

Production and Processing of Polymer-Based Nanocomposites

Loïc Hilliou, José A. Covas
University of Minho, Guimarães, Portugal

5.1 INTRODUCTION

Particularly during the first half of the 20th century, as new thermoplastic polymer materials were being synthesized and processing technologies were being developed, plastics were applied to packaging to replace paper, glass, and metals. Polyethylene (PE) was synthesized in the 1930s and polypropylene (PP) in the 1950s while linear low density polyethylene (LLDPE) and polyethylene terephthalate (PET) were introduced in the 1970s. The first commercial biodegradable plastic (Biopol) was launched in 1990, while polylactic acid (PLA) made from corn was presented to the packaging market in 2000. This rate of materials evolution was well matched by technology development. While thermoforming was patented as early as 1890s, “modern” single- and twin-screw extruders were made available in 1935 and 1937, respectively, and the patent for an injection molding machine using a plasticating screw was filed in 1933. Extrusion blow molding of containers was introduced in the late 1940s, enabling the creation of squeeze LDPE bottles (1945) (the iconic Heinz ketchup bottle is relatively new, being launched in 1983) and plastic spray bottles (1946). At about the same time, the Tupperware brand of food containers made from LDPE was created. PE bags manufactured from blown films, PS foams, and milk cartons using PE-coated paperboard were developed in the 1950s. The popular Bubble Wrap was created in 1960, while PET bottles appeared in the 1970s. The well-known triangular recycling symbols identifying plastics were introduced in 1988. The incorporation of nanoparticles (mostly chemically modified layered clays such as montmorillonite) in polymer matrices to increase the mechanical, thermal, and barrier properties of packages has been extensively studied since the late 1990s. This solution has great potential particularly for biopolymers due to current limitations of some of their properties, although safety concerns remain about the use of nanoparticles as food contact materials [1].

Not only polymers have established themselves as one of the most important types of materials, since the 2000s more than one-third of commercial plastics are used in packaging (in Europe 39.4% in 2013 [2]). Table 5.1 identifies the most important plastics used for packaging, together with their main applications. The order adopted in the list comes from the number in their corresponding triangular recycling symbols (from 1 to 6 for PET to PS, respectively). An additional number (7) is used to indicate all other polymer materials (including blends, multilayers, bio-based, and biodegradable polymers).

PET is essentially used in applications requiring good barrier properties, high strength, wide-ranging temperature resistance (high softening point but good mechanical resistance at freezing temperatures), while keeping acceptable transparency. HDPE is a versatile polymer as it can be easily shaped into a wide variety of products. Together with LDPE, which is extensively used in film packaging, HDPE accounts for more than half of the food packages found on the market. Low permeability to water, high resistance to tear (its elongation at break outperforms that of other plastics), and low heat seal temperature are major assets for using LDPE and HDPE. PVC has high chemical and good gas barrier properties, being often the material of choice to pack fatty foods or meat. PP is extensively used for thin walled containers and cups. Good strength, optical clarity, barrier properties, and heat resistance make this polymer suited for hot-filled or sterilized containers, as well as freeze and microwave able containers [3,4]. PP is progressively replacing PS in rigid packaging and thermoformed containers (e.g., yoghurt) [3,4]. However, the high permeability of PS still makes it popular for packing short shelf-life food (e.g., cheese), not mentioning its ability to be manufactured as hard foam for thermal insulation applications (e.g., disposable fast food packaging) and light weight but still stiff trays. The two most promising bio-sourced and biodegradable polymers currently available commercially are polylactic acid (PLA) and polyhydroxyalkanoates (PHA). However, food packages made of these polymers did not yet make their way through the market, essentially due to two reasons. First, PHA and PLA are still 1.5–4.5 times more expensive than the remaining polymers listed in Table 5.1. Second, they are far more difficult to convert into packages by means of conventional polymer processing technologies. Thus PLA and PHA are currently only found in niche markets.

The success of plastics in packaging applications relates not only with the continuous development of more performing and/or sustainable polymers, polymer blends, and additives but also with significant advances in polymer processing technologies. Efficient process control allows for thinner and consequently lighter packages. Coextrusion and lamination provide the

Table 5.1 Polymers Used in Food Packaging and Their Main Physical Properties

Polymer ^a	Packaging Types	T_g (°C)	T_m (°C)	T	ϵ_B	OP	Permeability		
							H ₂ O	O ₂	CO ₂
PET	Bottles, microwaveable and oven able trays, boil-in-the-bag products.	70–87	243–268	+++	20–300	++	++	+	+
HDPE	Jars and other rigid containers, pallets, films, or layers for dry food.	–125 to –90	135	++	100–>1000	+++	+	++	++
PVC	Wrapping films, bottles, trays, containers.	60–100	n.d.	+++	40–75	++	+	+	+
LDPE	Films (wrapping, carrier bags, pouches), bottles.	–125 to –110	112–135	+	200–900	++	++	+++	+++
PP	Cups and containers for frozen and microwaveable food, lids, thin walled containers (yoghurt).	–10	167–177	++	100–600	+	+	++	++
PS	Disposable cups, plates, and trays; boxes (egg cartons), rigid containers (yoghurt).	100	n.d.	+++	1–4	++	+++	++	++
PLA	Cups, bowls, bottles, trays, disposable cups, and cutlery.	5–60	150–175	+++	1–20	++	+	++	+
PHA	Jar, trays	<0–10 ^b	170–180 ^b	++	1–10 ^b	+	+	++	+

T_g , glass transition temperature; T_m , melting temperature; T , tensile strength; ϵ_B , elongation at break (%); OP, overall optical properties including haze, gloss, and transmission of visible light; permeability (H₂O, water vapor; O₂, oxygen gas; CO₂, carbon dioxide gas). n.d.: not defined. +: low, ++: medium, +++: high.

^aPolyethylene terephthalate (PET), high density polyethylene (HDPE), polyvinyl chloride (PVC), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS).

^bCommercially available poly(hydroxy butyrate-co-valerate) with valerate content up to 10 mol%.

(Range of values retrieved from data reported in J.E. Mark (Ed.), *Physical Properties of Polymers Handbook*, AIP Press, New York, 1996; J.D. Ferry, *Viscoelastic Properties of Polymers*, third ed., John Wiley & Sons, New York, 1980; R.J. Ashley, *Permeability and plastics packaging*, in: J. Comyn (Ed.), *Polymer Permeability*, Elsevier, London, 1989, pp. 269–308; J.I. Kroschwitz, *Encyclopedia of Polymer Science and Engineering*, John Wiley & Sons, New York, 1988; J. Brandrup, E.H. Immergut (Eds.), *Polymer Handbook*, third ed., John Wiley & Sons, New York, 1989; Z. Tadmor, C.G. Gogos, *Principles of Polymer Processing*, second ed., Wiley-Interscience, John Wiley & Sons, Hoboken, NJ, 2006; Matweb Material Property Data, www.matweb.com, 2017 (Accessed 12 January 2017); N. Peelman, P. Ragaert, B. De Meulenaer, D. Adon, R. Peters, L. Cardon, F. Van Impe, F. Devlieghere, *Application of bioplastics for food packaging*, *Trends Food Sci. Technol.* 32 (2013) 128–141; M. Cunha, B. Fernandes, J.A. Covas, A.A. Vicente, L. Hilliou, *Film blowing of PHBV blends and PHBV-based multilayers for the production of biodegradable packages*, *J. Appl. Polym. Sci.* 133 (2016) 42165.)

possibility to develop multilayer products, where each individual layer is tailored to ensure a certain property (barrier, mechanical resistance, aesthetic); biaxial orientation increases significantly the barrier and the mechanical properties of a film or bottle and triggers some interesting behaviors, such as those of shrink films. Converting technologies for flexible packaging allow the automatic manufacture of a wide range of innovative product designs. It is worth noting that polymer processing technologies are generally more energy efficient when compared with those of other materials due to the lower temperatures involved (typically below 300°C). These technological developments have enabled significant reductions in the weight of packages (on average, in the last decade the average plastic packaging weight decreased 28% [5]), which in turn brings about significant savings in transportation costs.

Future trends in plastics packaging will be probably determined by: (i) how these materials will continue to successfully comply with the progressively more stringent requirements for product protection; (ii) the processability of new biopolymers, that is, how amenable these materials will be to existing processing and converting technologies; (iii) market and legal issues; and (iv) by environmental sustainability (e.g., plastics packaging recycling and energy recovery rates in Europe have attained approximately 100% in a few countries and is generally above 60% in the remaining [2]).

Due to their practical importance, this chapter focuses on the main processing and converting technologies used for producing plastics food packages, with a focus on polymer-based nanocomposites (PNCs). The text is organized as follows. A first section details the polymer properties required for their conversion into packaging, which may bring the necessity to mix them with various additives and nanoparticles. The preparation of PNCs is treated in a second section, whereas the third section presents the main processing technologies used to convert them into food packages.

5.2 PROPERTIES REQUIRED FOR PROCESSING POLYMERS: THE ADVANTAGES OF (NANO) ADDITIVES

Most polymers used in food packaging are thermoplastic in nature, that is, they become viscoelastic fluids when sufficiently heated and hard when cooled, the cycle being repeated without significant changes in their structure and properties (this feature facilitates recycling but has practical limits, as each heating step can induce a certain degree of thermal degradation, the problem being frequently aggravated with biopolymers). Processing technologies take advantage of these characteristics by normally adopting the following approach:

- (i) The material is fed as solid pellets (about 3 mm in size);
- (ii) These are compressed and heated until molten;
- (iii) The melt is pressurized and mixed, so that its constituents (i.e., polymer and additives) become homogenized;
- (iv) The melt is shaped by means of pressure flow through a shaping tool;
- (v) The melt is cooled until its shape becomes consistent;
- (vi) The part is removed from the equipment.

Consequently, the thermal, mechanical, and rheological properties of a given polymer system define its processability. The shear viscosity of polymer melts suitable for melt processing is non-Newtonian (shear thinning) and typically varies between 10^3 and $100 \text{ Pa} \cdot \text{s}$ in the flow rate range corresponding to each process (from 50 to $5 \times 10^4 \text{ s}^{-1}$). In a few processes polymer melts should resist the stretching associated with shaping and cooling tools, that is, large enough melt elasticity and extensional viscosity are required, with preferably a strain hardening behavior. At large flow rates polymer melts exhibit viscoelastic instabilities that generate surface defects on the final products, and thus limit production speeds. Furthermore, thermal degradation (due to heat conduction and/or viscous dissipation) occurring during polymer processing will yield products with depressed optical and mechanical properties. Cooling of the melt during molding or after extrusion induces crystallization which in turn affects the viscous and elastic properties, as well as the mechanical, optical, and barrier properties of the final product. Thus crystallization kinetics needs to be maximized to allow fast cycle times in injection molding or to avoid the sticking of material on drawing and postextrusion tools.

In order to achieve the required properties for processing or under service, polymers are blended with other polymers and/or additives. This mixing operation is called compounding and allows producing plastics, that is, mixtures of polymers, chemicals, and solid particles. Table 5.2 offers a nonexhaustive list of additives, which are classified following their main purpose or function. The main function of each additive is identified together with its action mechanism. Many additives listed in Table 5.2 are actually solid materials with nanometer sizes, which mean that the compounding of the polymers with additives results in many cases in the production of a polymer nanocomposite (PNC).

Several additives are used to minimize the degradation of plastics during melt processing and life cycle. Other additives are specific to polymer blending (compatibilizers), to processing (lubricants), to composites (fillers, wetting agents), or to attributes needed for the final product (e.g., barrier or antimicrobial properties). Some additives are multifunctional. For instance, the

Table 5.2 Additives used in the Formulation of Plastics and Polymer Nanocomposites [3,4,6,7]

Function	Materials	Type of Action
<i>Processing aids</i>		
Thermal stabilizers	Alkyl phenols, aromatic amines	Antioxidants: absorb radicals leading to chain scission
	Aromatic phosphites, organic sulfides	Antioxidants: avoid chain branching after scission by decomposing hydroperoxides without formation of radicals
Lubricants	Chelating agents, sterically hindered phenols, amides, polyhydrazides	Metal deactivators: form less active compounds and radicals originating from catalysts, pigments, fillers, biocides, processing tools, etc.
	Fluoropolymers, oleamide, clays, talc, limestone, silica, zeolites	Promote slip at the tools surface by migration to the surface thus reducing melt fracture and allowing faster production rates, facilitating demolding and avoiding blocking of processing lines
	Calcium stearate, paraffin waxes	Plasticization of polymer particles (pellets): promote or delay the fusion of the pellets by controlling friction between pellets and thus heat
Viscosity enhancers	Paraffin waxes, fatty acids, short chain alcohols, metallic soaps, polymers, nanoparticles	Decrease the viscosity: diluent/solvent effect, addition of free volume (particles smaller than polymer size) ^a , non-Einstein effect (interactions and slip between nanoparticles and polymers) ^a
	Fumed silica, clays	Physical effect: add internal friction and hydrodynamic drag
Antifoaming agents	Stearic acid, peroxides, silanes, reactive polymers	Chemical effect: crosslinking and grafting chemical reactions on the polymer chain resulting in chain extension, ramification, and reticulation, eventually enhancing the viscosity
	Silicones, polysiloxane oils, surfactants, fatty acids	Reduce surface tension allowing breaking up the foam
Coupling agents	Stearate, titanate, anhydride	Physical or chemical modification of particles surfaces and polymers to promote the interaction with the polymer matrix thereby avoiding droplets and particles aggregation
<i>Stabilizers</i>		
Light (UV)	Carbon black/pigments, metal oxides (nanoparticles)	UV absorption, UV blockers
	Sterically hindered amines	Deactivation of UV-induced chromophores which trigger radicals giving way to chain degradation through oxidation (photooxidation)
	Nickel phenolates	Scavenging of free radicals formed by chromophores
	Benzotriazols, nickel phenolates Metal (Ni,P,Zn) complexes of sulfur containing compounds	Chromophore quenchers: absorb light energy Hydroperoxides decomposers (same mechanism as antioxidants)

Table 5.2 Additives used in the Formulation of Plastics and Polymer Nanocomposites—Cont'd

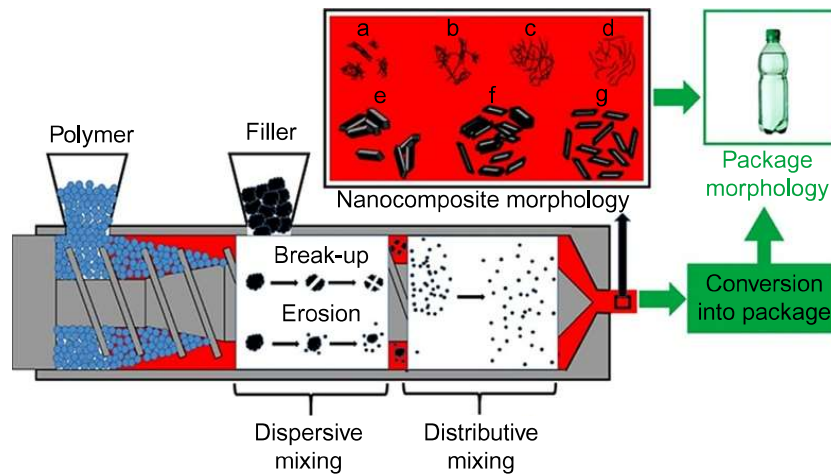
Function	Materials	Type of Action
Antiaging	Phosphates, thioethers, sterically hindered phenols	Antioxidants
Biostabilizers (antimicrobials, biocides)	Copper quinolate, metal oxide nanoparticles (zinc and titanium oxides), silver ions and salts, thio compounds	Disruption of microorganism membranes
<i>Modifiers of mechanical properties</i>		
Reinforcement	Solid fillers (glass and natural fibers, clays, salts, metals, polymer fibers, carbon nanotubes, graphene, etc.) Organic peroxides, organofunctional silanes	Composite technology: buildup of an elastic network, and strong adhesion between filler and polymer matrix to transmit the load Chemical crosslinking through generation of radicals
Plasticizers	Phthalates, phosphates, aliphatic/aromatic mono and dicarboxylic acid esters, polymers, vegetable oils	Addition of free volume, and reduction of polymer-polymer interactions thereby reducing elastic modulus while increasing strain at break
Impact modifiers	Rubbers, elastomers, triblock copolymers (SBS)	Multiphase (soft/hard) structure where the phase of the additive acts as local absorption of stresses or local damper
<i>Modifiers of other properties</i>		
Surface properties	Fatty chain glycols, polyther surfactants Ethoxylated amines, quaternary ammonium salts, phosphate esters, glycerides Ionic and nonionic surfactants Silica, oleamide, graphite, polytetrafluoroethylene	Antifogging agents Antistatic agents, adhesion promoters Wetting agents Antiblocking, slip promoter, antiwear additives (see lubricants)
Optical properties	Metal oxides, pigments, dyes SiO ₂ , talc, sodium benzoate, polymers	Colorants Nucleating agents thereby reducing crystals sizes and improving transparency
Permeability	Solid particles with platelet shapes (nanoclays, graphites, etc.)	Tortuosity: increase the diffusion path of permeating species
Electrical conductivity	Carbon black, metals, carbon and graphite fibers and nanoparticles, metallized fillers	Building a percolating conductive network in the polymer matrix
Flame retardants	Aluminum hydroxide, phosphorous compounds, antimony, brominated compounds, fluorine, and sulfur compounds	Physical action by favoring heat dissipation or shielding the gas phase (flame, oxygen, and volatile products of the combustion) from combustible by forming a charred layer in the condensed phase; chemical action by removing fire-propagating radicals (H and OH) in the gas phase
Blowing agents	Sodium bicarbonate (carbonates), azo compounds, nitroso compounds hydrocarbons, halocarbons, CO ₂ , N ₂	Chemical action Physical action

^aStill the matter of a vivid debate, see, for instance, H. Goldansaz, F. Goharpey, F. Afshar-Taromi, I. Kim, F.J. Stadler, E. van Ruymbeke, V. Karimkhani, Anomalous rheological behavior of dendritic nanoparticles/linear polymer nanocomposites, *Macromolecules* 48 (2015) 3368–3375.

incorporation of selected metal nanoparticles may confer heat dissipation (and inherently improved flame resistance), electrical conductivity, UV light blocking, mechanical reinforcement, and antimicrobial activity. However, a prerequisite to meet some of these properties is to achieve a homogeneous dispersion of the additives in the polymer matrix.

5.3 MANUFACTURE OF PNCs: THE QUEST FOR DISPERSION

Three decades ago, theoretical considerations showed that nanosized particles with large aspect and surface-to-volume ratios could percolate through a matrix to build three-dimensional networks at a very small volume fraction, typically between 0.01 and 0.05 vol% [8]. The use of nanofillers such as carbon nanotubes (CNT) in polymer matrices was therefore seen as very promising to achieve high electrical conductivity and reinforcement at much smaller filler loadings than those (typically between 10 and 40 wt%) used in conventional polymer composites. However, in practice, electrical conductivity in polymer-CNT nanocomposites prepared by melt mixing processes is only achieved with the incorporation of 0.1–5 wt% of CNT [9]. This large mismatch between theoretical and actual amounts of expensive CNT stems from the issue of the dispersion of the filler within the matrix to readily achieve nanosized morphologies. This has been identified as a major bottleneck to solve before bringing PNCs to large industrial applications [10]. As a result, the mechanism of dispersion of nanoparticles is a long but vivid research topic in polymer science [11] and engineering [12]. The basic concepts of fillers dispersion in polymer melts are depicted in Fig. 5.1, focusing on polymer melt extrusion, as this process is the most popular dispersion route used in the plastics industry to compound polymer composites. Pellets of polymer are first fed into the extruder and molten prior to the addition of the fillers in powder form (micrometric clusters of aggregated nanosized particles, i.e., the primary nanoparticles). Wetting of the clusters by the polymer melt first occurs and their dispersion into aggregates and primary particles takes place through cluster erosion and/or breakup. Following the dispersion step, particles are distributed within the polymer melt, eventually reaching a steady structure which depends on the complex interplay between the particles characteristics (shape, size, particle-particle interactions), the polymer melt viscoelasticity, the flow characteristics and history (total strain, extensional and shear velocities, velocity pattern), and the physical-chemical interactions between particles and polymer melt. Fig. 5.1 illustrates specific PNCs morphologies that can be formed with CNT and plate-like fillers (e.g., clay arranged in stacked platelets called tactoids, graphite flakes, etc.).



■ **FIG. 5.1** Compounding of a PNC with melt extrusion into a package. Nanocomposite morphology is represented by (A) bundles of wormlike CNT, (B) network of CNT aggregates and dispersed single CNT, (C) network of well-dispersed CNT, (D) nonconnected and fully dispersed CNT, (E) tactoids of clay platelets or flakes of graphite sheets, (F) a polymer network intercalated into expanded clay tactoids and exfoliated clay platelets, (G) exfoliated clay platelets or graphite sheets.

Polymer pellets (gray balls) are fed into the extruder and conveyed by the rotating screw to the hot zones of the extruder heated barrel. There, pellets melt into a homogeneous viscoelastic polymer fluid depicted in dark background. Filler powder (black clouds) is then fed into the polymer melt and dispersed by the rotating screw. The design of the latter promotes large stresses to enable rupture and erosion of filler clusters. The composite melt is then pumped into the distribution zone where the rotating screw spatially rearranges the PNC melt by separating and merging flow lines. Finally, the viscoelastic fluid is forced through the die which shapes the PNC into rods that are subsequently cut into pellets. At this stage, different nanocomposite morphologies corresponding to different levels of dispersion can be achieved. These are expanded in the window where the background represents the polymer melt filled with two types of fillers: CNT or clay. Different levels of dispersion are pictured, from microscopic (micrometric aggregates as in a, b, e) to truly nanoscopic morphologies (single CNT or exfoliated clay platelet as in c, d, g). The PNC is eventually converted into a package. During this stage, the nanocomposite structure is altered by an additional thermomechanical cycle resulting in a final package morphology. For instance, exfoliated and intercalated clay platelets can be oriented during the injection blow molding of PNC bottles for carbonated drinks.

The erosion and breakup mechanisms have been extensively modeled, based on the visualization of clusters and aggregates submitted to simple flow histories [13]. All models start from the computation of the hydrodynamic (viscoelastic) stress applied by the flowing matrix on the cluster. The cohesive

strength of the latter is a complex function of the forces acting between the primary nanoparticles (van der Waals forces, electrostatic forces, and steric/topological forces), the structure of the cluster (e.g., cluster porosity and connectivity between primary nanoparticles), and the possible impregnation of clusters by the polymer melt which may cause bridging between particles. Models showed that extensional flow is more efficient for dispersing solid fillers than shear flow [13]. Cluster breakup occurs when the critical hydrodynamic stress overcomes the cluster cohesive strength. This critical stress may [14] or may not [13] depend on the initial size and internal structure of the cluster, and on the size of primary nanoparticles. Erosion was seen to occur at smaller viscoelastic stresses, as small particle fragments are detached from the cluster, in opposition to breakup in two or more chunks [13]. However, dispersion by erosion would entail much longer times. Flow visualization experiments on different systems brought contradictory erosion results [14,15] which point toward the complex interplay between all parameters mentioned previously.

Once dispersion is initiated, all particles are distributed within the matrix and further dispersion may take place. Processing parameters such as screw speed and profile (different elements of the screw are designed for specific distributive or dispersive mixing, not mentioning the conveying of pellets and melt pumping, resulting in a screw profile adapted to a specific compounding application), the extruder temperature in each zone, the feeding rates of polymer and filler, and the residence time of materials in each mixing zone affect the morphology of the extruded PNCs. The characterization of cooled extruded samples by microscopic/submicroscopic imaging or scattering techniques reveals many relationships between processing parameters and quality of dispersion. Conclusions are rather specific to each polymer-nanoparticle system but overall indicate that no complete dispersion of single nanoparticles has been achieved to date by melt compounding [11,12]. Among the strategies investigated to enhance dispersion, modification of the interaction between the polymer and the filler is usually adopted. The modification of clay by ion exchange reaction with cationic surfactants leads to the partial reduction of the electrostatic attraction between clay layers. As a result, the interlayer distance is enlarged allowing the intercalation of polymer chains within tactoids, which leads to the exfoliation of organically modified clay platelets [16]. This concept can be even developed by blending such modified clay (also called organoclay) with monomer and then initiate the polymerization onto the surface of the exfoliated clay platelet. Such route was adopted for the first time by the Toyota Research Group to produce clay-Nylon nanocomposites for automotive applications [17] and is now utilized for delivering clay-PNCs for packaging

[18]. However, a fully exfoliated structure is only obtained with polymers containing polar functional groups. Polymer-clay nanocomposites are alternatively produced by melt compounding an organically modified clay with a functionalized polymer, for instance, a PP grafted with maleic anhydride (PP-g-MA). This modified polymer contains the necessary polar groups to bond to the clay platelets and also brings the necessary compatibility with a PP matrix added during the process [19]. Similar approaches have been used to enhance the dispersion of CNT or graphite into polymers [11,12]. However, either the functionalization of fillers by chemical routes or the simple addition of a modified polymer during the melt compounding produces PNCs showing both intercalated and exfoliated morphologies. Furthermore, the correct formulation of functionalized filler, modified polymer, and matrix should be optimized together with processing parameters to achieve the best PNC properties.

Tracking the structural evolution of the composite during melt compounding helps understanding the dispersion mechanism. One might stop the process, cool the barrel, and access the material by opening the equipment (in the case of clam-shell construction) [13]. This type of experiments was recently conducted with a small-scale prototype mixer coupled to a capillary rheometer [20,21]. Structural characterization showed that graphite nanoplates dispersed in a PP matrix tend to reaggregate upon stress relaxation. The functionalization of the nanomaterial with PP-g-MA enhanced the stability of the dispersion achieved by melt mixing as reagglomeration was delayed. In addition, the nanocomposite showed the same processability as the PP matrix, as inferred from the similarity in the flow curves measured in situ during mixing. Alternatively, the online sampling of a melt at different extruder locations gives access to structural information while continuously running the compounding. The advantage of online sampling is the fast cooling of small volumes of material as opposed to the slow cooling of the whole equipment, thereby ensuring the freezing of the PNC morphology. Such experiments were conducted to monitor the evolution of organo-clay dispersion in a blend of PP with PP-g-MA [22]. In particular, X-ray diffraction and electron microscopy revealed that dispersion develops quickly in the melting zone, whereas thermogravimetric data suggested that thermal degradation of clay surfactants and PP matrix are at the origin of reagglomeration along the twin-screw extruder. One might bring the online sampling even further, by coupling devices to the extruder, thereby delivering in-process material characterization. The online recording of small amplitude oscillatory shear data showed promising results for monitoring dispersion [23]. This is because the viscoelastic properties of a PNC are closely related to the structure of the elastic network built by the dispersed

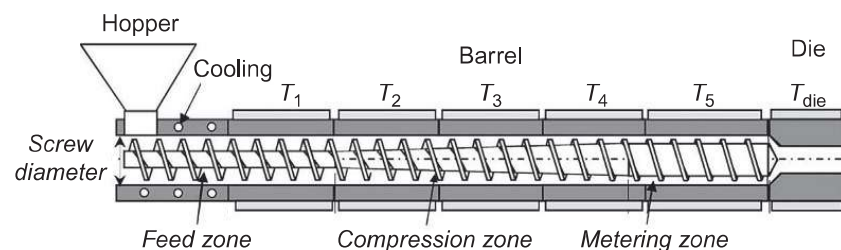
nanoparticles [24]. For instance, a prototype small-scale extrusion line was recently coupled to a rheo-optical slit die. The in situ recording of both shear viscosity and first normal stress difference of filled polymer melts and polymer blends was compared with the size of dispersed fillers and droplets returned by small angle light scattering and optical microscopy [25,26]. Such setup should contribute to develop in-process monitoring tools to readily control and optimize the dispersion of filler during the industrial melt compounding of nanocomposites.

5.4 MAIN PROCESSING TECHNOLOGIES

5.4.1 Extrusion (Film and Sheet)

Extrusion is a major polymer processing technology, used to obtain continuously products with constant cross-section, such as films, sheet, pipes and tubing, profiles, and also to coat substrates (e.g., paper or aluminum). Nevertheless, flexible drinking straws or nets typically used to pack root vegetables are also obtainable by extrusion. The equipment consists of an “extrusion line” that typically comprises an extruder, a shaping die and downstream equipment to cool down, stretch/blow, cut or wind the extrudate, depending on the actual product geometry and requirements.

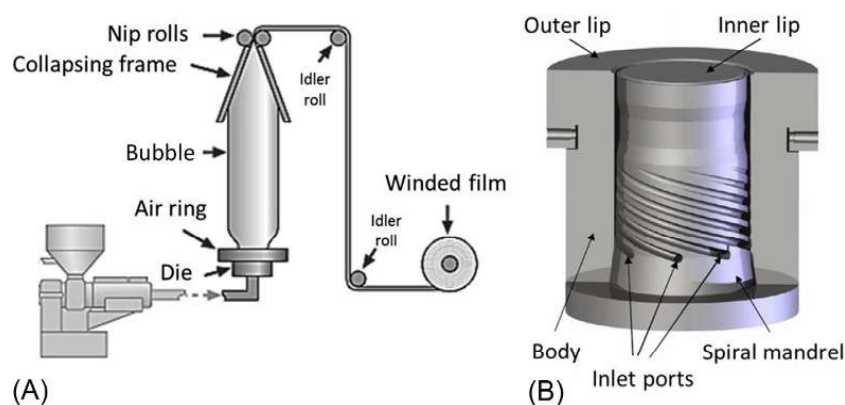
The extruder is in charge of melting, mixing, and pumping the material through the shaping die. As illustrated in Fig. 5.2, single screw extruders use an Archimedes-type screw rotating at a constant controllable speed inside a hollow barrel that is kept under a set temperature profile. The screw has three geometrically distinct sections, with constant and highest channel depth (feed zone), channel depth decreasing linearly in the extrusion direction (compression zone), and constant and smallest channel depth (metering zone), respectively. The barrel contains a lateral opening for material inlet through a vertical hopper, whereas a shaping die is fixed at the opposite end. The free space between barrel and screw root and flights forms a helical channel with a rectangular cross-section along which the material will flow



■ FIG. 5.2 Layout of a conventional single screw extruder.

from hopper to die. The pellets reach this channel by gravity flow in the hopper. Then they are dragged forward due to friction forces and eventually melt due to conducted and dissipated heat. The melt is progressively mixed and pressurized and subsequently flows through the die. Thus the geometry of the die dictates the contour and dimensions of the extrudate. Modern screw designs can contain double helices in the compression zone (this solution creates two parallel flow channels, one for the solids, the other for the molten material, thus increasing the dynamic stability of the process)—these are known as barrier screws and/or mixing sections in the metering zone (to improve dispersive and/or distributive mixing). A detailed analysis of polymer extrusion can be found in the specialized literature (e.g., Ref. [27]).

Postextrusion procedures will depend mostly upon the geometry and dimensions of the extrudate. As shown in Fig. 5.3A, in the case of blown film extrusion an annular die extrudes vertically upward a molten tube, which is then inflated with air into a thin bubble (thickness typically between 7 and 100 μm). The latter is pulled by a pair of nip rolls after being flattened by a table flap/collapsing frame. Then, the film descends with the assistance of various guide/idler rolls and is wound up. An air ring encircling the lower part of the bubble cools the film which will solidify and become cylindrical. The film has a certain degree of biaxial orientation due to stretching in the longitudinal and circumferential directions. Longitudinal orientation is imparted by the take-up ratio, that is, the ratio between the velocities of the nip rolls and of extrusion. Circumferential orientation is produced by the blow-up ratio, defined by the ratio between the bubble and die diameters. Accordingly, adequate settings of screw speed, die diameter, nip roll velocity, and air pressure give the possibility of producing films with a wide range



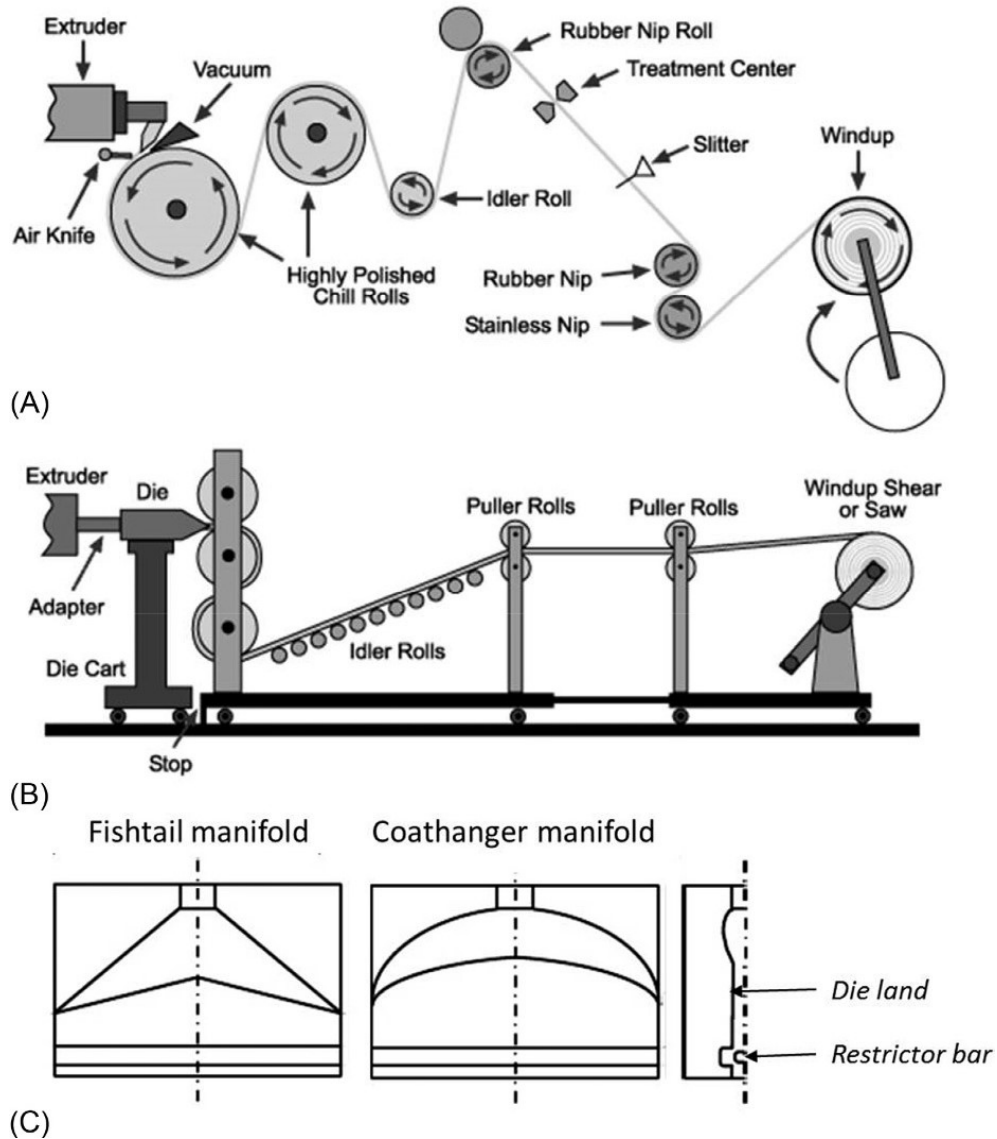
■ FIG. 5.3 Extrusion film blowing: (A) layout of the extrusion line; (B) spiral mandrel die. ((A) Adapted from www.eastman.com.)

of diameters, thicknesses, intensity, and balance of molecular orientation (i.e., physical and mechanical properties). The flattened tubular film geometry is particularly convenient for the manufacture of all sorts of plastic bags. Slitting the film longitudinally can result in large widths and these films are well suited for applications in agriculture.

Modern equipment is often capable of simultaneous external and internal bubble cooling, which not only increases production rates, but yields films with improved optical characteristics, since less time is given for crystallization. Die design has also received substantial attention, as it is important to ensure that the extrudate emerges with uniform thickness and temperature along its perimeter and that no welding lines resulting from impinging flows in opposite directions take place inside the die. Fig. 5.3B shows the geometry of a spiral mandrel die, which is commonly utilized in industry. The melt coming from the extruder arrives at several inlet ports and starts flowing along individual spiral channels. However, as these become progressively shallower, a growing portion of the melt initiates a vertical movement toward the die lips. A well-designed die will take into consideration the rheological behavior of the melt to ensure balanced flow across the perimeter and reduced local viscous dissipation. Even so, most dies allow for local gap adjustment. The fine tuning of the film thickness can also be obtained using air rings with adjustable airflow valves around the circumference.

This processing technique has two major drawbacks. Melt stretching to form the bubble requires sufficient extensional viscosity and strain hardening characteristics from the melt. In this respect, materials such as PP and LLDPE are weak and thus difficult to process in conventional lines. Vertical downward lines with quenching by contact with a cold mandrel were developed for PP and are also being presently applied to manufacture thick films (up to 300 μm). On the other hand, cooling by forced convection has limited efficacy, with possible consequences in terms of transparency (slower cooling allows time for larger degree of crystallinity and bigger spherulites) and thickness uniformity (gauges can vary from 5% up to 20%).

A competing processing method is cast film or sheet extrusion (sheets have thicknesses above 0.25 mm), in which a slit die shapes the melt into a wide and thin rectangular cross-section that is subsequently cooled by direct contact with temperature-controlled highly polished chill rolls. PET, PS, PA, PP, and PMMA are commonly processed in this way (film thickness can be as low as 15 μm , gauge usually varies between 1.5% and 5%). Since thickness affects the flexibility of the extrudate, the layout of film and sheet extrusion lines differs somewhat. Cast film (Fig. 5.4A) is often extruded



■ FIG. 5.4 Cast film/sheet extrusion: (A) layout of a cast film extrusion line; (B) layout of a cast sheet extrusion line; and (C) slit die geometry. ((A,B) Adapted from www.eastman.com.)

downward, contacts tangentially a first chill roll and then moves on to a second chill roll (kept at a lower temperature) in order to equally expose the opposite side to cooling by contact. To maximize cooling efficiency, an air knife and a vacuum box may be installed near to the die exit. The first forces the melt against the chill roll, thus increasing the contact angle between both. The second removes air that could become entrapped between film and roll, thus decreasing local cooling rates due to its thermal

insulating characteristics and causing surface defects. The film is pulled longitudinally by rubber coated nip rolls and wound up. The film dimensions are controlled primarily by the die geometry, extrusion rate, and takeoff speed. Molecular orientation develops in the longitudinal direction, its intensity depending on the ratio between nip rolls velocity and extrusion velocity. Sheet is extruded either horizontally or vertically onto the gap between two rolls of a three-roll stack of polishing rolls that are temperature controlled by circulating hot oil (Fig. 5.4B). This equipment exerts pressure by properly adjusting the gap between the rolls, which helps to regulate the thickness of the sheet and may also be used to texturize it (in this case, one of the rolls is embossed with the desired pattern). The sheet then progresses toward a series of cooling rolls in a frame and is next wound up.

Even when the film or sheet emerges from the die with uniform thickness and temperature across the width, differential stretching and elastic relaxation at the center and edges before the first chill roll decreases the width (neck-in effect) and tends to thicken the extrudate at the edges (this phenomenon is known as dog bone effect). This is why the edges are frequently trimmed off before winding (and subsequently incorporated back into the hopper after shredding). A poor performing die will emphasize this defect. Yet, designing dies for slit extrusion that guarantee uniform flow velocity, temperature, and residence time across the width at the outlet is far from straightforward. Indeed, since the flow path of a fluid element in the center is much shorter than that of an element flowing toward the edge, higher velocities at the center would be anticipated a priori. As depicted in Fig. 5.4C, most dies contain a manifold with a relatively large cross-section that distributes the incoming melt across the width before it flows through the shallow land, toward the die exit. Thus a central fluid element flows a short distance in the manifold and a longer length in the land, whereas a flow element near to the edge benefits from a lengthier flow path in the manifold and a shorter flow path in the land. In both cases, for a balanced flow the total pressure drop should be equal. The design of the manifold depends on the rheological response of the fluid. Initially manifolds were T-shaped, but evolved into fishtail and coat hanger shapes, which are the most common nowadays. Anyway, as variations in flow rate, polymer properties, and local temperatures will affect the flow balance, in practice dies are generally fitted with a restrictor bar downstream of the manifold as well as with adjustable die lips. The local vertical settings can be adjusted by screws. These can also be coupled to step motors or replaced by piezoelectric bolts for automatic thickness control, based upon in-line thickness measurements after the cooling rolls. In order to increase the range of possible

extrudate widths, dies may also be equipped with sliding rulers that displace the lateral channel walls.

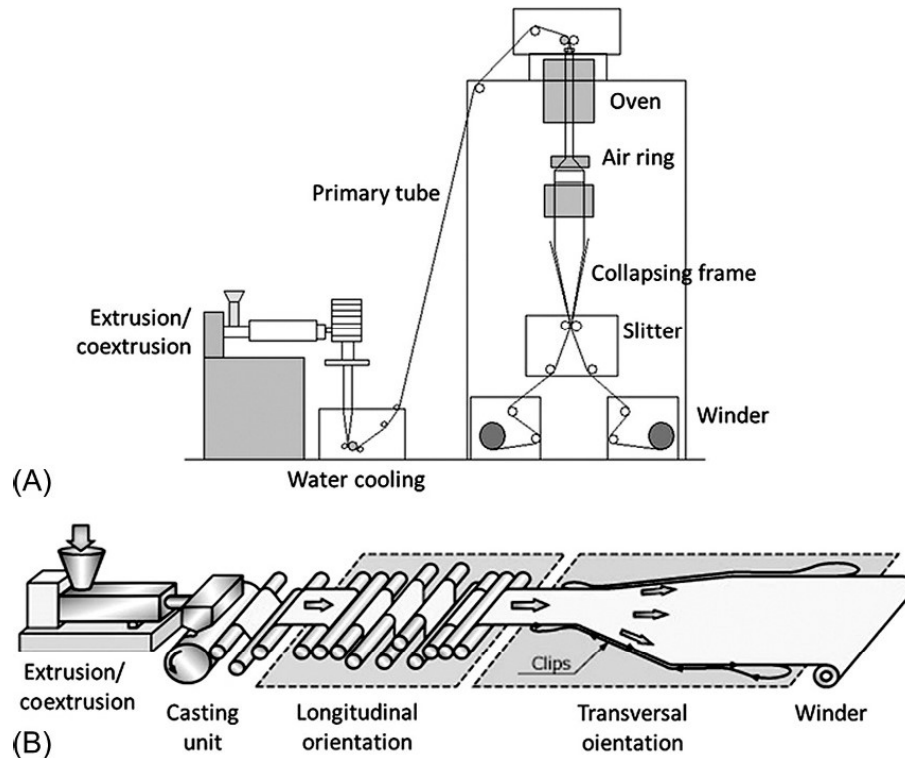
The manufacture of multilayered film or sheet is readily available by coextrusion. In this technology, each polymer is melted and pumped in an individual extruder and then the various polymers are joined upstream (using a feed block) or at the die. The downstream equipment remains unchanged relative to conventional extrusion. The number of extruders is not necessarily equal to that of individual layers, as the same polymer melt can be made to generate more than one layer (this is typically the case of adhesive or tie layers), depending on feed block or die design. Currently, combinations of up to 12 layers are not uncommon. For optimal performance, layers should have uniform thickness along the length and width, interfaces of contiguous layers should remain smooth in order to guarantee good optical properties, and good adhesion between layers is important for mechanical properties. These requirements are more easily met if the various melts have similar viscosities and elasticities within a common processing temperature window, as well as some degree of chemical compatibility. When the latter does not exist between any pair of polymers, an additional adhesive layer has to be created.

Multilayered blown film is generally produced using coextrusion spiral mandrel dies. Most designs contain concentric individual spiral mandrel channels, the melts being joined close to the die exit in order to minimize the length of channel along which they flow together. The “pancake” solution is based upon the concept of horizontal (rather than vertical, as represented in Fig. 5.3B) planar spiral mandrels. Not only the design is more compact, if additional layers are needed the corresponding individual modules can be stacked vertically. Due to the complexities of the design and melt flow in sheet dies, the feed block solution is generally adopted, as it enables the use of conventional extrusion dies. Adjustable feed blocks containing exchangeable modules allow changing the number of layers and/or the relative position of each layer.

As mentioned previously, cast film/sheet extrusion yields a mono-oriented extrudate, while film blowing induces biorientation. However, the intensity of this orientation is limited, as most of it develops within a very short time/length, while the material is being cooled. High orientation levels require high stretching during sufficient time, at sufficiently low temperature (if the polymer is semicrystalline, just below the melting temperature to ensure enough molecular mobility of the amorphous phase). Thus significant orientation usually requires reheating the extrudate, stretching and cooling.

Conventional film and sheet lines can be retrofitted with longitudinal stretchers (e.g., to manufacture shrink wrap). Biaxial orientation (not necessarily balanced in the two directions) involves stretching the film both longitudinally and transversely, which requires dedicated equipment. Mono and multilayered films containing PE, PVC, PA, EVOH, and polyvinylidene chloride (PVdC) are commonly biaxially oriented using the double-bubble process or one of its variants (a triple bubble process producing high barrier films with 11 layers for coffee and meat packaging was recently launched commercially), while PP, PA, PET, PS, and PLA are often bioriented in simultaneous or sequential (by far the most common) stretching tentering lines. Draw ratios usually range between 5 and 10.

Fig. 5.5A illustrates the layout of a coextrusion line for the production of PE-based biaxially oriented blown films. A tube is extruded vertically downward, calibrated and cooled with water. It is worth noting that eventual nonuniformities in this tube will be amplified during the subsequent blowing step, hence they must be carefully minimized. The tube is subsequently pulled toward the top of a tower by means of a pair of nip rolls, being steered by a few guide rolls, and then changes direction and progresses vertically downward. Now the tube is reheated in a radiation oven and simultaneously blown by means of air pressure and stretched axially by a pair of nip rolls located underneath. This is followed by bubble cooling using external air rings and winding. Gauge along the circumference and bubble diameter is measured in-line, the data being used for manual or automatic control. Fig. 5.5B presents the layout of an extrusion line for the production of biaxially oriented PP-based cast film. The first part of the line is conventional, that is, it encompasses extruder(s), slit die, and chill rolls. Cooling may be complemented with a water bath in the case of thick films. Then, the material is stretched longitudinally in a section containing horizontally staggered rolls. The first rolls comprise the preheating zone, which reheats the film to the optimal stretching temperature; the next rolls run at higher speeds to stretch the film axially; the film is cooled in the last rolls. In the next step, the film is stretched in the transversal direction. To achieve this, the film is clipped on both sides by magnetic or mechanical operating claws that run at constant speed on a diverting chain track. The entire system is enclosed in a large oven, the tentering chamber. Each claw clips the film upstream, moves along the track, opens at the exit, and returns at the same speed to the initial position to clip the film. The bioriented film traverses a gauge measurement station (for automatic control of die aperture) and is wound. These lines can reach production speeds above 500 m/min and manufacture films with thickness between 12 and 60 μm and width up to 10 m. Consequently, the dimensions of the equipment are quite significant (e.g., one manufacturer advises installation of its largest machine in a room with dimensions 150 \times 30 m).



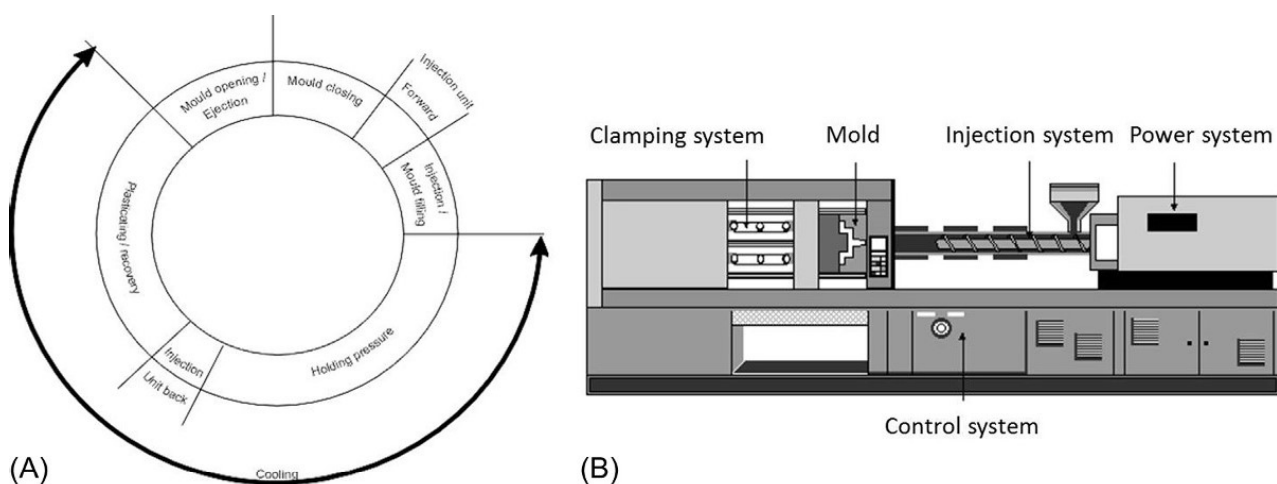
■ FIG. 5.5 Biaxial orientation film extrusion lines: (A) blown film; (B) cast film. (Adapted from www.jsw.co.jp.)

5.4.2 Injection Molding (Containers, Lids, and Caps)

Injection molding is a widely used polymer processing technique whereby a melt is forced into the cavity (or cavities, if several parts are produced simultaneously) of a mold, followed by cooling and extraction. The technique is suited to the mass production (because molds are generally expensive) of parts with complex 3D shapes and accurate dimensions. Pots, tubs, buckets, pails, and other containers, as well as their lids and caps (often threaded), are normally injection molded. Melting, mixing, and pumping are carried out by a plasticating unit, which is an equipment similar to a single screw extruder, but containing a reciprocating screw, with the ability to move axially backward and forward. As the screw rotates, the material fed by a vertical hopper melts and accumulates between the nozzle (the orifice linking the plasticating unit and the cavity of the mold) and the tip of the screw, pushing the latter backward. When the predefined volume of melt becomes available, the screw stops rotating and moves forward as a ram, creating pressure and forcing the melt through the nozzle and into the mold cavity which will become fully filled. The tip of the screw contains a check ring (also known as nonreturn valve) that hinders back flow along the helical screw channel.

Once the cavity is filled, pressure is maintained (this is known as holding pressure) to compensate for material shrinkage upon cooling and the eventual creation of voids in the bulk. This pressure is kept until solidification of the material in the channel linking the nozzle and the cavity. Now, while the mold remains closed until the part becomes sufficiently strong to be extracted, the next shot (i.e., the next production cycle) can start to be prepared. The screw retracts and begins rotating, receiving and melting new material. In the meantime, the mold opens and the part is removed. This sequence of events to produce one part (again, or various parts if the mold contains various cavities) is called a cycle and is represented schematically in Fig. 5.6A. The breadth of each box is proportional to its typical duration. The importance of cooling—the mold remains closed—is evident, as it encompasses various steps. The thicker the part, the longer the cycle is. In practice, injection molding is usually limited to parts <3 mm thick. For food packaging applications, thin parts (with thickness under 0.8 mm) can be manufactured with high yields (injection rates of up to 2 kg/s).

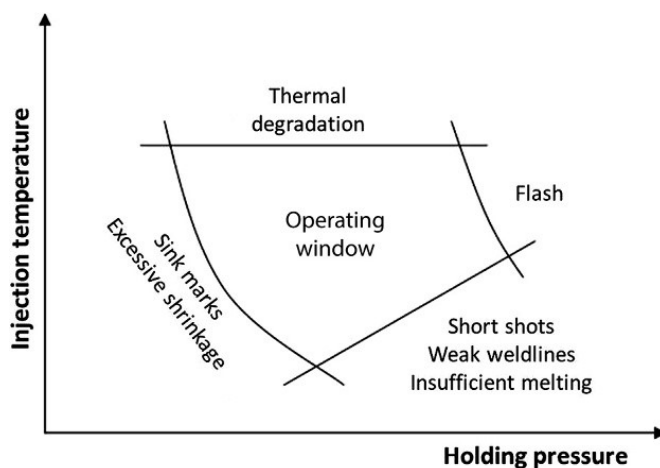
An injection molding machine usually comprises four systems mounted on a common base (Fig. 5.6B): (i) the injection system containing the plasticating unit; (ii) the hydraulic, electric, or combined power system that controls the movements of the screw and platens; (iii) the clamping system, containing two vertical platens that hold, open, close, and lock the mold; and (iv) the control system, that is used to setup, control, and manage the process parameters, including speeds, pressures, times, temperature, and displacements of moving parts. Hydraulic injection molding machines use a hydraulic pump to provide pressure and hydraulic valves to control the moving components.



■ FIG. 5.6 Injection molding: (A) the production cycle; (B) the various systems of a machine.

Electric machines contain individual servomotors to operate each component. These are usually cleaner, more energy efficient, accurate, and reliable. Clamping units can be very sophisticated, being capable of closing/opening the mold very quickly, but assuring gentle contact between the mold parts to preserve their service life. Injection molding machines are usually rated by their maximum clamping force (usually between 5 and 10,000ton) and shot size, which is the maximum amount of melt than can be injected in a single shot. The clamping force depends on the material used, on the size of the part (particularly the projected area in a vertical plan), and on the operating conditions. These include: (i) temperatures of the barrel, nozzle, and mold; (ii) maximum injection pressure and holding pressure; (iii) injection time, holding time, and holding pressure time; and (iv) shot size, determined by the axial screw travel. Fig. 5.7 shows that a proper combination of values of these variables creates a feasible operating window.

Too high temperatures will prompt thermal degradation, while the reverse can cause insufficient melting, partially filled cavities (known as short shots) or weak regions in the part (e.g., merging flow fronts coming from opposite directions will cause weak weld lines). The last two result from the higher viscosity levels associated to lower temperatures (in the case of the weld lines, high viscosity prevents the entanglement at macromolecular level of the two flow fronts). If the pressure exceeds the clamping force flow will leak through the partition between the mold halves (this is called flash); conversely, too little holding pressure or time may allow for too much shrinkage, or the appearance of sink marks. High injection rates, thin walls, and intricate geometries require polymers with relatively low viscosities,



■ FIG. 5.7 The injection molding diagram.

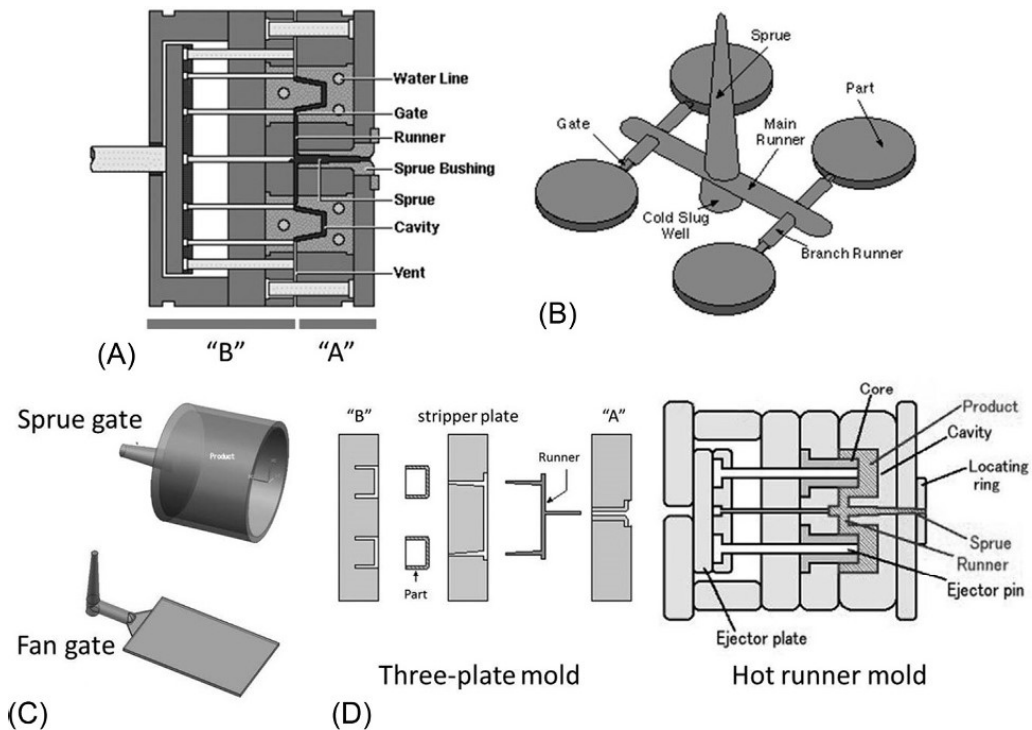
that is, higher melt flow rates (MFR). Lids produced by injection mold often exhibit warpage. This is caused by operating conditions leading to uneven residual stresses in the part. Although the topic goes beyond the objective of this chapter, it seems important to mention that residual stresses in injection molded parts result from the combined effect of flow and heat transfer. Flow induces orientation in the flow direction (whose intensity decreases across the thickness), cooling induces a sharp temperature gradient also across the thickness. Orientation increases strength, but also greater shrinkage on cooling. Warpage on the finished product occurs when the temperature is raised high enough for molecular relaxation to take place. High injection and mold temperatures, together with slow cooling and thicker parts would decrease orientation and generate lower stresses, but these conditions are of course associated to low production yields and poor process economics.

The mold is fixed to the clamping unit of the injection molding machine and takes in the molten plastic, shapes it and cools the material until it becomes solid again and the part can be removed. More specifically, the mold is designed to perform five major tasks:

- (i) to provide a pathway for the melt to flow from the injection unit to the mold cavity(ies);
- (ii) to shape the melt into the required geometry, dimensions, and surface finish of the part(s);
- (iii) to allow the air trapped inside the mold by the advancing melt to escape through the partition between the mold platens, thus preventing the appearance of air bubbles in the final part(s);
- (iv) to cool the part until extraction is possible without damaging it;
- (v) to eject the part(s).

Nowadays, mold construction has reached a high degree of standardization in terms of modular components, which decreases significantly the time required for its fabrication.

One of the mold platens is secured to the fixed platen of the machine (and often denoted as the “A” half), the other to the moving platen (“B” half)—see Fig. 5.8a. Considering a mold for the manufacture of a cup, the “A” half will contain the hollow cavity side, while the “B” half will contain the convex core. The former includes also the runner system that transfers the material from the nozzle to the cavity. As illustrated in Fig. 5.8b, the runner system comprises the sprue (the channel directly in contact with the injection nozzle during injection and packing), the runner (links the sprue to the cavity entrance), and the gate (defines how the melt enters the cavity). This means that the runner system consists of excess material that needs to be separated from the part (and eventually recycled). Fig. 5.8b also shows that



■ FIG. 5.8 The injection mold: (A) mold components; (B) runner system; (C) sprue gate and fan gate; and (D) three-plate mold and hot runner mold.

for a balanced flow in the mold, the flow resistance (i.e., the flow path) associated to each individual cavity should be identical. Otherwise, incomplete filling of the more distant cavities will occur. Fig. 5.8c shows two examples of gates. The sprue gate is the simplest and is used to inject cups from the center of the base. Melt flows radially in the base and along the lateral walls, all flow lines being equal and no weld lines being created. However, this gate can be difficult to separate from the cup and leaves a large mark. The fan gate is appropriate for rectangular plaques (if applied to the cup, it would create a weld line on the opposite side wall) and leaves a small mark. The "A" side also has leader pins (perpendicular to the mold partition wall) that ensure good alignment between the "A" and "B" halves during mold opening/closing. When the plastic cools, the part tends to stick to the "B" side due to shrinkage. Thus this half contains an ejector system. When the mold opens, ejector pins protrude perpendicularly from the core surface and push the part out either totally or partially (in this case, a robot will automatically pick up the part). Finally, cooling channels are machined in both the "A" and "B" halves that keep the mold walls at constant temperature by water or oil circulation.

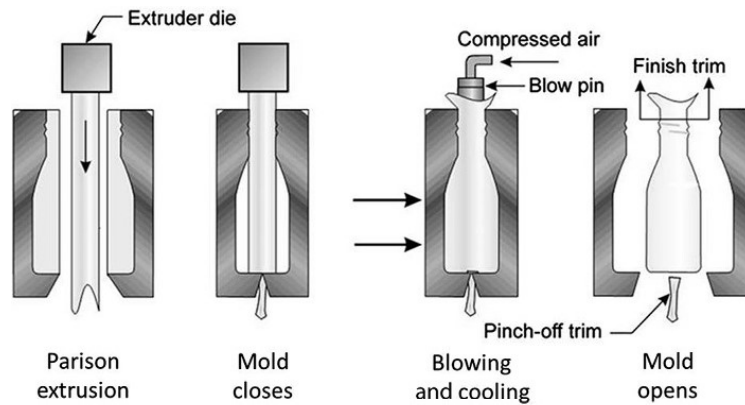
In general, molds can be classified as two-plate molds, three-plate molds, and hot-runner molds. The first were described previously. Three-plate molds (Fig. 5.8d) have an intermediate plate, the stripper plate, between “A” and “B.” While the sprue is necessarily part of the “A,” the remaining runner system channels are machined in the stripper plate. When the mold opens, the runner system is separated from the part and both are extracted (in two-plate molds this separation can require an additional operation, depending on the gate used). As the name implies, hotter runner molds (Fig. 5.8d) are able to keep the material in the runner molten, avoiding, or minimizing, the generation of excess material.

Injection molding has seen impressive technological developments not only in terms of precision, reproducibility, and control capacity, but also in diversity of process variants yielding parts with a wide variety of characteristics. Gas-assisted injection molding produces hollow parts (popular for the automotive industry); in structural foaming a gas is introduced in the melt prior to filling the mold, thus yielding foamed parts; insert molding enables to insert a component of the part in the mold before filling the cavity; in in-mold labeling the label becomes part of the container, instead of using an adhesive applied in a second operation. Multimaterial molding techniques include, for instance, bi-injection or coinjection molding (two materials are injected into a cavity creating a sandwich structure, e.g., with recycled material in the core) and multishot molding (two materials are injected sequentially into separate cavities by means of a rotating mold, becoming side by side; a practical example would be caps with articulated lids of different color or transparency).

5.4.3 Blow Molding (Bottles)

Blow molding is widely used to manufacture bottles of many sizes and shapes, jars, drums and, in general, hollow parts including fuel reservoirs, automotive ducts, cases, kayaks, toys, and so on. Generally, the process consists in using air pressure to blow a hot tube against the contour of the cavity of a cold mold. When the material cools down sufficiently, the mold opens and the vessel is removed. The method has two main variants, extrusion blow molding and injection blow molding, which differ in the way the tube is obtained.

In extrusion blow molding (Fig. 5.9) a single screw extruder melts the plastic pellets and extrudes vertically downward the tube (here known as parison). The two halves of the mold close on the parison. When doing this, the lower part of the mold (known as pinch off) seals the parison, while a hot wire or knife above the mold separates the top of the parison from the material being



■ FIG. 5.9 Extrusion blow molding. (Adapted from www.silganplastics.com.)

extruded. The mold is transferred to a blowing station, where a blowing pin or a needle blows air through the open top of the parison. Pressure forces it to expand against the wall of the mold cavity. Once the plastic has solidified (the mold contains cooling channels with circulating water), the mold opens. Simultaneously, a new length of parison has been made available for a new production cycle.

The process is simple and economic, and thus widely used to produce mid-size (200 mL) to large containers. Output rates can be increased significantly by generating several parisons in parallel, which are then blown in multicavity molds (tandem arrangements are also available, where one parison is used to generate two bottles). Also, coextrusion can be used to generate multilayer parisons. For example, this allows to introduce a layer of recycled material or to use an expensive pigment only in the outer layer for better economics, to provide barrier layer(s) for specific food packages, or to generate a vertical viewing stripe in an opaque bottle. However, extrusion blow molding has a number of important limitations:

- it produces a considerable amount of scrap, known as flash (usually up to 25% of the bottle weight, corresponding to the portions of parison above and below the bottle plus the material cut out to make a hollow handle, if existing);
- the melt should have sufficient extensional viscosity, otherwise the parison will sag significantly due to its own weight and difficulties in blowing will arise—processing aids are often added to polymers to improve their performance;
- final parts may exhibit a significant thickness distribution. This results from the combined effect of two phenomena: (i) extrudate swell (both in diameter and thickness) and sagging due to gravity creates a thickness distribution along the length of the parison; (ii) upon blowing, the

parison will touch first those regions of the mold cavity with smaller diameter, which will become thicker, while zones with higher diameter will become thinner. For similar reasons, manufacture of bottles with oval cross-section or with variations in diameter along the height can be problematic (in the first case, usually the die extrudes an oval parison).

Deflashing can be easily automated, and then the excess material is grinded and incorporated at constant percentage with the raw material. The second limitation is crucial during the manufacture of large containers. In this case, it is usual to resort to intermittent extrusion, whereby the melt provided by the extruder is deposited in an accumulator, from which it is periodically extruded at a fast rate to form the parison. The optimal mechanical performance of a bottle is not necessarily associated to uniform thickness. However, the optimal thickness profile is rarely coincident with that resulting from the process. Parison programming was developed to control thickness distribution. It uses dies with a conical annular gap. By moving up or down the mandrel during extrusion, the die gap is made to vary and so does the thickness of the parison. Hence, it is possible to generate a parison with a geometry yielding the desired wall thickness in the bottle. The most sophisticated systems use laterally deformable dies, so that the ovality of the parison can also be adjusted.

Technological developments allow producing progressively more complex hollow parts, for example, by moving the open mold as the parison is gradually laid down onto the cavity (known as 3D blow molding), eventually assisted by vacuum in the open end to avoid premature sealing, by using sequential extrusion to produce parts having sections with distinct flexibility, or by using molds with movable parts (or plungers) that upon closing in a given sequence create complex contours. Blow-fill-seal technology provides aseptic packaging, that is, enables the manufacture, filling with a product and sealing of a package under sterile conditions, thus eliminating the need of a sterilization stage after filling. The process takes advantage of the temperatures involved in polymer processing to assure an aseptic environment and comprises the following steps:

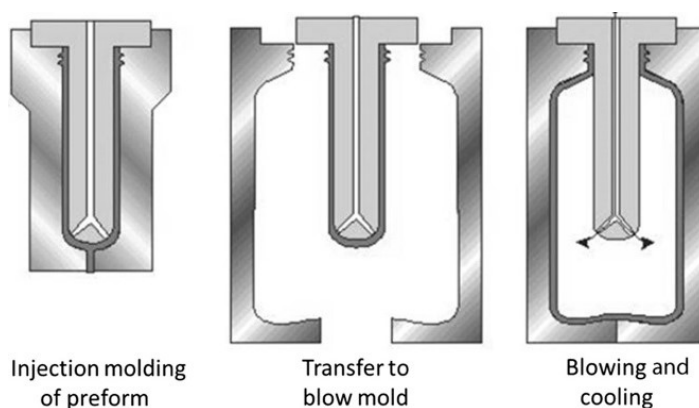
- (i) the parison is extruded vertically downward, the mold closes, the lower part of the parison is sealed by the mold pinch off, the top is separated from the parison being extruded, the mold is transferred to the blowing station;
- (ii) a modified blowing pin lowers into the parison and blows sterile filtered air, thus shaping the container (with volumes in the interval 0.1–1000 mL). The pin delivers a precise amount of product into the container and retracts to the original position;

- (iii) the two halves of an independent seal mold close to form the top and hermetically seal the container;
- (iv) the mold opens and the container is removed.

Hot filling of bioplastics is generally not possible as they have a tendency to deform at low temperatures (in the case of PLA, as low as 60°C).

Injection blow molding is a two-step process (Fig. 5.10). First, a preform with the geometry of a test tube is injection molded. Hot runner molds are usually employed. The molds consist of two halves and a movable core rod that holds the preform. After molding, two possibilities exist: (i) the mold opens as soon as the preform is cold enough to keep its shape, the core rod is transferred and clamped to the blow mold, air is blown through the core (air pressure is higher than in extrusion blow molding because of the cooler parison and corresponding higher viscosity [4]), and cooling and stripping from the core rod take place successively, or (ii) the preform is cooled down, stored or shipped, and converted into a bottle only when needed (this is often the case for bottles for seasonal drinks, since storage of preforms occupies much less volume than bottles). In this situation, the preform will be reheated and blown.

Injection blow molding needs a higher investment in equipment and molds, but produces little scrap and provides a much better control of wall thickness of the body (the preform can be produced with an appropriate thickness distribution), neck, and screw top of the container. Coinjection molding can be employed to produce multilayered preforms, for example, containing EVOH layers for oxygen barrier. Also, in-mold labeling techniques (already referred to for injection molding) can be applied. Conversely, it is not easy to manufacture containers with handles and virtually impossible if these are

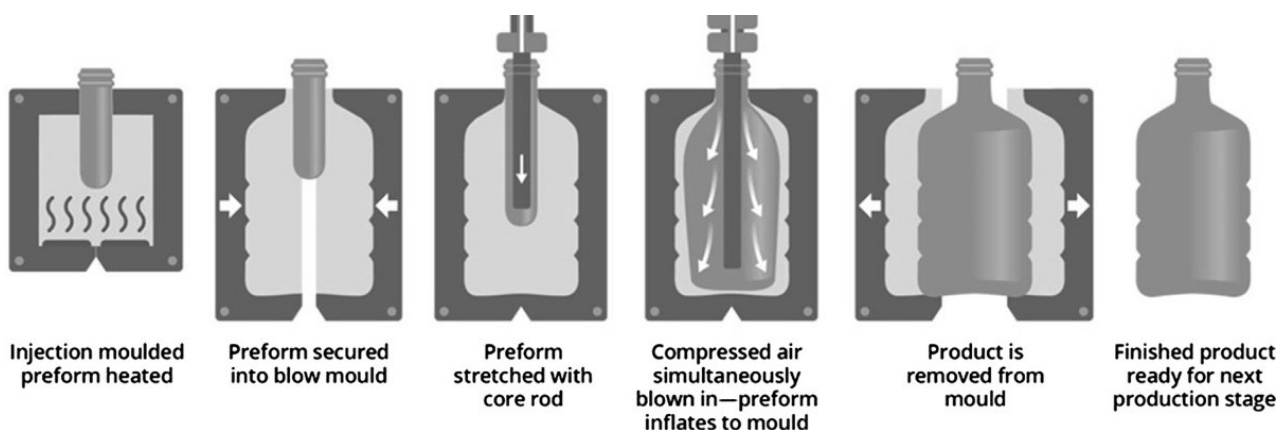


■ FIG. 5.10 Injection blow molding.

hollow [4]. Production rates can be increased by injecting preforms in multi-cavity molds and/or using rotary tables with injection molding, blowing, and ejection stations.

The bottles and containers produced by extrusion and injection blow molding exhibit predominant circumferential molecular orientation, which is induced during the blowing stage. Biaxial orientation offers containers with higher optical clarity and gloss, lower permeability, and improved mechanical properties. Injection stretch blow molding became the customary technique to produce biaxially oriented bottles (Fig. 5.11). As in the conventional cycle, this is a two-step process. First, the preform is injection molded. After being clamped in the blowing mold, the hot preform is stretched axially and then expanded into the shape of the mold cavity by means of air pumped through the same rod. Orientation is induced at temperatures above T_g and below T_m (for PET between 88°C and 116°C, for PP between 104°C and 127°C, for PVC between 99°C and 116°C [4]). For example, for PET the axial stretching ratio (bottle body length/preform body length) is 2.5–3 and the hoop stretch ratio (bottle diameter/preform diameter) is 4–5. This technology, together with improved bottle design, has enabled significant savings in weight, while maintaining the performance of the bottle: a 0.5 L Nestlé water bottle weighed 24 g in 1990 and 9.5 g in 2012. Coca Cola liter bottles reduced from 41.1 g in 2008 to 38.1 g in 2012.

An interesting variant of injection stretch blow blowing is the Pressblower process (Ossberger GmbH+Co, Germany) that is used to fabricate plastic collapsible tubes, small bottles, and ampoules for the food, cosmetics, and pharmaceutical industries. In the first step, the top, neck, and part of the



■ FIG. 5.11 Injection stretch blow molding. (Adapted from robinsonpackaging.com/plastics/injection-stretch-blow-moulding/.)

body are injection molded. Then, the latter is drawn axially, thus inducing a strong molecular orientation in this direction; this parison is then blown, to impart circumferential orientation, and cut to the desired dimension.

5.4.4 Thermoforming (Trays, Cups, and Containers)

Unlike the preceding technologies that convert solid pellets into a package, or package component, thermoforming starts with a film or sheet (this is why it is sometimes classified as a secondary shaping operation rather than a processing technique). However, tandem, in line and rotary arrangements can integrate the extrusion and thermoforming stages. Thermoforming consists in heating the film or sheet (above T_g for amorphous polymers or slightly below T_m for semicrystalline materials) by radiation (by means of ceramic heaters, quartz lamps, or metallic resistance rods), forcing it against the contours of a mold cavity by means of pressure or vacuum (sometimes assisted mechanically), and trimming the part from the original sheet. The scrap (the sheet skeletal after removing the parts) can vary from 15% to 50% of the original sheet. This excess material can be reground and added to the raw material at a fixed percentage. Sheet coextrusion is also widely utilized, either to insert the scrap material in the middle layer, or to provide a barrier layer, frequently made of EVOH.

Thermoforming competes in many applications with blow molding and injection molding due to its favorable economics: equipment and molds are less expensive because of the lower forces involved, high production yields are attained using multicavity molds, and automated operations are readily available. Thick gauge sheet (thickness above 3 mm) is used to manufacture large parts, such as refrigerator liners, bathtubs, automotive door panels and cargo box liners, or aircraft windscreens. Thin sheet/film can yield cups, trays, packs (e.g., meat/fish trays, egg trays, microwave and deep freeze containers, ice cream tubs, margarine tubs, yoghurt cups, sandwich and salad packs, drink cups, plates, etc.), blister packs (where the product is encapsulated between a transparent plastic blister and a paperboard or plastic backing), and skin packs (similar to the blister construction, but here the product was used as mold). Form, fill, and seal equipment is also available.

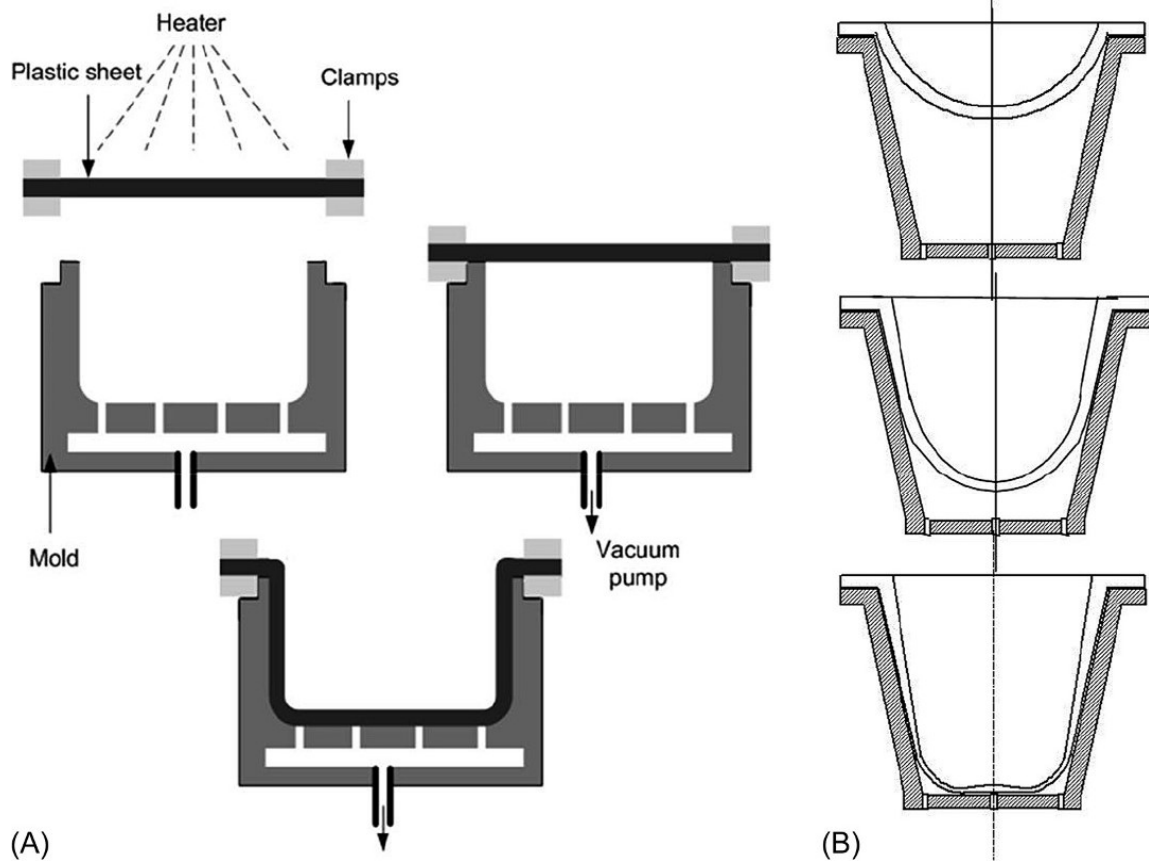
Thermoforming cannot offer tight tolerances or significant undercuts. Containers should have tapered lateral walls, they should be as shallow as possible (to avoid ultrathin thicknesses, as explained later), and corners should have generous radii. The material deformations sustained in thermoforming, as well as the operating temperature range are similar to those in blow

molding, that is, in both cases a soft material is blown against the contours of a cold mold. Thus thermoforming:

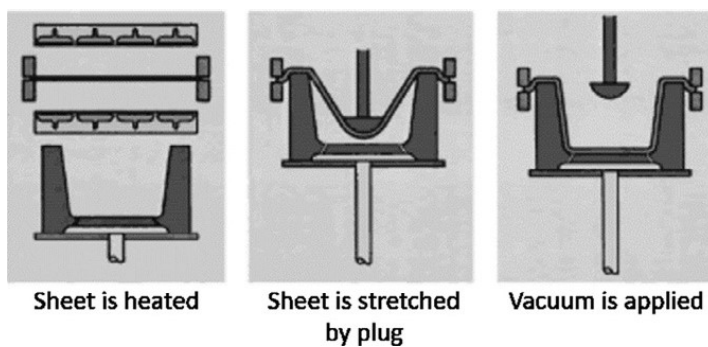
- necessitates materials with extensional strain hardening characteristics. If the draw ratio, given by the ratio of the depth of the draw to the mold opening at the rim, is too high, the container may become too thin locally. Simultaneously, materials should show good capacity to reproduce detailed mold surface features. For example, PLA has a very short temperature range for thermoforming, between “still too cold” for processing and “degradation started,” and becomes very brittle after forming.
- generates a thickness distribution both in the lateral walls and bottom. During shaping, a thin hot membrane is brought into contact with a cold mold. As soon as contact arises, that portion of membrane solidifies and stops deforming, which means that the remaining free membrane must cover the remaining area of the mold.

Fig. 5.12 illustrates vacuum thermoforming for the manufacture of a cup. The female mold contains a series of small holes at the bottom, which are connected to a vacuum reservoir and a vacuum pump. First, the sheet is clamped on top of the mold in such a way that it entraps the volume of air between itself and the contour of the mold cavity. After heating the sheet, vacuum is applied and the forming stage involving sheet deformation takes place very quickly. In fact, this deformation progresses in three stages: due to the pressure difference below (vacuum) and above (atmospheric pressure) the sheet, a free thin bubble is formed; this bubble has a thickness gradient from the base to the pole, the thinnest spot. As the bubble advances downward, it freezes upon touching the lateral mold walls; thus the wall thickness of the product decreases from top to bottom. In due course, the bubble will touch the bottom center of the mold. Now, the annular bubble will progress radially to the corners, and the bottom corner will become the thinnest part of the cup.

Given the negative consequences of this thickness profile on the mechanical performance of the product, several variants of this technology have been developed in order to either minimize thickness differences or make them more convenient. Only a few will be briefly presented here. Pressure forming employs a male mold, so that the sheet is positioned near to the bottom of the cup. Consequently, cups with a thick base and lateral walls becoming thinner from bottom to top are obtained. Plug-assist vacuum thermoforming (see Fig. 5.13) is a popular technique that combines the previous two variants, to produce deep cups with a favorable thickness distribution. Initially, the sheet is drawn downward by a plug (the male mold) while avoiding



■ FIG. 5.12 Vacuum thermoforming: (A) the technique; (B) formation of the wall thickness gradient. (Adapted from robinsonpackaging.com/plastics/injection-stretch-blow-moulding).



■ FIG. 5.13 Plug-assist vacuum thermoforming. (Adapted from www.fvf.co.jp).

contact with the lateral walls. Thus a relatively thick sheet becomes available closer to the bottom and lower lateral walls when vacuum is subsequently applied. The resulting cups usually exhibit a thick base and lateral corner, a thick top rim, and a lateral wall with decreasing thickness downward until above the lateral corner. Reverse draw thermoforming with plug assist and vacuum is also commonly used in industry. In this case, the plug-assist vacuum forming sequence is preceded by blowing the sheet upward, as this prestretching will significantly reduce thickness variations in the final part.

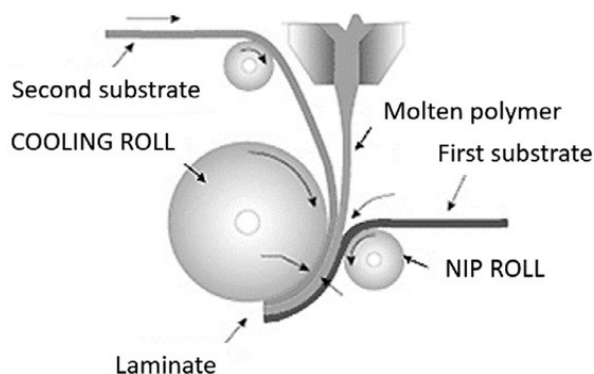
5.4.5 Converting Flexible Films

Converting films for packaging can be broken down in a series of unit operations, which include surface treatment, printing, coating, laminating, and heat sealing. Due to the wide range of machinery, only coating, lamination, and heat sealing will be briefly discussed here.

Extrusion (or coextrusion) coating consists in laying a molten flat film over a polymeric or nonpolymeric substrate (e.g., paper, fabric). The equipment layout is similar to that for cast film extrusion (see Fig. 5.4), with two major differences: (i) an unwinding station upstream of the die pulls the substrate toward the chill roll; (ii) upon contact with the chill roll, molten extrudate and substrate are pressed against each other by a nip roll.

Lamination combines individual films (polymeric or nonpolymeric) into multilayer structures by means of low molecular weight polymeric adhesives (suspended in water or diluted in a solvent). In dry lamination the adhesive is applied to one substrate, dried with hot air, and then the other substrate is layered onto the first one by a hot compression nip roll. In wet lamination the adhesive is applied to one substrate, the two substrates are joined together via a nip roll, followed by drying with hot air. This technique requires that one substrate is sufficiently porous to allow evaporation of the water or solvent from the adhesive.

Extrusion lamination merges the previous two techniques into a single process. The extruder(s) provide the molten film that will coat a multilayered substrate formed by individual components joined together by a nip roll (Fig. 5.14). In this case, the melt also works as adhesive. Extrusion laminating lines are frequently configured to produce specific food, medical, and industrial packages. Tandem extrusion lamination lines, consisting of two or more individual lines in series, are capable of producing complex multilayer substrates with the required functional and protective requirements. Usually, these packs combine films of LDPE, PP (often biaxially oriented), PET, PA, PLA, paper, or aluminum foil. They also incorporate corona



■ FIG. 5.14 Extrusion lamination.

discharge stations to promote mutual adhesion of the substrates and/or ulterior adhesion of printing inks.

Heat sealing in plastics packaging consists in welding two films by the action of heat and pressure. This is a common method for forming bags and pouches, but is also frequently the last step of making a package, from closing overwraps to form-fill-seal operations. Various techniques are available, the method of choice depending on the type of materials, package design, and product. For example, thermal sealing uses heated bars to press together the films. In the case of impulse sealing, the bars are heated intermittently by electrical impulses. It is also possible to use a hot wire to simultaneously weld and cut the films. In all cases, temperature and pressure melt the polymer and good entanglement should develop between the macromolecules of the layers being sealed. Materials for hot sealing should present low seal initiation temperature, good hot tack resistance, and good thermal stability. PE is a widely used heat-sealable polymer, either by itself or as the inside layer of multilayer films. Conversely, cellulose acetate and thermoplastic polyesters are not heat sealable. PLA has a relatively high T_g and T_m , which limit its heat sealability. Blending with other biopolymers or incorporation of plasticizers can be helpful in this respect [27].

5.5 CONCLUSIONS

Only few PNCs have made their journey from basic research up to the highest level of technology readiness for food packaging application. Polymer-clay nanocomposites are currently the main type of PNCs incorporated in commercial food packaging. PNCs are essentially used in markets where improved barrier (organoclays) and antimicrobial (silver nanoparticles) package properties are needed to enhance the shelf life of foods and drinks. The manufacture of PNCs and their conversion into a package is a complex process which demands specific material properties. Cost-efficient

production routes and good processability with conventional techniques are the two prime requirements for bringing more PNCs on the food packaging market. Adaptation of existing processing lines to cope with specific materials properties, as for instance those exhibited by biosourced and biodegradable polymers, requires a significant investment. As such, this route is economically less attractive than adjusting the material properties to the requirements of current industrial machinery. Therefore the modification of biodegradable polymers by the addition of nanoparticles aiming at improving their processability has received much attention over recent years. The production of these biodegradable PNCs for their conversion into smart, active, and sustainable food packaging seems to be the major drive in this research field. However, this cannot be done without a better fundamental understanding of the relationships between processing parameters and materials properties that allow for the delivery of truly nanosized dispersed PNC.

ACKNOWLEDGMENTS

This work is funded by FEDER funds through the COMPETE 2020 Programme and National Funds through FCT—Portuguese Foundation for Science and Technology under the Project UID/CTM/50025/2013. L.H. *acknowledges* the support from FCT through Investigador FCT contract IF/00606/2014.

REFERENCES

- [1] J.-W. Rhim, H.-M. Park, C.-S. Ha, Bio-nanocomposites for food packaging applications, *Prog. Polym. Sci.* 38 (2013) 1629–1652.
- [2] PlasticsEurope, *Plastics—The Facts*, PlasticsEurope, Brussels, 2014.
- [3] J. Brandsch, O.G. Piringer, Characteristics of plastic materials, in: O.G. Piringer, A. I. Baner (Eds.), *Plastic Packaging*, second ed., Wiley-VCH Verlag GmbH & Co., Weinheim, 2008.
- [4] S.E.M. Selke, J.D. Culter, *Plastics Packaging: Properties, Processing, Applications and Regulations*, third ed., Carl Hanser Verlag GmbH & Company KG, München, 2016.
- [5] PlasticsEurope, *Plastic Packaging: Born to Protect*, PlasticsEurope, Brussels, 2012.
- [6] Z. Tadmor, C.G. Gogos, *Principles of Polymer Processing*, second ed., Wiley-Interscience, John Wiley & Sons, Hoboken, NJ, 2006.
- [7] H. Zweifel, R. Maier, M. Schiller, *Plastics Additives Handbook*, sixth ed., Hanser, München, 2009.
- [8] I. Balberg, N. Binenbaum, N. Wagner, Percolation thresholds in the 3-dimensional sticks systems, *Phys. Rev. Lett.* 52 (1984) 1465–1468.
- [9] T. McNally, P. Pötschke (Eds.), *Polymer-Carbon Nanotube Composites: Preparation, Properties and Applications*, Woodhead Publishing Limited, Cambridge, 2011.

- [10] S.K. Kumar, B.C. Benicewicz, R.A. Vaia, K.I. Winey, 50th anniversary perspective: are polymer nanocomposites practical for applications? *Macromolecules* 50 (2017) 714–731.
- [11] J. Jancar, J.F. Douglas, F.W. Starr, S.K. Kumar, P. Cassagnau, A.J. Lesser, S. S. Sternstein, M.J. Buehler, Current issues in research on structure-property relationships in polymer nanocomposites, *Polymer* 51 (2010) 3321–3343.
- [12] F. Hussain, M. Hojjati, M. Okamoto, R.E. Gorga, Polymer-matrix nanocomposites, processing, manufacturing and application: an overview, *J. Compos. Mater.* 40 (2006) 1511–1575.
- [13] I. Manas-Zloczower (Ed.), *Mixing and Compounding of Polymers: Theory and Practice*, second ed., Carl Hanser Verlag GmbH & Co., Munich, 2009.
- [14] V. Collin, I. Boudimbou, E. Peuvrel-Disdier, New insights in dispersion mechanisms of carbon black in a polymer matrix under shear by rheo-optics, *J. Appl. Polym. Sci.* 127 (2013) 2121–2131.
- [15] A. Scurati, D.L. Feke, I. Manas-Zloczower, Analysis of the kinetics of agglomerate erosion in simple shear flows, *Chem. Eng. Sci.* 60 (2005) 6564–6573.
- [16] S.S. Ray, M. Okamoto, Polymer/layered silicate nanocomposite: a review from preparation to processing, *Prog. Polym. Sci.* 28 (2003) 1539–1641.
- [17] A. Okada, Y. Fukushima, S. Inagaki, A. Usuki, S. Sugiyama, T. Kurashi, O. Kamigaito, U.S. Patent 4739007, 1988.
- [18] Nanocor Commercializes a Clay-Nylon MXD6 Nanocomposite Under the Trade Mark Imperm™ for Bottling Gaseous Drinks, http://www.nanocor.com/Cases/case_imperm.asp, 2017.
- [19] M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, A. Okada, Preparation and mechanical properties of propylene-clay hybrids, *Macromolecules* 30 (1997) 6333–6338.
- [20] R.M. Santos, C. Vilaverde, E. Cunha, M.C. Paiva, J.A. Covas, Probing dispersion and re-agglomeration phenomena upon melt mixing of polymer-functionalized graphite nanoplates, *Soft Matter* 12 (2016) 77–86.
- [21] E. Cunha, M.C. Paiva, L. Hilliou, J.A. Covas, Tracking the progression of dispersion of graphite nanoplates in a polypropylene matrix by melt mixing, *Polym. Compos.* 38 (2017) 947–954.
- [22] J.M. Barbas, A.V. Machado, J.A. Covas, Evolution of dispersion along the extruder during the manufacture of polymer-organoclay nanocomposites, *Chem. Eng. Sci.* 99 (2013) 77–87.
- [23] S.T. Mould, J.M. Barbas, A.V. Machado, J.M. Nobrega, J.A. Covas, Monitoring the production of polymer nanocomposites by melt compounding with on-line rheometry, *Int. Polym. Process.* 27 (2012) 527–534.
- [24] Y. Song, Q. Zheng, Linear rheology of nanofilled polymers, *J. Rheol.* 59 (2015) 155–191.
- [25] P.F. Teixeira, J.M. Maia, J.A. Covas, L. Hilliou, In-line particle size assessment of polymer suspensions during processing, *Polym. Test.* 37 (2014) 68–77.
- [26] P.F. Teixeira, J.M. Maia, J.A. Covas, L. Hilliou, A small-scale experimental extrusion set-up for exploring relationships between process-induced structures and characteristics of multiphase polymer systems, *Macromol. Mater. Eng.* 300 (2015) 1278–1289.
- [27] C.C. Yang, R. Bhardwaj, C. Alkiewicz, Biopolymers for paperboard extrusion coating and converting, TAPPI Conference, Fort Worth, TX, 2016.

FURTHER READING

- [1] J.E. Mark (Ed.), *Physical Properties of Polymers Handbook*, AIP Press, New York, 1996.
- [2] J.D. Ferry, *Viscoelastic Properties of Polymers*, third ed., John Wiley & Sons, New York, 1980.
- [3] R.J. Ashley, *Permeability and plastics packaging*, in: J. Comyn (Ed.), *Polymer Permeability*, Elsevier, London, 1989, pp. 269–308.
- [4] J.I. Kroschwitz, *Encyclopedia of Polymer Science and Engineering*, John Wiley & Sons, New York, 1988.
- [5] J. Brandrup, E.H. Immergut (Eds.), *Polymer Handbook*, third ed., John Wiley & Sons, New York, 1989.
- [6] Matweb Material Property Data, www.matweb.com, 2017.
- [7] N. Peelman, P. Ragaert, B. De Meulenaer, D. Adon, R. Peters, L. Cardon, F. Van Impe, F. Devlieghere, Application of bioplastics for food packaging, *Trends Food Sci. Technol.* 32 (2013) 128–141.
- [8] M. Cunha, B. Fernandes, J.A. Covas, A.A. Vicente, L. Hilliou, Film blowing of PHBV blends and PHBV-based multilayers for the production of biodegradable packages, *J. Appl. Polym. Sci.* 133 (2016) 42165.
- [9] C. Rauwendaal, *Polymer Extrusion*, fifth ed., Carl Hanser Verlag, Munich, 2014.
- [10] www.eastman.com.
- [11] www.jsw.co.jp.
- [12] www.silganplastics.com.
- [13] robinsonpackaging.com/plastics/injection-stretch-blow-moulding.
- [14] www.substech.com.
- [15] www.fvf.co.jp.