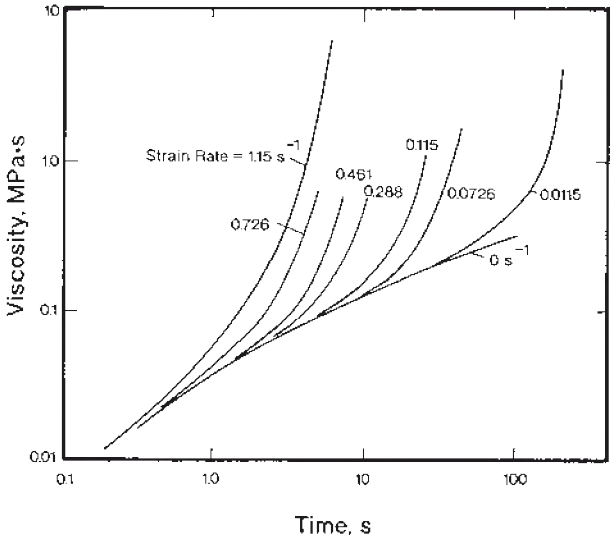


Figure 11.3: Time-dependent extensional viscosity for high-density polyethylene (HDPE), showing the effect of chain entanglement to produce strain rate hardening

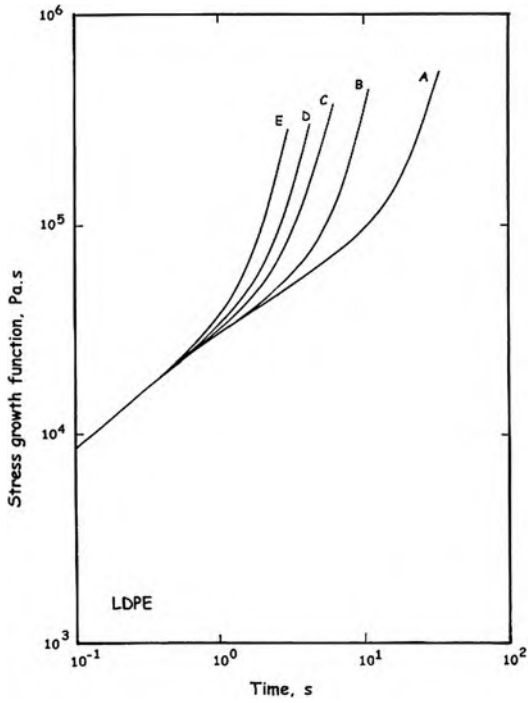


Figure 11.4: Time-dependent extensional viscosity for low-density polyethylene (LDPE), showing the effect of long chain branching to produce strain rate hardening. Strain rate values in s^{-1}: A = 0.1, B = 0.3, C = 0.5, D = 0.7, E = 1.0

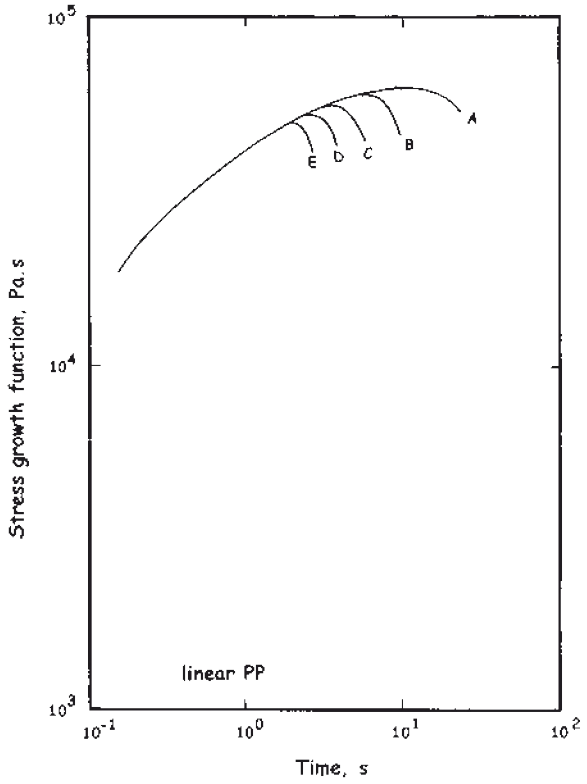


Figure 11.5: Time-dependent extensional viscosity for homopolymer polypropylene (homoPP), showing the absence of strain rate hardening.
Strain rate values in s^{-1}: A = 0.1, B = 0.3, C = 0.5, D = 0.7, E = 1.0

such as its crystalline melting temperature, its rate of heating slows, because the inputted energy is used to melt the crystallites. Once the crystallites are melted, the polymer rate of heating once again parallels that of the reference sample. When the polymer is cooled from its melt state, its rate of cooling parallels that of the reference sample until the polymer undergoes a transition, such as recrystallization. The rate of cooling increases as the polymer recrystallizes. Again, once the polymer has completed its transition, the rate of cooling parallels that of the reference sample. Figure 11.7 shows heating and cooling profiles for three polyolefins.

The heating and cooling curves for HDPE are depicted to the left in Fig. 11.7. HDPE melts around 280 °F (137 °C) and recrystallizes around 265 °F (130 °C). The heating and cooling curves for LDPE are depicted in the center of Fig. 11.7. LDPE melts in the general range of 230 °F (110 °C) and recrystallizes around 210 °F (100 °C). The heating and cooling curves for homoPP are depicted to the right in Fig. 11.7. Homopolymer PP melts around 320 °F (160 °C) and recrystallizes around 250 °F (120 °C).

Polyethylenes characteristically recrystallize very rapidly. As a result, their recrystallization temperatures are very close to their melting temperatures. On the other hand, PP characteristically recrystallizes slowly. As is apparent in Fig. 11.7, recrystallization temperatures are

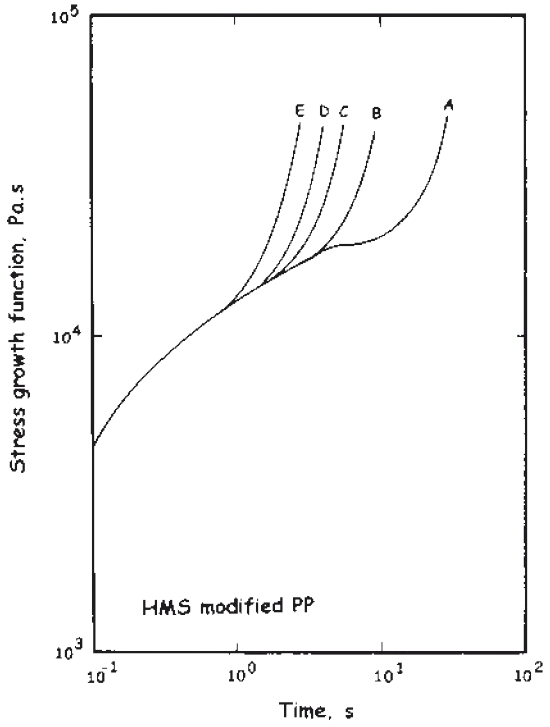


Figure 11.6: Time-dependent extensional viscosity for high-melt strength polypropylene (HMS-PP), showing the presence of strain rate hardening.
Strain rate values in s^{-1}: A = 0.1, B = 0.3, C = 0.5, D = 0.7, E = 1.0

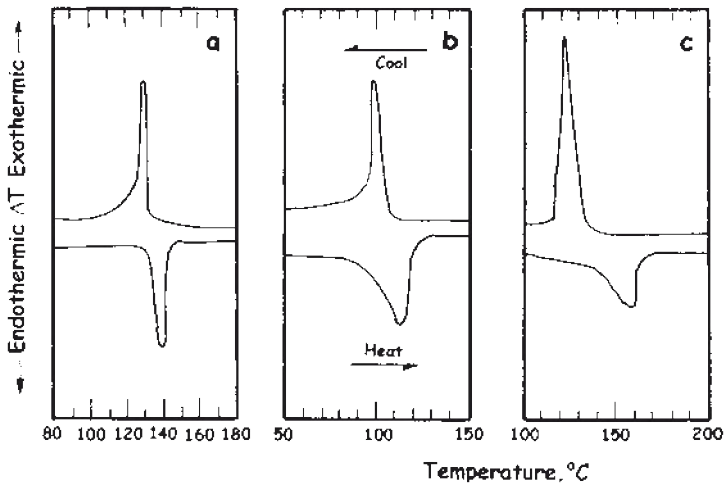


Figure 11.7: Differential scanning calorimetry heating and cooling curves for three polyolefins.
a: HDPE. b: LDPE. c: Homopolymer PP.
The heating and cooling rates are 7 °F/min (4 °C/min)

Table 11.4: Additive Effect on PP Recrystallization Temperature (ppm = parts per million)

Copolymer melting temperature	**155 °C**
Recrystallization temperature, °C	
• No clarifier	92
• Dibenzylidene sorbitol (DBS)	105 @ 1800 ppm
• Methyl dibenzylidene sorbitol (MDBS)	107 @ 1200 ppm
• Millad 3988 (unknown chemistry)	108 @ 600 ppm
Homopolymer melting temperature	**165 °C**
Recrystallization temperature, °C	
• No clarifier	102
• Dibenzylidene sorbitol (DBS)	115 @ 1800 ppm
• Methyl dibenzylidene sorbitol (MDBS)	120 @ 1800 ppm
• Millad 3988 (unknown chemistry)	121 @ 1200 ppm

substantially below PP melting temperatures. The slow crystallization rate often dramatically affects the final dimensions of thermoformed parts. Crystallization may continue for hours after the parts have been trimmed from their web and even after the parts have been inspected, packaged and warehoused. This often results in unwanted part distortion and warpage and wholesale rejection of finished products.

Small amounts (~0.1% wt) of additives such as sorbitols and phosphanates increase the rate of PP recrystallization by nucleating microcrystallites, as seen in Table 11.4. The crystallites thus formed are much smaller than those formed without the additives. As a result, the finished product has dramatically improved clarity, with haze levels typically below 5%.

11.3.9 Other Polyolefins

TPOs

There is growing interest in the general family of thermoplastic olefins (TPOs). TPOs usually consist of a polyolefin such as polyethylene, homopolymer PP, or copolymer PP, and a synthetic rubber such as ethylene-propylene-diene rubber (EPDM), or an ethylene-styrene-butadiene rubber (ESBR). For many applications such as automotive interior fascia, the TPO also includes filler such as talc or milled glass fiber. If the olefin is the greater organic component, it is the continuous phase and the rubber is the discrete phase. The resulting product is tough and semi-rigid to rigid. If the rubber is the greater organic component, it is the continuous phase and the olefin is the discrete phase. The resulting product is flexible and is often referred to as a thermoplastic rubber (TPR). If the rubber is reactive and can be crosslinked, the final product is essentially a thermoset and is called a thermoplastic vulcanizate (TPV).

TPOs are thermoformable. The level of required applied forming force increases with increasing filler content. TPRs are also thermoformable, but the depth of draw is restricted and formed parts may experience short-term rebound or recovery once the forming pressure is removed. They often experience long-term stress relaxation as well. Most TPVs have some degree of mobility at elevated temperatures and so are thermoformed into relatively shallow-draw parts.

COCs

Cycloolefins (COCs) have been developed recently by reacting ethylene with cyclopentadiene to produce norbornene. Norbornene is then reacted with ethylene using a metallocene catalyst to produce the amorphous polymer, COC. The temperature-dependent elastic modulus of COC is shown in comparison with other thermoformable polymers in Fig. 11.8. Unlike other polyolefin polymers, the glass transition temperature of COC can be dramatically altered by changing the ratio of norbornene to ethylene, as seen in Fig. 11.9. Because COCs are olefinic, they have good UV resistance and excellent chemical resistance. Because they are amorphous, they have wide forming windows as seen by the very flat plateau at temperatures above 100 °C. So far, they are quite expensive.

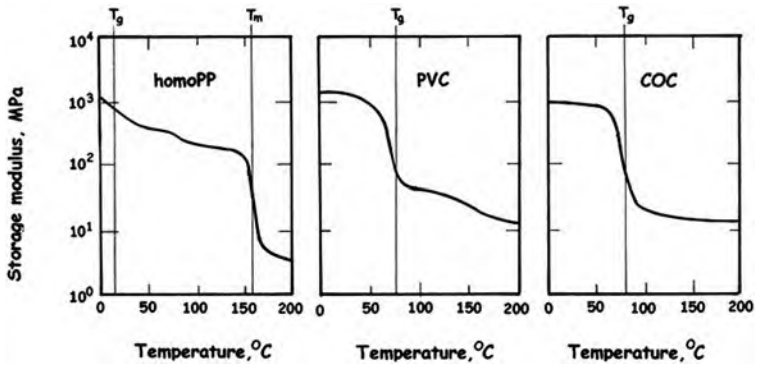


Figure 11.8: Temperature-dependent storage moduli of homopolymer polypropylene (homoPP), polyvinyl chloride (PVC) and cycloolefin (COC) from Ticona Topas Advanced Polymers, Florence, KY

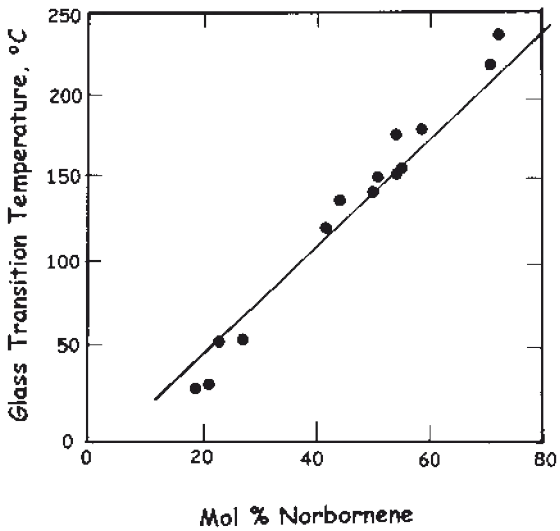


Figure 11.9: The effect of norbornene concentration on glass transition temperature of cycloolefin, from Ticona Topas Advanced Polymers, Florence, KY

EVA

Ethylene vinyl acetate (EVA) is a relatively low-melting (~200 °F or 95 °C) very flexible polyolefin containing about 10–15% (mol) vinyl acetate. Although it is normally used as a film, it has been thermoformed into flexible semi-rigid packages. Because it is FDA-approved, it competes well with flexible PVC and nylon in food packaging. Although it has exceptional elongation to break, low permeability to most oil-based essences, and excellent gloss, it has very high surface adhesion and friction. As a result, it is very difficult to handle in roll form without antistatic and antiblocking agents.

11.3.10 Formable Biopolymers

The global success of plastics as disposable light-gauge protective packaging is also causing consternation and concern. Once used, a substantial portion of the packaging resides in landfills or is discarded into the environment. As a result, there is growing interest in biodegradable and compostable polymers [36][24]. Nearly all such polymers contain, at least in part, some type of biological polymer and so are called *biopolymers*.

Most biopolymers tend to be moisture sensitive, have low melting or softening points, have poor mechanical properties, and are more expensive than the hydrocarbon-based polymers with which they compete.

Based on cellulose, starch, or polylactic acid

There are many types of biopolymers. The very earliest were based on cellulose – camphorated cellulose nitrate, cellulose acetate, and others, as described above. Starches have been polymerized for many decades. And more recently, polylactic acid (PLA) has been commercialized.

PLA properties

To produce PLA, lactic acid is extracted from bacterial fermentation from natural crops such as corn and sugar cane. The lactic acid is then catalytically oligomerized, dimerized, and polymerized. There are two stereospecific forms of PLA. L-PLA is about 35% crystalline, with a glass transition temperature of about 160 °F (70 °C) and a melting temperature of 350 °F (175 °C). These properties are increased by melt-blending up to 40% (wt) D-PLA. Blends of L-PLA and D-PLA are transparent. As with most biopolymers, PLA is moisture sensitive and must be thoroughly dried before extrusion. Rollstock and regrind must also be moisture-protected. PLA is also thermally sensitive. Extrusion temperatures must be carefully monitored. Low D-PLA concentration PLAs extrude like stiff polystyrenes. Gels are potential problems with light-gauge sheet and film. PLA does not degrade in a traditional manner. It continues to crystallize in landfills. At around 150 °F (65 °C), it crumbles to powder in about 30 days.

Although polystarches have been produced in laboratories for decades, they tend to be very moisture sensitive and very difficult to extrude into quality sheet. Recently, polystarches have been combined with poly-e-caprolactone to produce a thermally stable polymer. Poly-e-caprolactone is produced by oxidizing cyclohexanone with peracetic acid to produce e-caprolactone,

[24] The terms *biodegradable* and *compostable* are not identical. ASTM defines a biodegradable plastic as one "in which the degradation results from the action of naturally occurring micro-organisms such as bacteria, fungi, and algae". ASTM defines a compostable plastic as one "that undergoes biological degradation during composting to yield carbon dioxide, water, inorganic compounds and biomass at a rate consistent with other known compostable materials and leaves no visually distinguishable or toxic residues". For more details, see L. F. Doty, "Compostable, biodegradable not identical", Plastics News, July 16, 2007.

then reacting e-caprolactone with a catalyst to produce the polymer. Both polystarch and poly-e-caprolactone are biopolymers but may not necessarily be biodegradable. Degradation occurs by hydrolysis.

PHB and PHV

There is growing interest in genetically modified microorganism- and plant-generated biopolymers. Two biopolymers of current interest are polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV). Combinations of these polymers, called PHA or PHBV, are also of interest. PHB is quite stiff and very brittle. It has a glass transition temperature of about 50 °F (10 °C), melting temperature of about 340 °F (170 °C), and is transparent. Currently, the dried leaves of a genetically modified watercress produce about 15% (wt) PHB. Genetically modified e. coli bacteria also produce substantial amounts of PHB.

Other biopolymers include those synthesized from polypeptides. Two very early polymers were based on amino-acids obtained from gluten or animal protein and gliadin or vegetable protein.

Table 11.5: Biopolymer Glass Transition and Melt Temperatures (Courtesy of Engineer Anne-Marie Clarinval, CRIF-WTCM, Brussels, Belgium, 2001, www.CRIF.be)

Biopolymer Name	T_g [°C]	T_m [°C]
Cornflour 1	NA	63
Cornflour 2	NA	75
Cornflour + Wax 1	NA	62
Cornflour + Wax 2	NA	74
Corn amylase	NA	80
Wheatflour 1	NA	51
Wheatflour 2	NA	64
Potato starch 1	NA	52
Potato starch 2	NA	73
EcoPLA 4040D	51	130
Galactic LA33JZE	42	168
Galactic LA07JZE	72	180
Biopol PHB	~0	177
Biopol PHBV 8% HV	~0	152
Biopol PHBV 12% HV	~0	143
PHB Metabolix	5	178
PHO Metabolix	–30	62
Capa 650 (Solvay)	–65	63
EastarBio 14766	–29	108
Bionolle PBS	–30	112
Bionolle PBSA	–45	90

Casein was first synthesized from the amino acids in milk. Zein is synthesized from maze gluten. Polymers have been synthesized from vegetable proteins in soy bean, castor bean, and blood and from hair, wool, and silk. Nearly all of these polymers were reacted with formaldehyde or other crosslinking agents to produce moldable thermoset products. And most or all of these early polymers were supplanted by synthetic ones with superior properties and lower costs. All of these polymers could be biodegradable if they are not crosslinked. The high cost of extraction and the low yield of the basic building block from the animal or plant structure remain the primary economic barriers to more development and wider application of these biopolymers. The temperature characteristics of several biopolymers are given in Table 11.5.

11.3.11 Other Formable Polymers

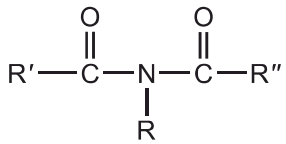
If a polymer can be produced in sheet form, it can usually be thermoformed into a functional product. Although the great majority of polymers are identified in detail above, there are niche applications for many other polymers. Some polymers that have found commercial success include:

- Fluoropolymers such as polyethylene terephthalate (PTFE) and fluoroethylene polymers (FEPs). Despite their high cost, these highly crystalline polymers are sought for their extreme chemical resistance and elevated temperature applications. The sheet is usually cast rather than extruded. Fluoropolymers require very high forming temperatures and must be heated very carefully. Because sheet at elevated temperature cools very quickly in environmental air, forming must take place very quickly. Fluoropolymers are quite soft. As a result, trimming is very easy. — Fluoropolymers
- Polyamides (PAs) or nylons are high-temperature crystalline polymers that have excellent chemical resistance. However, most have very poor melt strengths and are therefore not thermoformable. Recent development work has focused on improving nylon melt strength for both blow molding and thermoforming. Toughened or rubberized nylon is a copolymer of EPDM and polyamide with a melting temperature of about 315 °F (157 °C). A block copolymer of polyphenylene oxide and poly-e-caprolactam (nylon 6 or PA6) exhibits two crystalline melting temperatures indicative of the two crystalline moieties. To date, these nylons have found limited use because of their relatively high cost. — Polyamides
- Thermoplastic polyurethane (TPU) is a segmented block copolymer thermoplastic elastomer containing the traditional urethane hard and soft sectors. The hard segment is typically an aliphatic isocyanate. The soft segment is either a polyester or a polyether. TPUs used in aqueous applications are polyester-based. TPUs used in oil applications are polyether-based. TPUs are weldable and can be colored, printed, and sterilized. They have low temperature flexibility and some grades have moderate UV resistance and optical clarity. Their chemical inertness in contact with human skin allows them to be thermoformed into medical devices such as gloves and condoms that compete with natural rubber latex products. — TPUs
- High-nitrile resin (HNR) is usually an amorphous copolymer of modified acrylonitrile and ethyl or methyl acrylate, with a glass transition temperature of about 210 °F (100 °C). It finds application as a thermoformed rigid package where moderate to good oxygen — HNR

and carbon dioxide gas barrier properties are needed. While its film barrier properties are not as good as those of polyvinyl dichloride (PVDC) or ethylene vinyl alcohol (EVOH), it provides a barrier in a single layer sheet rather than in a difficult-to-recycle multilayer sheet. It extrudes and thermoforms as a relatively stiff SAN.

PSO

- Polysulfone (PSO) is a high-temperature amorphous polymer with a glass transition temperature of 365 °F (185 °C) and a continuous use temperature in air of about 285 °F (140 °C). It is a tough, ductile polymer with an elongation at break of 50%. It is chemically resistant to most acids, bases, and hydrocarbons but is attacked by ketones and certain chlorinated hydrocarbons. Although PSO is transparent, it typically has a yellow-to-amber tint, even in thin gauges. PSO sheet should be heated to at least 579 °F (300 °C) and should be formed against molds heated to around 210 °F (100 °C). Steel tooling is usually recommended. Because PSO is quite notch sensitive, thermoformed parts should be designed to have generous radii, particularly in potential impact areas.
- Polyimides (PIs) have the following basic structure:



PI

where R′ and R″ are linear aliphatic chains for linear PI or they are aromatic or cyclic chains for heterocyclic PI. Polyether-imide (PEI) is amorphous with a glass transition temperature of 783 °F (417 °C). If it is available in sheet form, it can be thermoformed using hot matched steel tooling.

When PI is copolymerized with aromatic polyamide, the result is an amorphous high-temperature polyamide-imide having a glass transition temperature of 525 °F (275 °C). It is normally thermoformed in a pre-imidized state and the trimmed part is then fully imidized in a controlled temperature oven.

PPS

- Polyphenylene sulfide (PPS) is a crystalline high-temperature polymer that can be thermoformed, albeit with difficulty, provided that sheet product is available. Its melting temperature is 545 °F (285 °C). It has moderate-to-poor melt strength. As a result, it is often glass or mineral filled. Highly filled PPS must be pressure-formed. It is one of the most chemically resistant polymers known, being inert to most solvents and organic acids and alkalis, even at elevated temperatures. Unfilled PPS structures pass FDA and NSF[25] regulations for food and potable water contact.

Again, there are many other polymers that, when available in sheet form, are thermoformed into products that have niche applications.

[25] NSF = National Sanitary Foundation

11.4 Multilayer Polymers

Vinyl-acrylic blend polymers were discussed earlier. Heavy-gauge laminated PVC-PMMA sheet is often recommended for sanitary products, including shower stalls, soaking tubs, bathtubs, whirlpools, and spas. Because both of these polymers are amorphous with glass transition temperatures between about 175 °F (80 °C) and 210 °F (100 °C), the laminate thermoforms quite easily. The greatest concern is delamination, caused by differential expansion at the laminate interface. This is best controlled by reducing the rate of heating to achieve a more uniform temperature profile through the sheet. Drawdown into sharp corners must be minimized to prevent delamination and *read-through* of the backing sheet.

Cap sheet

Acrylic (PMMA) is extensively used as a cap sheet for ABS in heavy-gauge exterior applications such as construction products and vehicular components. The cap sheet is usually greater than about 0.006 in (0.15 mm) in thickness. As the cap sheet is stretched during forming, it may thin substantially. If the cap sheet is not colored the same as the substrate, the substrate color may *read through*, particularly in sharply radiused corners. Fluoropolymers (FEPs) are also used as cap sheets on HIPS or ABS substrates on products where abrasion or solid particle erosion may be a problem. Fluoropolymer cap sheets are typically less than about 0.012 in (0.3 mm) in thickness.

Achieving specific property combinations by upto 9 layers of dissimilar polymers

Many types of multilayer structures are used to produce light-gauge products. Often dissimilar polymers are laminated to provide characteristics that are not achievable with a single polymer. For example, to achieve a combination of stiffness, moisture barrier and oil resistance, polystyrene (PS) may be laminated with a polyolefin (PO). To achieve small molecule diffusion resistance, a barrier polymer such as ethylene vinyl alcohol (EVOH) may be sandwiched between two polyolefin (PO) sheets. Often, tie layers such as ethylene vinyl acetate (EVA) or amines are employed between plies to ensure adhesion during heating, shaping, trimming, and end use. As a result, light-gauge multilayer sheet may have three layers, at a minimum, to perhaps as many as seven or nine layers of dissimilar polymers.

When forming multilayer sheet, all layers draw locally to the same extent, regardless of their individual thicknesses. As an example, consider thermoforming a 0.006 in (0.15 mm) thick cap sheet on a 0.120 in (3 mm) substrate. If the sheet is drawn locally to 33% of its original thickness, the local substrate thickness will be 0.040 in (1.0 mm) and the local cap sheet thickness will be 0.002 in (0.050 mm). If, as is the case of acrylic-capped ABS, the cap sheet is there to protect the substrate from ultraviolet or UV damage, the barrier may be compromised if the cap sheet is too thin.

In some cases, care must be taken to ensure that very thin plies of high-forming temperature polymers are at their forming temperatures. If not, the higher temperature polymers may delaminate, form microcracks, or microscopic pinholes may form as the plies are drawn. In any case, the barrier resistance may be compromised.

Example

The formability of multilayer sheet depends on a combination of factors such as the forming temperature range of the higher-modulus polymer, the thickest ply, and the ply requiring the highest forming temperature. As an example, consider a multilayer sheet consisting of a moderate temperature amorphous polymer of substantial thickness, a very thin high-temperature amorphous barrier layer, and a moderately thick ply of high-temperature crystalline polymer. It is apparent that the forming temperature of the entire sheet will depend on the