

22 Chaotic Advection and Its Application to Extruding Micro- and Nanostructured Plastic Materials

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22.1 Applicability and Fundamentals

Chaotic advection-based processing of plastics is a new plastics processing technology that offers opportunities to enhance physical properties, impart functionalities, or create decorative patterns in extrusions. It can be used with existing polymer resins and is well suited to melt processing of shear-sensitive materials. Droplet dispersions or solid particle mixtures can also be produced. Both miscible and immiscible polymer combinations can be used although structural outcomes differ. Structured plastics can be extruded that can contain, for example, thousands of layers, sponge-like assemblies, interconnected layers, percolating networks, ribbons, abundant submicron fibers, or oriented particles. Dispersions of droplets or solid particles can also be produced. Physical property enhancements that have been demonstrated include barrier (resistance to permeation) [1–3], toughness [4,5], and electrical conductivity [6,7]. Functionalities that have been demonstrated include controlled release of additives [8] and strain-sensitive electrical resistivity [7]. Plastics have also been produced with the appearance of realistic wood grains both inside and on surfaces of extrusions [9]. Both realistic (e.g., wood grains and stone appearances) and abstract patterns are obtainable. Because a large variety of microscale and nanoscale structures can be formed in extrusions even at fixed material compositions, opportunities are afforded for improving simultaneously several physical properties or performing optimization in tandem with minimization of material costs. Machinery and methods have special applicability to nanotechnology because nanostructured materials can be extruded in large quantities and in many forms such as film, sheet, tube, pipe, and fiber. In situ structure formation is controllable and repeatable so product optimization can be done efficiently. As with all blending processes, chemical reactions between material components, large viscosity differences, and polymer incompatibility can lead to processing difficulties.

Plastic materials that consist of two or more polymer types or that are composites of a polymer and a solid additive are typically manufactured by mixing or coextrusion through dies. These processing methods intrinsically restrict the variety of structural outcomes and compositions so that

plastic materials may not have optimal physical properties or minimized cost. Functionalities may also be difficult to obtain. The goal of mixing is to break down domains of polymer components often to give a dispersion of droplets, whereas coextrusion arranges polymer components only into discrete layers. Often, a desired fine-scale internal structure in a plastic can be obtained only at particular compositions. Applied to polymer processing, *chaotic advection* provides a means to form a wider variety of microscale and nanoscale internal structures in plastics even at a fixed material composition [5]. Plastics are regarded as composite materials and not simply as mixtures or coextruded layers with the realization that structure of a composite can influence physical properties more than composition. Machinery and control systems have been developed that induce chaotic advection in polymer melts for extruding cast and blown film, sheet, rod, tubing, fibers, and other plastic products. Because the fine-scale structure in extrusions can be controlled during their manufacture and a greater variety of structure types are attainable than with mixing, machines have become known as *smart blenders*. Methods are applicable to polymers and other materials such as ceramic slurries that are processable in a liquid or liquid-like state and that are thermally compatible. Solids are incorporated by first mixing with a polymer to obtain a masterbatch which is supplied to the smart blender in lieu of a pure polymer component melt.

Chaotic advection is a subject of fluid mechanics that denotes the chaotic movements of passive particles in response to even simple flow fields [10,11]. Because of chaotic advection, it is now understood that complex particle motions in fluids do not require complex flow fields. Even where discrete particles do not exist in a polymer melt, this understanding is useful because small melt domains move, or *advection*, in a similar fashion. Simple flow fields allow controllable formation in melts of structures that can have both fine-scale features while also being physically expansive. For example, two polymer components can be arranged into thousands of thin alternating layers or into a blend consisting of long, submicron fibers. From a machinery perspective, device simplification and more controllable in situ structure development are made possible. A variety of

blend morphologies are obtainable by *progressive structure development*, which is defined as the formation of structured materials via sequential in situ transitions from one structure type to another.

Progressive structure development is shown in Figure 22.1. By subjecting melts to chaotic advection, initially large melt domains (e.g., resin pellet size or larger) or melt streams are stretched and folded (steps 1–3) into alternating multilayers. Such stretching and folding is a characteristic of chaotic advection [12] and is a consequence of shear deformations and reorientations by the simple velocity fields. Simple velocity fields in smart blenders act on melt domains by shear deformation. Time-periodic changes or space-period changes in these velocity fields reorient the deformed domains to fold them. Shear deformation and folding cause domain sizes to reduce exponentially fast. Characteristic sizes of melt domains can reduce by several orders of magnitude as they move only distances of several centimeters in smart blending machines toward an extrusion point. Individual layer thicknesses can decrease rapidly to microscale or nanoscale. (1 micron = 10^{-6} m. Nanoscale is commonly regarded as <0.1 micron = 100 nm). Unlike multilayers obtained by

conventional coextrusion, imbedded folds are present and stretching and processing can be continued to give a desired layer thickness in an extrusion.

While multilayer extrusions having very numerous thin layers have important applications such as permeation barriers, light interactive media, and impact resistant materials, they also serve as a template from which other structured plastics can be obtained [13,14]. Stretching and folding of polymer melt layers in a smart blender can be continued until individual layers rupture (Figure 22.1, steps 5 and 6). The ruptures grow due to interfacial tension forces. Because the number of layers is large and layers are geometrically similar, volumetric transformations in shape occur. In a blend of two immiscible polymers, simultaneous layer rupture in a multilayer melt gives an interpenetrating blend morphology [13]. Where one polymer component is present in an appreciably smaller amount, ruptures occur only in the minor component polymer. The ruptures coalesce preferentially in the direction of shear to give numerous long fibers of the minor component (Figure 22.1, steps 8–10). These structures can be broken into droplet dispersions such as those typically resulting from conventional mixing (Figure 22.1, step 7).

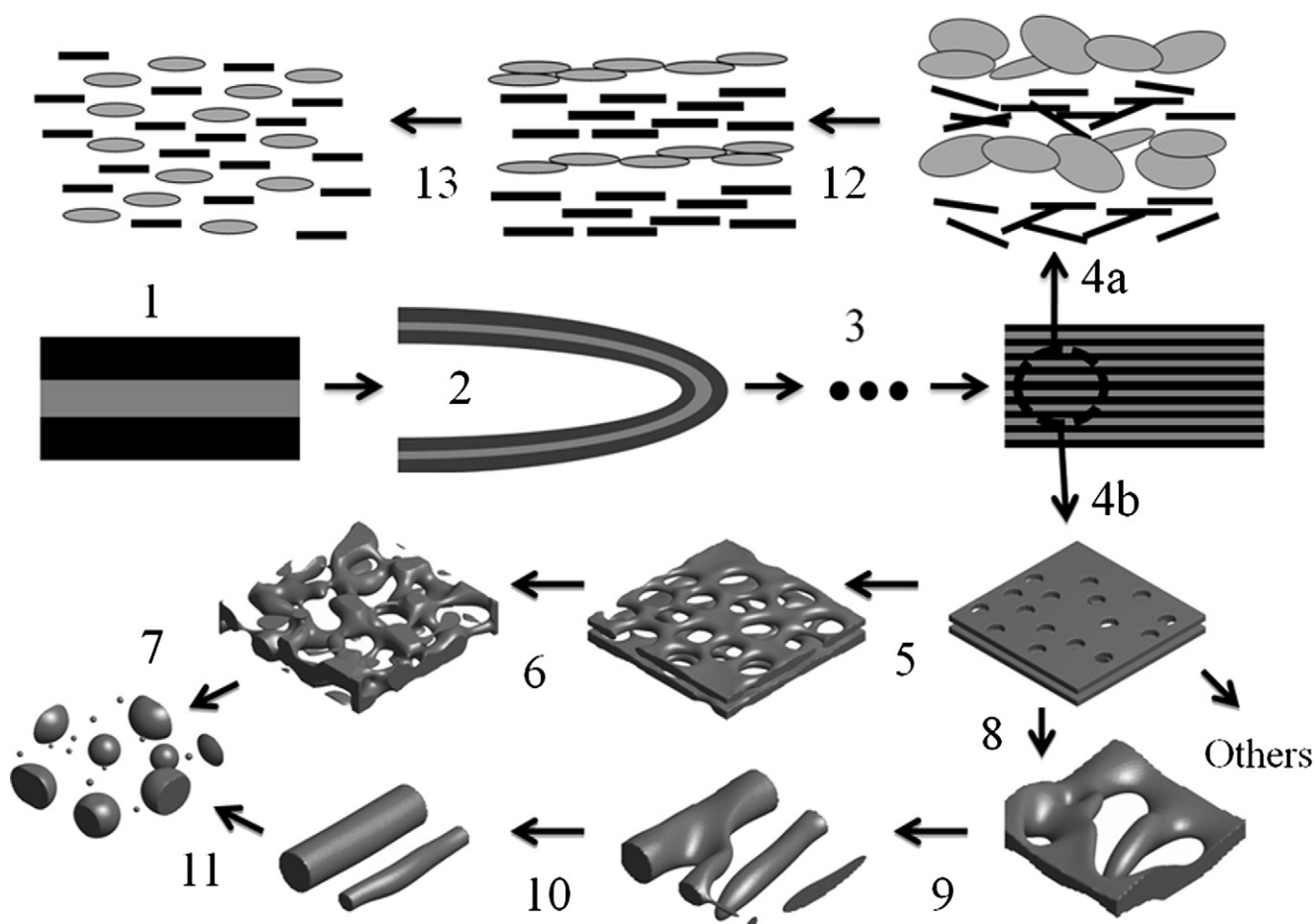


Figure 22.1 Stretching and folding by chaotic advection of initial melt bodies in a two component polymer melt give initially multilayer melts that transform by *progressive structure development* to a wide variety of polymer blend morphologies.

Characteristic dimensions (e.g., rupture size, fiber diameter, and droplet diameter) of these various blends are related to the parent layer thicknesses and thereby can be correspondingly small. Additionally, unlike mixing, numerous structure types are possible even at a fixed material composition. Any of these structure types can be captured in an extrusion. This attribute is important because physical properties can differ for each of the blend morphologies in Figure 22.1. For example, because melt flows through the ruptures in a multilayer melt, layers of the same polymer type become interconnected via coalescence and resulting extrusions are less prone to layer delamination.

Processing methods also offer new opportunities when applied to plastics containing small solids, such as carbon black and inorganic platelets or fibers and nanotubes. As shown in Figure 22.1 (steps 4a, 12), such solid particles can be localized in numerous thin layers that can have thicknesses less than 100 nm. Orientation results that can promote network formation more effectively impede diffusion or impart strength. Dispersions are also obtainable by continuing stretching and folding until layer thicknesses become smaller than the transverse dimensions of the solid particles (Figure 22.1, step 13). Such dispersions are theoretically optimal due to the underpinning chaotic motions that produce them.

22.2 Machinery and Process Control

Smart blenders have been developed for various purposes such as extruding cast film or sheet, filaments, or fibers or for manufacture of tubular extrusions such as blown film or pipe [16,17]. These machines can also be used for nanosolids dispersion and shear-sensitive material processing. They are often installable into manufacturing lines with little disturbance between existing screw extruders and downstream equipment such as chill rolls or bubble collapsing frames. They can discharge to combining blocks to produce extrusions that include melts supplied from separate screw extruders. In cast film or sheet and fiber applications, attached dies serve only to form an extrusion into a desired shape and dimension because melt structuring (Figure 22.1) occurs in the smart blender.

A basic smart blending system is given schematically in Figure 22.2. Polymer melts are supplied to a feed throat of the smart blender by screw extruders in prescribed proportions to give a desired composition in the extrusion. The melts enter a region in the blender where chaotic advection is induced by time-periodic changes in rotational speeds of stir rods controlled by a process control computer. The stir rods can be of simple geometry. Cylindrical stir rods are typically employed that are hydrodynamically tapered near a die attachment. As melt advances along the stir rods, melt domains are stretched and folded recursively by chaotic advection so that a layered arrangement first arises. Thick

multilayers reduce in thickness as stretching and folding progress and the melt moves toward an extrusion point. Blend morphology changes can eventually occur in the melt due to layer breakup as discussed earlier (Figure 22.1). Morphology changes are depicted in Figure 22.2 by broken layers adjacent to the stir rods. Many derivative morphologies are attainable from multilayer breakup [5,14,15]. A particular morphology can be placed into an extrusion by operating the smart blender such that it occurs in the vicinity of the die entrance. At the extrusion point, the melt is formed by an attached die into a desired extrusion form such as a film, plate, or filament. By attaching a spinneret, multiple fibers can be produced. Unlike conventional processes, the die serves to impart only the final form. Consequently, die design is simplified and a single die can be used to produce plastic products having a wide variety of physical properties. Smart blenders for annular extrusions such as blown film differ in construction and are described later in this section.

The amount of melt structuring in the smart blender is specified through selection on a process control computer (Figure 22.2) of the number N of time-periodic speed changes of the stir rods. For example, small N yields a multilayer blend morphology whereas larger N and further stretching and folding by chaotic advection can lead to layer ruptures in immiscible polymer combinations and resulting morphology transformations. Particular blend morphologies are typically obtained with $N < 30$. By organizing polymer components into multilayers and refining the layers, one morphology type can lead in sequence to many derivative morphologies. Such progressive structure development can also be performed with melts containing solid additives such as carbon black, nanotubes, silica, or graphene platelets [6,7,18]. The smart blender system in Figure 22.2 can make use of structure–property–composition results, rheological measurements, and process parameters of prior studies. Such information can be compiled in a data base. As more information is collected, the smart blender can be used with increasing efficiency to obtain extrusions having internal structures associated with desired physical properties. In practice of course, such databases can become proprietary.

Chaotic advection is induced in a manner analogous to a twin vortex model used to describe concepts of chaotic advection [10,19]. In the twin vortex model, fluid motion and chaotic advection occur when adjacent idealized point vortices are repetitively activated. In an analogous fashion, chaotic advection is induced in the smart blender in response to periodic rotations of stir rods. The manner in which stir rods are rotated periodically is referred to as the *rod rotational protocol*. Requisite conditions for inducing chaotic advection in driven flows have been widely studied [20–23] and similar methods have been used in the design of smart blending machines [4,5,24–26]. Due to a pressure-driven axial flow and rod-driven circumferential flow, the

flow field in a smart blender is three dimensional. However, the simple geometry of the stir rods instills chaotic advection principally within planes parallel to the cross-section of the smart blender barrel. The extent of melt structuring along the barrel by progressive structure development is selectable via specification of a number N denoting pairs of rod rotational speed changes while melt is resident in the smart blender. To clearly define N [4], let one rod in Figure 22.2 be designated as R_1 , the other rod be designated as R_2 , and Ω denote the number of rotations for a designated rod. For added generality, counter-clockwise

rotations are given by $\Omega < 0$ and clockwise rotations are given by $\Omega > 0$ and let η_i equal the rotational displacement of rod i . In terms of these parameters, designation of R_1 rotating $\eta_1 = 3$ complete rotations and R_2 rotating simultaneously $\eta_2 = 1$ complete rotation is denoted by $[R_1(\Omega = 3) + R_2(\Omega = 1)]$. As an example, a specific rod rotational protocol for the smart blender consists of a periodic sequence of rod motions of N repetitions given by $[R_1(\Omega = 3) + R_2(\Omega = 1); R_1(\Omega = 1) + R_2(\Omega = 3)]$. For $N = 3$, rod rotations occur according to $[R_1(\Omega = 3) + R_2(\Omega = 1); R_1(\Omega = 1) + R_2(\Omega = 3)]; [R_1(\Omega = 3) + R_2(\Omega = 1); R_1(\Omega = 1) +$

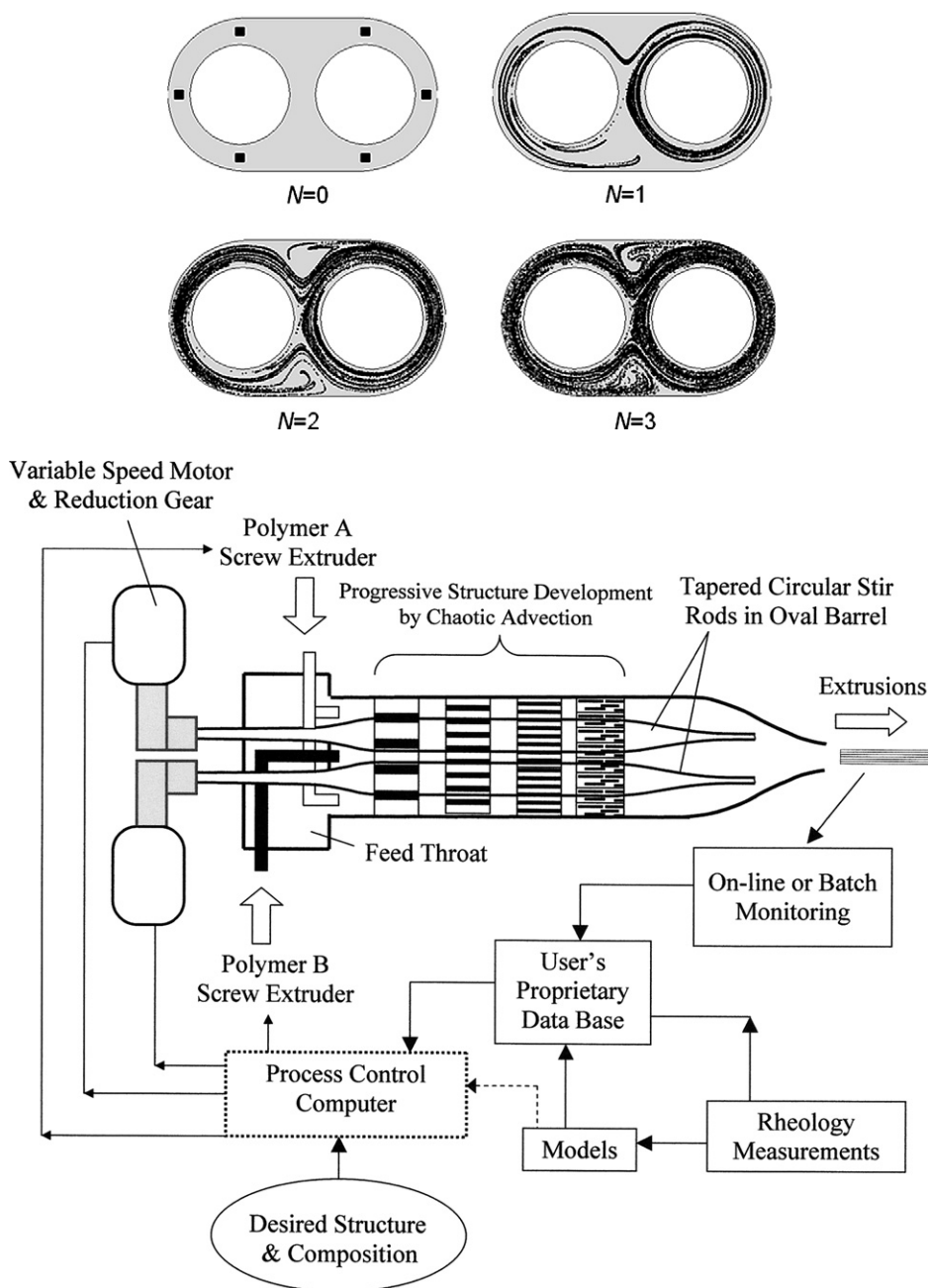


Figure 22.2 Schematic representation and process control features of a smart blending system.

$R_2(\Omega = 3)$; $R_1(\Omega = 3) + R_2(\Omega = 1)$; $R_1(\Omega = 1) + R_2(\Omega = 3)$. For a selected extrusion rate, rod speed is selected such that the desired value of N can be obtained while melt is resident in the blending section of the smart blender.

Chaotic advection in the smart blender is shown in the inset of Figure 22.2. Results were obtained through finite element modeling with a procedure analogous to those employed in chaotic mixing studies [27] where numerous particles are located initially within clusters. The shaded area represents injected major component polymer A. Six clusters are also shown. These represent injection of minor component polymer B melt from the feed throat of the smart blender. Because polymer A and polymer B are not yet subjected to chaotic advection, $N = 0$ for the initial injected melts. At $N = 1$, polymer A and B melts have moved a short distance along the stir rods and partial blending has occurred. Compositional uniformity is poor. Continued stretching and folding (Figure 22.1) lead to larger number of layers and improved compositional uniformity at smaller length scales. In effect, both polymer A and B are folded about each other [13] although layering may be most visually apparent in the minor component. The evident particulate structure for $N = 3$ actually corresponds to a highly layered blend morphology. Discrete layers are no longer evident because layer thicknesses have reduced to below the printed particle size in the illustration. It can be discerned though that smart blenders can be effective mixing machines where a mixed condition is achieved by structuring melts to reach fine scales. Layers can be produced of smaller thicknesses than the smallest material particles [28,29]. When extensive chaotic advection is specified, structured plastic materials result with internal characteristic dimensions at the microscale and nanoscale.

Examples of industrial smart blenders are shown in Figures 22.3 and 22.4 [17,30]. Both units are scalable to a desired melt flow rate. The smart blender in Figure 22.3 is similar to the configuration given in Figure 22.2. Polymer melts from two or more screw extruders are supplied to a feed throat that discharges to a blending zone. Chaotic advection is induced by time-periodic rotations of stir rods rotated by variable speed motors. Minor and major component melts move toward an extrusion point where various types of dies can be fitted at a die attachment flange to form extrusions of desired forms. This smart blender has primary application for extruding cast films, sheet, fibers, and filaments and can be used to supply melt to a combining block. The smart blender in Figure 22.4 is used to produce tubular extrusions such as blown film, piping, and tubing. Because these units can replace conventional dies and internal moving surfaces can be controlled to give a variety of structured plastics (Figure 22.1), they are also known as *smart dies*. As with conventional dies, the smart die is supported by a cart that can be mounted on tracks. The cart houses variable speed motors such as in Figures 22.2 and 22.3. The motors rotate six cylindrical stir rods that are mounted within an annular

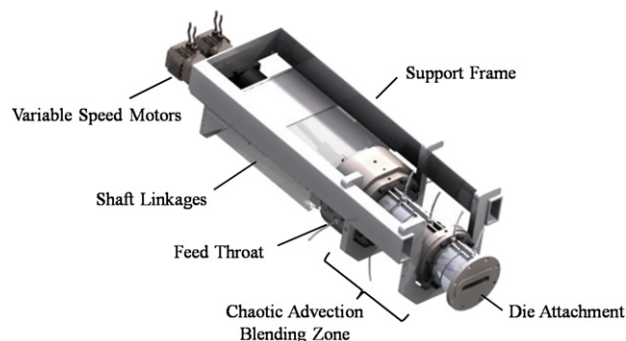


Figure 22.3 Industrial smart blending machine with two stir rods such as shown in Figure 22.2. Various types of extrusion dies can be attached to give extrusions such as film, sheet, rod, or filaments.

blending volume formed between a mandrel and the barrel. Air is supplied to the interior of the tubular extrusion as with conventional annular dies to equalize the pressure internal to the annular extrusion with ambient pressure. Polymer melts from screw extruders are introduced into the blending zone with spiral melt distribution blocks such as used in conventional multilayer blown film dies. Spiral melt distribution gives a uniform melt injection into the annular blending chamber without melt weld lines so favored features of conventional dies are incorporated. Injected melts move upward along the stir rods. Current units allow attachment of two or three screw extruders. Because layers are folded about one another by chaotic advection and blended melts can be produced, tie layers can be omitted so fewer screw extruders are needed in comparison to conventional annular dies. After forming the desired structure in the melt such as the examples in Figure 22.1, the melt exits the blending zone and is extruded via an annular die lip.

Data bases in Figure 22.2 can be organized in the form of a morphology map where key processing variables are related to a particular polymer blend morphology. A significant attribute of smart blending is that an approximate morphology map for process control purposes can be conveniently developed from trial runs. A smart blending system can be operated in a *transient operating mode* to rapidly identify all possible morphologies formable at specific compositions. To understand the control features and map construction, consider the simple morphology map in Figure 22.5 for polypropylene (PP) and low density polyethylene (LDPE) blend morphologies [4]. The amount of melt structuring in this map is designated by the number N defined previously that is related to the stir rod motion. Various morphologies are depicted symbolically for LDPE volume fractions (ϕ) of 10, 20, and 30%. In the transient operating mode, the stir rods are kept initially stationary until the minor and major component melts flow steadily through the smart blender barrel (Figure 22.2) and emerge in the extrusion as coarse, continuous streaks. This condition is

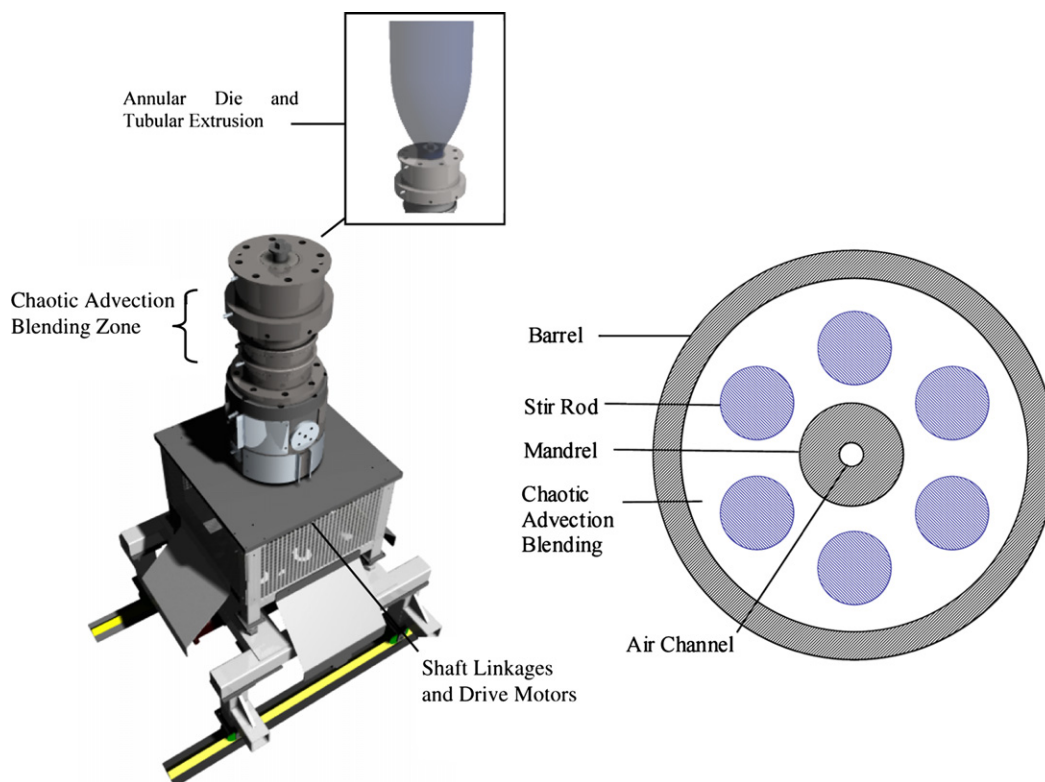


Figure 22.4 Industrial smart blender for manufacture of blown film and other tubular extrusions. Because the smart blender substitutes for conventional dies and allows online control of structure in an extrusion, it is also referred to as a “smart die”.

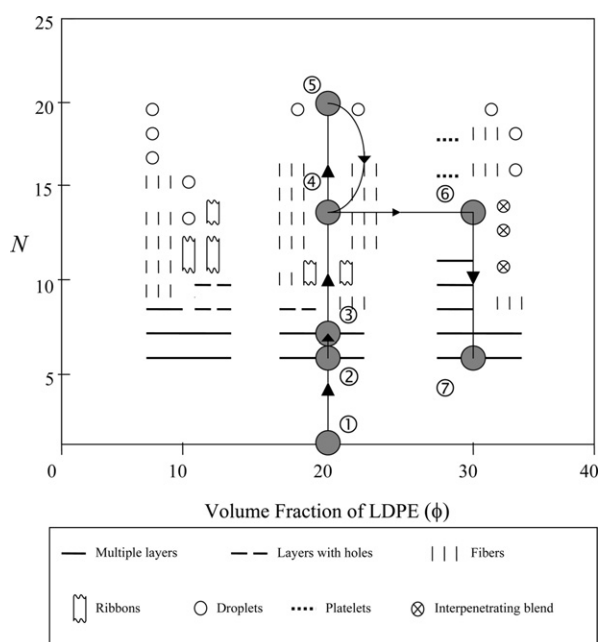


Figure 22.5 Example of a blend morphology map that can be compiled to guide machine operation. Databases can be developed in terms of pertinent melt properties to reduce trial-and-error used typically in polymer processing. Chaotic advection blending machines are thereby referred to also as *smart blenders* or *smart dies*.

designated *state 1* in Figure 22.5. Afterward, rod motion is started. In the subsequent extrusion, the extent of structuring from this point forward is related to the initial location of the melt within the smart blender barrel when rod rotation was begun. For example, melt near the exit of the blender is subjected to little structuring whereas melt located closer to the feed throat will become more structured as it travels within the barrel. Structure development occurs progressively. The polymer A and polymer B melts are stretched and folded by chaotic advection (Figure 22.1) to give the multi-layer morphology at *state 2*. Few layers lead to larger number of layers (*state 3*) and subsequent morphologies are obtained via sequential morphology transitions made possible by progressive structure development. Fiber morphologies eventually emerge from their parent layers (*state 4*), followed by droplet morphologies (*state 5*).

To illustrate the dynamic operation of a smart blender and use of the morphology map, the designated value of N on the process control computer can be changed to restore *state 4* from *state 5* in Figure 22.5 if desired. Additionally, screw extruder flow rates can be changed to increase ϕ to 30% and reach *state 6*. Multilayers at *state 7* can be attained by reducing N , as shown. Such dynamic operation facilitates cost and property optimization of extruded plastics and can lead to more efficient research and development for new products.

22.3 Micro- and Nanolayered Plastics

Examples of multilayer blend morphologies with layers having thicknesses of less than a few microns are shown in Figure 22.6. All were extruded as cast films using a smart blender similar to the one shown schematically in Figure 22.2. Such morphologies can be useful in barrier, light interactive, or toughened plastics. In Figure 22.6a, a multilayer blend structure is shown in a blend consisting of 30% by volume ethylene vinyl alcohol copolymer (EVOH) and LDPE where the EVOH is used to suppress oxygen permeation [2]. Due to component immiscibility and the absence of a tie layer, EVOH and LLDPE layers detached upon fracture of the imaged sample that had been immersed in liquid nitrogen to improve component contrast in the scanning electron microscope image. However, to reduce delamination, the multilayer morphology of Figure 22.6a can be transformed to ruptured layers and ribbons that can impart good oxygen barrier properties. Notably, droplet morphologies typically result from mixing of these

polymers and are associated with poor barrier properties in contrast.

In Figure 22.6b, an example is shown of very thin and numerous layers in an extruded 500 micron-thick film composed of 20% by volume ethylene propylene diene terpolymer (EPDM) and PP [29]. Individual layer thicknesses were about 100–200 nm and several thousand layers were present. The viscosity ratio (EPDM/PP) at the processing temperature of 235 °C ranged from 4 to 8 for shear rates during processing from 0.2 to 2 per second. Because of the propylene monomer unit in EPDM, interfacial tension with PP was small (1.07 dyne/cm). This multilayer morphology had very large interfacial area on the order of 10^6 – 10^7 cm²/ml. Instabilities that seek to reduce interfacial area can give rise to a variety of derivative morphologies (Figure 22.1). These can initially retain the very small dimensions of parent layer thicknesses [14].

Whereas examples in Figure 22.6a and b pertain to immiscible polymer melts, Figure 22.6c pertains to a miscible polymer pair [31]. Submicron layers were formed in a blend of 30%

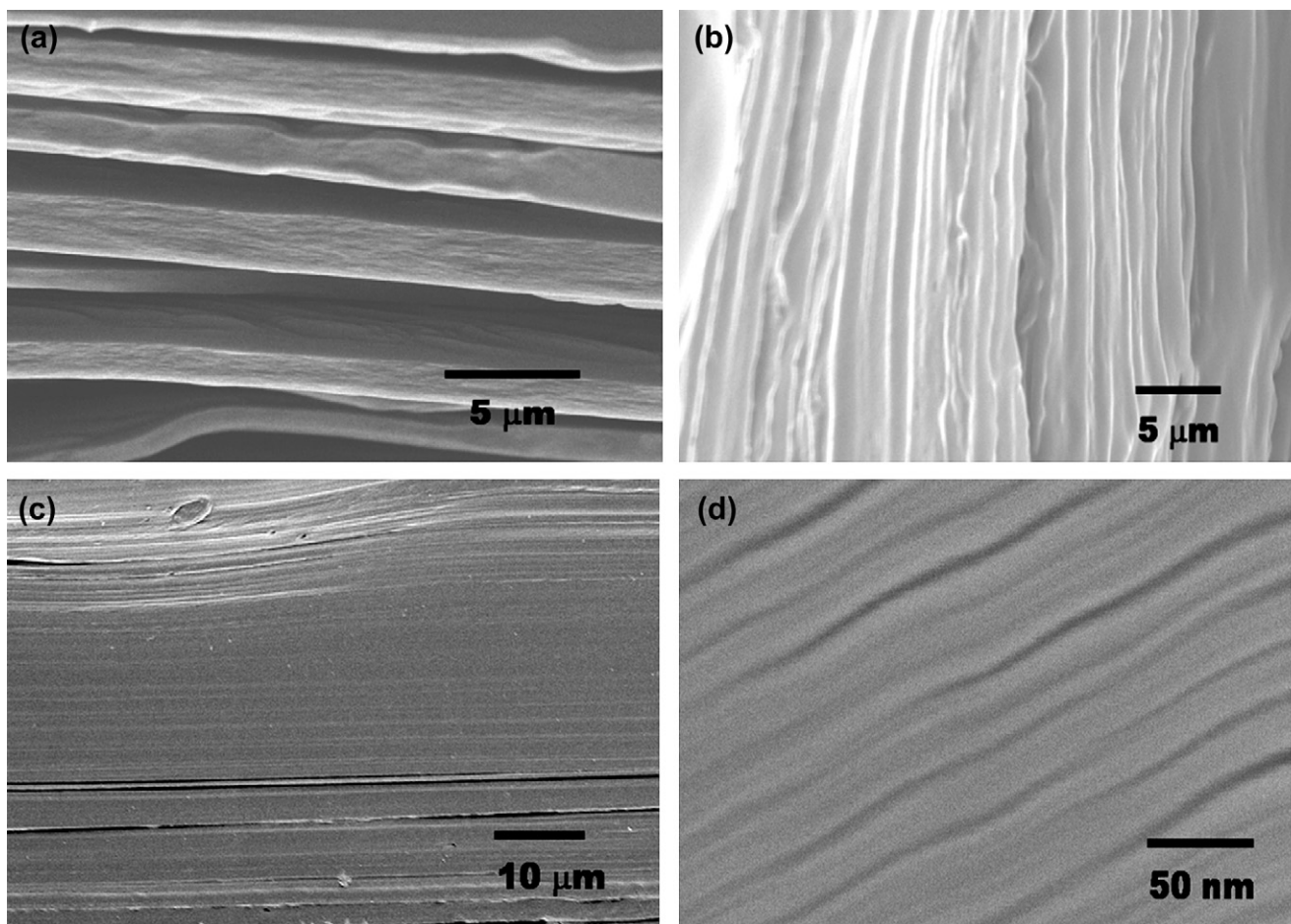


Figure 22.6 Scanning electron microscope images of microlayered and nanolayered plastics: (a) LLDPE and 30% by volume EVOH after cryogenic fracture, (b) 20% by volume EPDM and PP after cryogenic fracture, (c) 30% EVOH by volume and PA with EVOH removed by dissolution, and (d) 15% by volume LDPE and HDPE.

by volume EVOH and polyamide (PA). To improve phase contrast in the scanning electron image, samples were etched in a solvent so that some or portions of EVOH layers were removed. Thicknesses of layers were determined by separate transmission electron examinations to be less than 0.5 micron. The potential amount of layer refinement obtained with a smart blender is demonstrated for a blend consisting of 15% by volume LDPE and high density polyethylene (HDPE) [5]. Because interfacial tension was very low due to molecular similarity between these polymer types, very thin layers readily formed. Samples were fractured after immersion in liquid nitrogen for at least 5 minutes to reveal internal structure. Individual layers of less than 12 nm thickness in an extruded film of 500 micron thickness are shown in Figure 22.6d. The extruded film contains more than 25,000 layers. A progression from thicker and fewer layers to thinner and more numerous layers was documented and correlated to increasing N .

22.4 Polymer Blends

Instead of small flow clearances associated with screw extruders, comparatively large spaces can exist in a smart blending device so that physically expansive melt structures with small-scale features evolve. For example, the polymer component melt streams in Figure 22.2 are converted initially to melt layers that are expansive in the spanwise layer direction but are also very thin such as in Figure 22.6. The melt layers, while of practical importance such as when extruded to yield multilayer films, are parent structures to other morphologies via sequential morphology transitions (i.e., progressive structure development). By creating physically expansive and numerous multiple layers, a morphology transition that occurs at one location also generally occurs at other locations having the same degree of layer refinement. Specific locations within a multilayer melt having many layers lack uniqueness so morphology transitions can occur approximately volumetrically.

Where interfacial tension exists between melt components, the multilayers give rise to derivative blend morphologies such as depicted in Figure 22.1. Morphology results for PP–LDPE blends are given in Figure 22.7 at a LDPE volume composition of 30% [4]. These results and others at 10% and 20% LDPE are the basis for the morphology map in Figure 22.5. All such blends were extruded as films of 500 microns thickness with a smart blender similar to the one represented by Figure 22.2. By inspecting micrographs available for each N or fractional increment of N if necessary for clarity, the relation of parent morphologies to derivative morphologies was determined. Morphology development for $N < 10$ is similar to morphology development at the lower compositions of 10–20%. Initial PP and LDPE melt streams were converted to alternating layers such as shown for $N = 8$ in Figure 22.7. Rupture formation in a layer of one polymer component is accompanied by coalescence of adjacent layers

of the other polymer component. Layer coalescence is evident for $N = 10$ where oval domains are remnants of LDPE layers in which adjacent ruptures form and enlarge. Hole growth in layers of one polymer component is accompanied by melt drainage from adjacent layers of the other polymer component. Melt drainage leads to layer thinning and promotes rupture formation in the adjacent layers [15]. The multilayer melt with $N = 8$ is eventually converted volumetrically to an interpenetrating blend for $N = 12$ in agreement with computational simulations [14]. The interpenetrating blend is a parent morphology to LDPE platelets and ribbons at $N = 18$ and to droplets at $N = 20$. In contrast, only a droplet morphology is obtainable by conventional processing methods such as screw extrusion.

A fibrous blend is shown in Figure 22.8 that consisted of 55% by volume polystyrene (PS) and PP [25]. This blend was extruded as a 2.5 mm filament. Numerous and long internal fibers are present with diameters less than 5 microns. Close inspection indicates that smaller diameter fibers are encapsulated by larger diameter fibers so that the extruded filament has a hierarchical fibrous structure [32]. Fibrous blend morphologies have been produced in other polymer combinations as well. For blends of Figure 22.7 but with lower LDPE concentrations of 10% and 20%, ruptures also occur among layers but separation distances between LDPE layers is greater so the interpenetrating blend morphology at $N = 12$ does not form. Instead, LDPE layers convert to long fibers which yield 1 micron droplets with increasing N . A comparative morphology development has been reported [4].

Fibrous blends can serve as internal reinforcements or perhaps electrical conductors, depending on the polymer characteristics comprising them. Where very thin fibers can be formed ($< 1 \mu\text{m}$) for example, opportunities exist for enhancing crystallinity and tensile properties of the resulting blends especially when extrusions containing them, which themselves can be fibers, are drawn to promote polymer chain orientation [33].

22.5 Polymer–Solid Composites and Nanocomposites

Inorganic solids such as carbon black, nanoclays, graphene, nanotubes, and nanofibers are added to plastics to allow them to be used in applications traditionally reserved for metals and ceramics or to improve the performance of plastics to meet more demanding requirements. Solids addition can also allow expanded use of commodity polymer resins to give new plastic products at reduced cost. Examples of physical properties that can be improved include electrical conductivity, permeability, resistance to crack propagation, flammability, thermal stability, and flexural rigidity, and light interactive characteristics such as refraction index and polarity. When conventional processing methods are used with solid additives, the focus is typically on the degree of

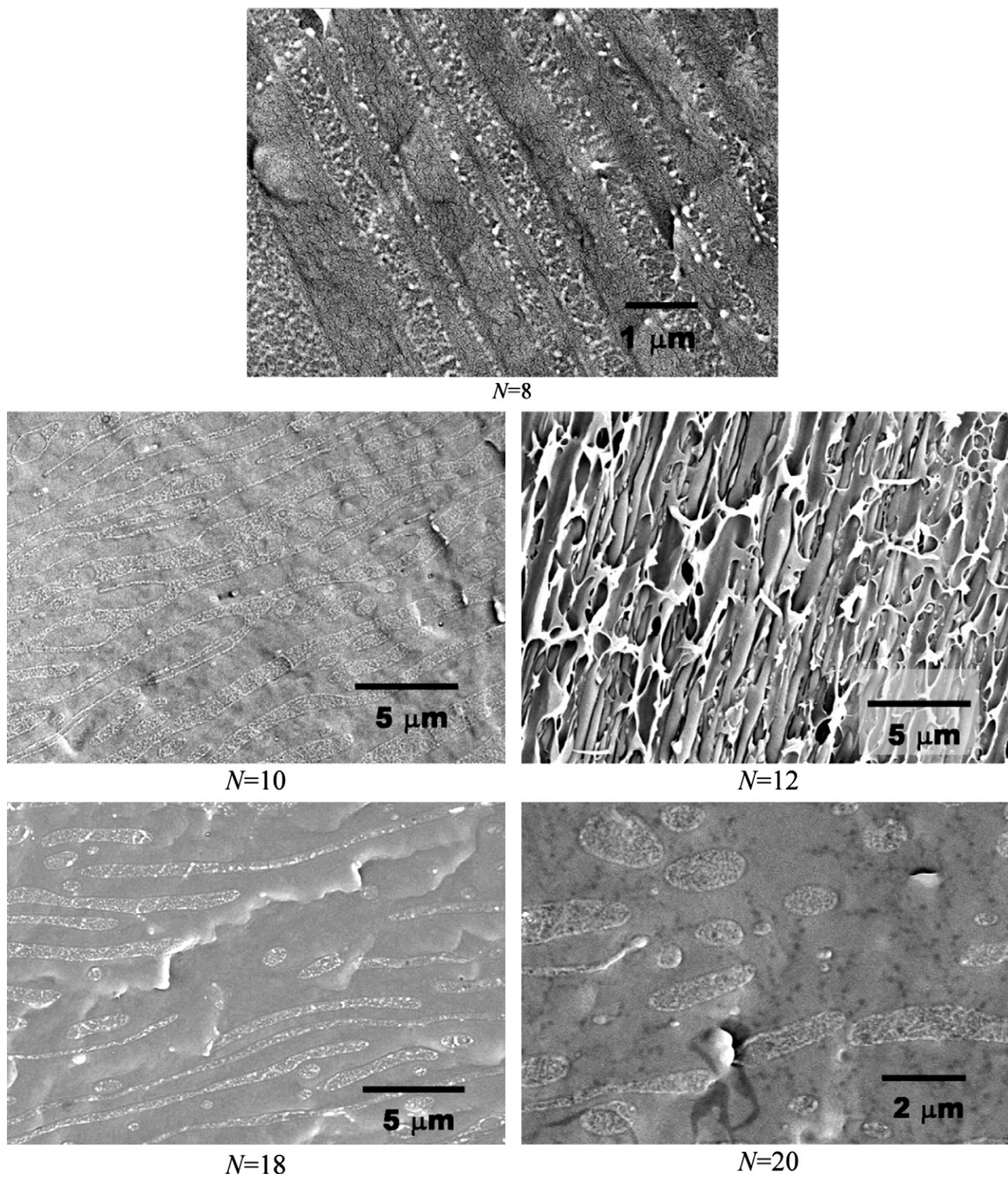


Figure 22.7 Example of progressive structure development resulting from an initial multilayer blend morphology and the primary derivative morphologies producible in a PP/LDPE blend at a constant 70/30% volume composition.

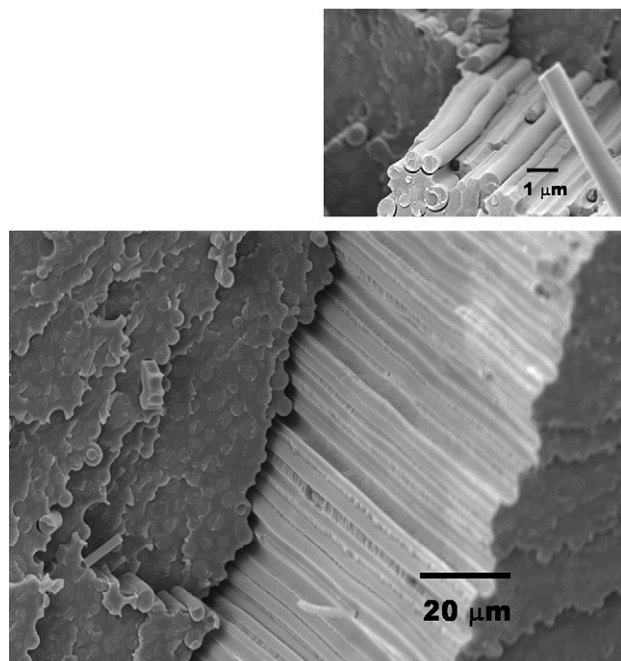


Figure 22.8 Low and high magnification views of a fibrous blend formed in an extruded monofilament consisting of PP and PS. Internal fibers contain smaller diameter fibers so the filament has a novel hierarchical structure that may be associated with physical property enhancements.

mixing so that structural outcomes and opportunities for property enhancements can be limited. In contrast, solid additives are arranged into specific structural types within a plastic by chaotic advection that are associated with physical property enhancements in recognition of the fact that structure can be more influential in determining physical properties of a composite than its composition.

Optical micrographs of composites consisting of linear low density polyethylene (LLDPE) and 3% carbon black by weight are given in [Figure 22.9](#) where internal structures are revealed in thin translucent sections by cryogenic microtomy [7]. Such composites can be produced by supplying a smart blender with LLDPE as polymer A and a masterbatch composed of carbon black and LLDPE as polymer B in [Figure 22.2](#). The masterbatch and LLDPE are stretched and folded by chaotic advection into multiple layers ([Figure 22.1](#)) until layer thicknesses become comparable to the sizes of carbon black particles such that extended particle networks form. The structured composite melt can be extruded from the smart blender in a desired form. The examples in [Figure 22.2](#) were extruded as cast film. Electrical current flow is provided along the many thin striations. By changing the amount of chaotic advection in terms of the parameter N (Section 22.2), interconnectivity among striations is adjustable to alter directional conductivity properties and conductivity levels. In effect, percolating networks can thereby be constructed in situ in lieu of being simply stochastic outcomes dependent on particle concentration. The striated structure in [Figure 22.9a](#) is

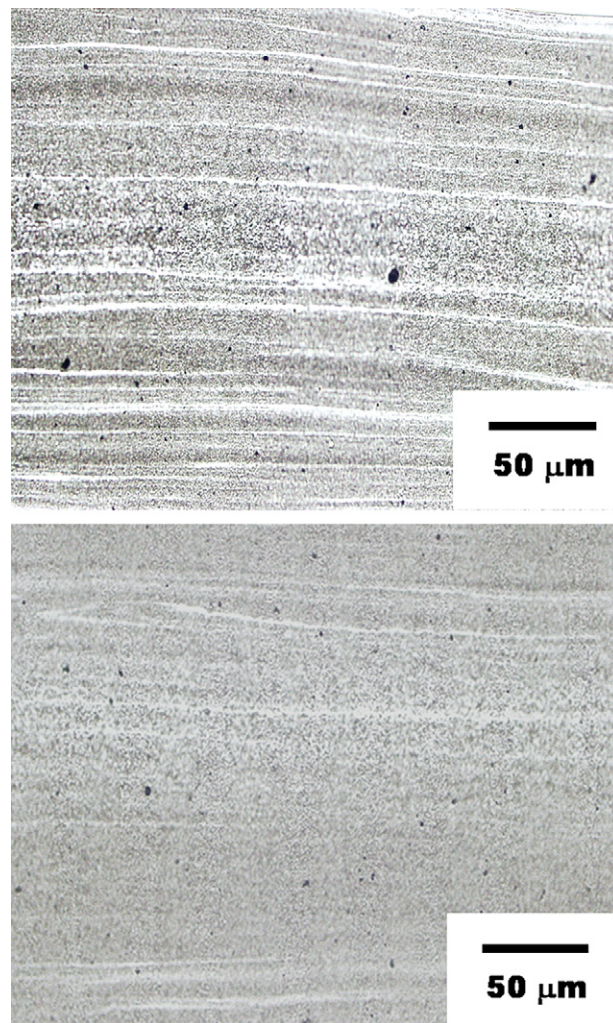


Figure 22.9 Optical micrographs of translucent 100 nm thick sections taken from extruded films with addition of 3% by weight carbon black. Interconnectivity of carbon black is controllable to impart distinct electrical properties.

convertible, for example, to a structure such as in [Figure 22.9b](#) having less property anisotropy.

An example of a novel clay nanocomposite is shown in [Figure 22.10](#) that may be especially well suited to high barrier packaging, low permeation storage vessels and piping, impact resistant materials [5,18], and light interactive media. It makes optimal use of inorganic material in terms of physical property enhancement by localizing and orienting it within numerous layers. Clay particles when broken down through a process referred to as exfoliation consist of very thin (~ 1 nm) silica platelets having high frontal area ($0.01 \mu\text{m}^2$) and very low mass diffusivity [34]. When present in sufficient number in a plastic and especially when oriented, the platelets can effectively impede molecular diffusion, for example [35]. To produce the nanocomposite in [Figure 22.10](#), a twin screw extruder is used to prepare a masterbatch of PA and nanoclay. Nanoclays and guidelines

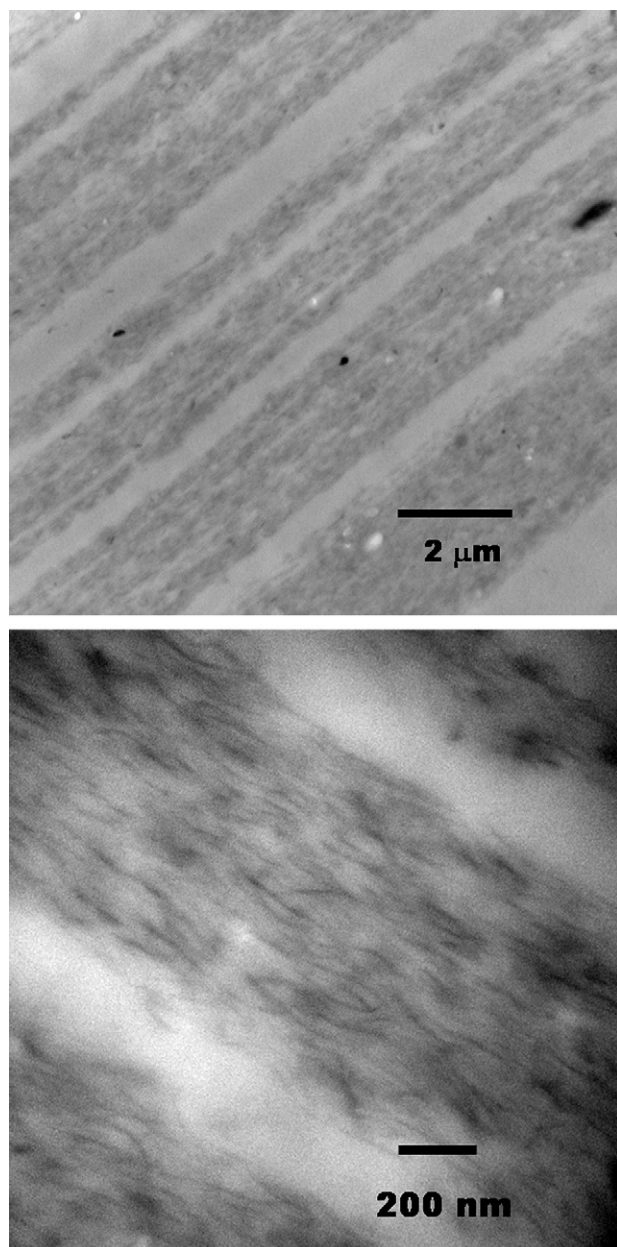


Figure 22.10 Novel nanocomposites extruded in film form with silica platelets both oriented and localized in numerous internal layers to give plastics with low permeability and other property enhancements. (Layers of matrix polymer separate both the platelets and platelet-rich layers. Internal layers and platelets are optimally oriented parallel to the film surface).

for their use are available from several manufacturers. The masterbatch and PA are supplied to the smart blender as polymers A and B (Figure 22.1) and can be extruded in a desired form such as film, sheet, or tubing using smart blenders such as shown in Figures 22.3 and 22.4.

The particular example in Figure 22.10, which was extruded as cast film, was produced with a masterbatch of 4% nanoclay by weight to give an overall 2% nanoclay loading in

the resulting nanocomposites. A multilayer structure of platelet-rich layers and PA layers results such as in Figure 22.10a for $N = 10$. Platelets are oriented throughout the film such that their frontal areas are parallel to the extruded film surface and net permeation direction. Due to orientation and localization within numerous multiple layers, the clay additive is most influential in affecting physical properties for a given overall clay loading. The optimal structure allows reductions in nanoclay concentrations for a particular level of physical property enhancement. The average thicknesses of PA and platelet-rich layers are selectable via specification of N to the process control computer in Figure 22.2. The PA layers in the upper micrograph of Figure 22.10 are reduced from about 1 micron thickness to less than about 125 nm thickness in the lower micrograph by specifying a larger N . In tandem, the mean lateral separation distance between platelets within a platelet-rich layer is increased. The physical properties of resulting nanocomposites are thereby adjustable during smart blender operation so that product optimization can be performed efficiently.

Orientation of thin or oblong particles results from the alternating shear flows in smart blenders described in relation to Figure 22.1. Orientation can occur nearly volumetrically because chaotic advection effectively shuffles melt to different locations during blending and flow fields are simpler than those arising in mixing machines and screw extruders. Equivalently, particle orientation can be considered an outcome of decreasing layer thicknesses as chaotic advection proceeds. In effect, platelets, nanotubes, or oblong particle clusters orient in response to stretching and folding to reside with the layers containing them. As with carbon black and clay additives, processing methods can also be applied to nanotubes and nanofibers. Smart blending also offers a means to place nanotubes or nanofibers within minor or major components of polymer blends such as those shown in Figures 22.6–22.8 to impart additional structural effects to polymer blends. With smart blenders, physical properties of nanocomposites are not solely an outcome of the nanoscale dimensions of solid additives such as provided when conventional mixing is used but instead are also derived from structure at the nanoscale. The nanocomposites in Figures 22.9 and 22.10 are such examples.

22.6 Mixtures and Nanodispersions

Chaotic advection can be effective in dispersing a minor polymer component or solid additive in a major polymer component. Results of numerous chaotic mixing investigations have been reported that consider chaotic motions in passive tracer particles in a liquid [20–23,27,34]. For polymer blends, dispersions of small droplets in the minor component are often the goal of conventional processing methods such as mixing with twin screw extruders. Colorants and functional solids such as carbon black, nanoclay, graphene, and nanofibers are

similarly mixed with host polymers to produce masterbatches or specialty plastic resins. (As mentioned in Section 22.1, however, structured plastics can have superior properties for an equivalent net composition because properties of a composite can depend more on structure than on composition.) A smaller droplet size in a blend is often pursued by operating mixing equipment at higher shear rates, promoting extensional flows via machine design and prolonging melt residence time. Unfortunately, the reduction in droplet size can be less than sought because droplet deformation and resulting breakup become more difficult to induce as the viscosity of the major component decreases as a consequence of shear thinning behavior. Molecular breakdown (i.e., chain scission) from viscous heating can also prove problematic especially in shear-sensitive fluids.

Droplet dispersions in a polymer blend are obtained differently in smart blenders than in conventional mixing machines. The general sequence to obtain droplets is depicted in Figure 22.1 based on experiments and computational models. Chaotic advection causes minor and major component polymer melts to become arranged into numerous and expansive multilayers. As the layers decrease in thickness and increase in number by continuing chaotic advection, breakup eventually occurs in the thinner minor component layers. Minor component droplets result that have diameters related to the thickness of their parent minor component layer. An example droplet dispersion in a blend of 20% by volume LDPE in PP is shown in Figure 25.11a where average droplet diameter is about 1 micron [4]. At 30% composition, somewhat larger droplets result (Figure 22.7, $N = 20$). Processing was performed for both examples with shear rates less than 1.5 per second so viscous heating was negligible. Droplet dispersions can also be formed at higher shear rates by chaotic advection as demonstrated in blends of PP and PA [37].

To obtain dispersions of solid particles, one or both polymer melts that are supplied to the smart blender in Figure 22.2 can contain an initial mixture of solid particles. The initial mixture can be a masterbatch produced with a twin screw extruder. Both polymer melts are stretched and folded to give structural arrangements such as shown in Figure 22.9a with carbon black and Figure 22.10 with nanoclay [38]. By continuing chaotic advection further and focusing on Figure 22.10, the PA layer can be reduced to a vanishingly small thickness so that the multilayer structure is no longer evident and an excellent dispersion of platelets results such as in Figure 22.11b. The dispersion consists of volumetrically oriented platelets due to stretching and folding of chaotic advection (Section 22.5). It can be shown mathematically that such nanodispersions are theoretically optimal dispersions due to the chaotic motions that underpin their formation.

Dispersions are obtained by specifying to the smart blender large values of the parameter N (Section 22.2). Even so, a variety of structural types are formed in the smart blender prior to the extrusion point due to progressive structure development. An extrusion with droplets such as in

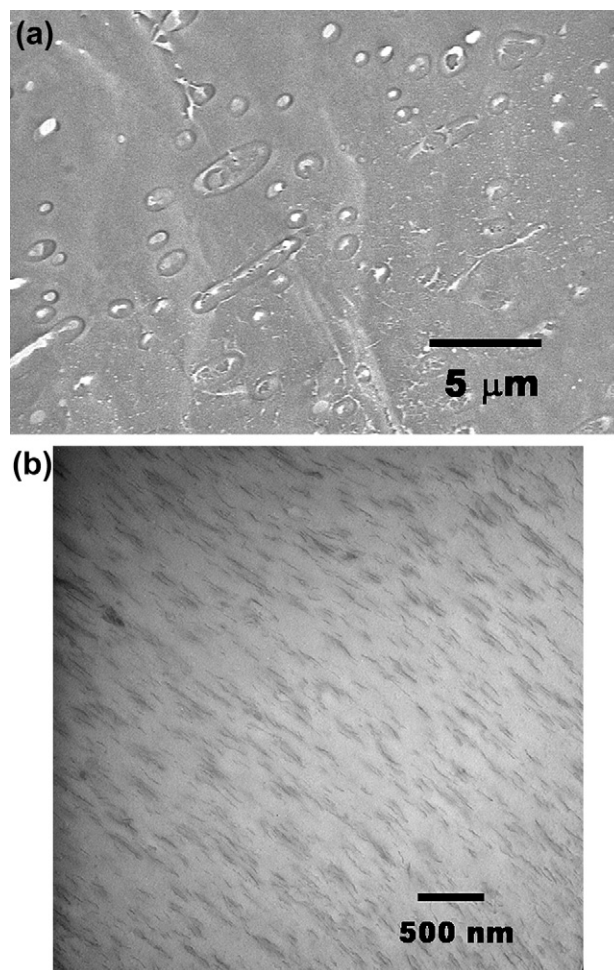


Figure 22.11 Examples of dispersions: (a) LDPE droplets in a blend of 20% LDPE and PP and (b) nanodispersion of silica platelets in an extruded film where platelets are volumetrically oriented.

Figure 22.11a can be transformed to one having other blend morphologies such as depicted in the morphology map of Figure 22.5. Similarly, extrusions with the platelet dispersion of Figure 22.11b can be changed to extrusions that have platelets localized within many layers such as the example in Figure 22.10.

22.7 Decoration

The natural world has an infinite variety of patterns in woods, rocks, and other materials. Similarly, due to progressive structure development of smart blending (Sections 22.1 and 22.2) and chaotic advection, extrusions can be produced with literally an infinite variety of appearances using machines such as those in Figures 22.2–22.4. Examples of simulated wood grains extruded as cast film are given in Figure 22.12 [9]. This example was produced in conjunction with an investigation of electrically conducting plastics to show early structure formation in an extrusion [7] with carbon black as an additive.



Figure 22.12 Realistic simulated wood grain patterns formed controllably in extruded film. Because chaotic motion underpins the process used to form them, each extrusion can have a unique pattern if desired. Stone-like and abstract patterning can also be imparted.

To produce these decorative plastics, the smart blender is operated to give ribbons that wrap in a helical format around stir rods (Figure 22.2). Such helical ribbons can be obtained by using a smaller rotational displacement η_i than specified (Section 22.2) for expansive layers such as shown in Figure 22.6. Desired colors are obtained by using pigmented polymer resins such as those from colorant manufacturers intended specifically to impart wood appearance. By extruding this structured melt through a die, the various wood grain patterns in Figure 22.12 form. Additionally, as with trees that have a layered structure in the form of tree rings disturbed by branches, chaotic advection introduces subtle and attractive intricacies into the simulated grain. Like cut wood, the simulated grain appears both on the surface and interior of extrusions. By dynamically changing the manner in which stir rods are rotated, simulated wood grain patterns can be repeated at intervals along an extrusion while the pattern within the interval remains unique everywhere. Alternately, the smart blender can be operated such that the wood grain changes continuously along an extrusion length. Repetition at specified length intervals can be useful where it is desired to match grain patterns at exposed joints of thick extrusions such as sheet or in ends of laminates. Nonrepeating wood grains can be desirable where large surfaces or lengths are involved such as in wall or floor coverings.

The ability to produce an infinite variety of simulated wood patterns is done via online control with no physical changes to the smart blender. Similar opportunities are available to form simulated rocks and abstract patterns in

plastics or in ceramic materials processable as slurries. Due to pattern uniqueness and their chaotic advection basis, counterfeit proofing of products may also be achievable using these approaches. Many patterns that appear in extrusions have fingerprints of the chaotic motions used to create them.

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