

SMART BLENDING: FUNCTIONAL FINE-SCALE STRUCTURES FORMED BY INTELLIGENT AGITATIONS IN MULTI-COMPONENT MELTS

D. A. Zumbrunnen
Department of Mechanical Engineering and the
NSF Center for Advanced Engineering Fibers and Films
214 Fluor Daniel Building
Clemson University
Clemson, SC 29634-0921
E-mail: zdavid@ces.clemson.edu

ABSTRACT

In viscous melts, turbulence often does not arise. Consequently, opportunities exist for controllably organizing melt components into functional structures that can have very small feature sizes. In this paper, concepts and results of smart blending are described. Smart blending entails the controllable development in situ of a variety of fine-scale structures by intelligently agitating melts. Once formed, structures are captured in applicable products by extrusion and solidification. Chaotic advection is an enabling recent sub-field of fluid mechanics for smart blending since it provides a means to stretch and fold melt domains and evolve a multi-layer structure leading to derivative arrangements, or indirectly manipulate solid additives. Applications include the production of plastics with enhanced mechanical properties, electrically conducting plastics and glasses, barrier films, and nano- and molecular-scale composites.

INTRODUCTION

When engineers develop new processes or materials, they draw from existing knowledge and experience. Plastics are an interesting example. During the last century, it became possible to synthesize a wide variety of polymer molecules with specific characteristics. Some of these polymers were thermally stable and nonreactive. As such, they could be heated to a liquid state and extruded or pressed into desired shapes. Their high molecular weight, however, posed processing challenges. Melt viscosities were typically one-million times greater than the viscosity of water. Consequently, in order to make use of polymers to make plastic products, engineers enlisted equipment originally intended in the 1800s to convey viscous

soap and grains [1]. This equipment incorporated a helical shaft (i.e., or screw) inside a cylindrical barrel. By heating the barrel and rotating the screw, polymer pellets were melted and conveyed. It is recognizable today as a screw extruder to many engineers and has become one of the most commonly used manufacturing devices.

In modern times, the majority of plastic products consists of two or more polymer types and may also include additives. Particulate or short fiber additives are used for internal reinforcement or to improve electrical or thermal conductivity, for example. Like any composite material, the physical properties of polymer blends and polymer composites are strongly dependent on the structural arrangement of the components. In this regard, it is interesting that the basic configuration of screw extruders offers little means to controllably develop desired structures, or morphologies, in polymer blends or among solid additives. Nevertheless, the synthesis and processing of polymeric materials is a notable achievement of the past century. Plastics have become common materials and have underpinned advances in diverse fields.

It is time to think anew about polymer blending. New smart blending machines can now be constructed in which blend morphology develops more controllably in response to applied intelligent agitations. Smart blending is enabled by work done in 1984. H. Aref did some independent thinking and articulated in a seminal paper [2] the potential importance of what had been regarded as rather strange fluid motion. When a Lagrangian perspective is taken and in consideration of dynamical systems theory, he noted that the equations of motion for passive markers in a fluid can produce nonintegrable

(i.e., chaotic) dynamics. An unsteady flow field is required for flows restricted to two spatial dimensions, whereas chaotic dynamics can occur even in steady, three dimensional flows. This type of fluid motion was appropriately dubbed, *chaotic advection*.

Chaotic advection has been used primarily to elucidate mixing mechanisms and also to enhance mixing of viscous fluids [3]. With this application in mind, the term chaotic mixing has become widely used [4]. Investigators studied almost exclusively patterns formed among passively advected particles or in blobs that were identical to the major component fluid except for color or another passive identifier. To simplify experiments and analyses, flows were often confined to two spatial dimensions or only deformations in small circular blobs were considered. Striations patterns ensued. These had little relevance to polymer blending where melt domains are typically stretched to sheets and interfacial tension and component viscosity differences exist. Moreover, the linear character of striations strongly limits the variety of derivative shapes that can be obtained. For example, a droplet might be extended to a filament, but only droplets can be obtained from its subsequent breakup. As will be shown, the situation is much different if initial minor component bodies are converted to multiple layers.

Although chaotic advection refers specifically to passively advected particles in a fluid, very important characteristics of blending become evident when the aggregate motion of a cluster of particles is considered. A cluster becomes stretched and folded to give patterns denoting horseshoe mappings or baker's transformations. The stretching and folding can occur recursively such that initially large clusters become converted to numerous layers of very small thicknesses. Stretching and folding are very relevant to polymer blending. Due to very high viscosities, refinement due to turbulence effects is not possible. Instead, present day processes attempt to refine polymer components by deforming and reorienting them in response to complex flows in screw extruders. Chaotic advection now allows more controllable refinement in devices of simpler construction [5-8]. It has been used to create a variety of blend morphologies with less restrictions on composition [9]. Because morphology development can be controlled, structure-property optimizations can be readily done [10,11]. It has also been used to build in situ particle networks to render plastics electrically conducting [12,13]. This line of inquiry has been recently characterized as a new area of chaotic advection research that may hold particular promise [14].

METHODOLOGY

A conceptual representation of a smart blending device (SBD) is given in Fig. 1 [8]. The SBD consists simply of a cylindrical barrel and two internal rods. Separate melt flows of polymer A and polymer B enter the device. These can be supplied from metering pumps to ensure a steady polymer flow which are in turn fed from present-day extruders. Chaotic advection can be induced by rotating each rod alternately and periodically. Careful selection of the rotational displacements, rod positions, and other design aspects are necessary for effective performance. Many other physical configurations and rod rotational protocols are possible. These can be estimated from computational simulations of passively advected particles [3,15]. The goal of such studies is to determine component

arrangements and operating procedures such that chaotic advection occurs throughout the smart blending device volume and differences in local stretching rates are minimized. The polymer melt streams of Fig. 1 are initially distributed and flow along the rods. Refinement and reorientation occurs in response to chaotic advection. Thick layers are stretched and folded to give thinner, more numerous layers as the combined melt flows move toward an extrusion point. The amount of refinement depends on the melt residence time and rod rotations.

Instead of small flow clearances associated with screw extruders, comparatively large spaces exist in SBDs in which physically expansive structures with small scale features can evolve. For example, both polymer component melt streams in Fig. 1 are converted to layers that are expansive within their individual planes but can be very thin. The number and thickness of individual layers can be regulated through process control. The layers, while of great practical importance, also are parent structures to other morphologies. Interfacial instabilities arise among the layers leading to morphology transitions and the formation of a variety of derivative morphologies in sequence. *Interestingly*, by creating physically expansive and numerous multiple layers, a morphology transition that occurs at one location also generally occurs at all other locations having the same degree of layer refinement. Moreover, transitions proceed interactively so that structure uniformity can be promoted. Such *progressive morphology development* [7] is in stark contrast to existing blending processes where morphology development is localized and transitory. Structure in these processes is broken down instead of evolved. As such, the processing conditions of Fig. 1 offer new opportunities for more controllably creating structures in viscous melts.

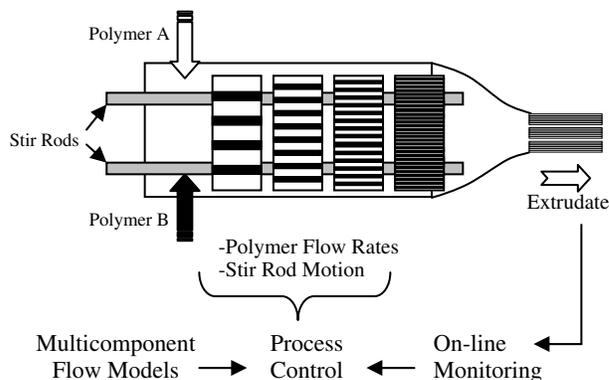


Fig. 1 Conceptual representation of a smart blending device.

SBDs receive inputs from computational multicomponent flow models. Modeling morphology development in these devices is challenging due to rapid reductions in length scales and interfacial interactions. As will be shown, layers can develop with thicknesses of only tens of nanometers. Consequently, molecular scale effects such as van der Waals interactions and thermal vibrations in the melt can become important in addition to shear stresses, interfacial tension, and non-Newtonian behavior such as viscoelasticity and shear thinning viscosity. Real-time simulations for process control are currently only possible for early morphology development or for assessing rod motions that give effective chaotic advection conditions.

Multicomponent flow models are implemented currently in parallel with experimentation with SBDs to elucidate progressive morphology development and morphology transitions. For computational approaches, the lattice Boltzmann method (LBM) is computationally efficient for low Reynolds number flows [16] applicable to smart blending. Unlike continuum-based approaches and a Eulerian viewpoint, the LBM is based on the kinetic theory of gases and has also been developed heuristically with cellular automata as a guide [17]. When a sufficiently large number of particles are considered and physically appropriate constraints are placed on their interactions, the LBM correctly represents real fluid motion. It has proved effective in tracking complex morphology changes applicable to smart blending devices [18]. As a new computational fluid dynamics method, restrictions on model parameters such as component viscosity ratio and interfacial tension currently exist. Volume-of-fluid methods [19] for interface tracking and continuum surface force representations [20] for interfacial tension have also been used to study simpler morphology transitions and minor component body interactions in chaotic advection [21-23].

NOVEL POLYMER BLENDS

In conventional blending processes, polymer components are deformed uncontrollably into disorganized cylinders and sheets often of small spatial extents. The variety of derivative shapes that are obtainable from their breakup is limited. A key concept in smart blending is to instead organize components into alternating layers. As shown in Fig. 1, an alternating layer morphology is a natural consequence in SBDs which make use of chaotic advection. An example is shown in Fig. 2 of very thin and numerous layers in an extruded 500 micron thick film composed of 20% by volume ethylene-propylene-diene terpolymer (EPDM) and polypropylene (PP) [24]. Individual layer thicknesses are about 100 to 200 nm. Several thousand layers were present. Similar layered morphologies have also been formed in extruded 2.5 mm monofilaments where processing conditions were identical except for differences in dies. Details of processing conditions have been described [8].

Instabilities that seek to reduce interfacial area in blends such as the one shown in Fig. 2 can give rise to a variety of derivative morphologies. These can initially retain the very small dimensions of the parent layer thicknesses. By inspecting scanning electron micrographs of blend specimens, insights have been gained of how morphology transitions occur. Continued layer refinement as melt moves toward an extrusion point (Fig. 1) leads eventually to the formation of holes. *Significantly*, if the number of layers is large, changes that occur at one location are also likely to occur at other locations in a multi-layer morphology. Holes thereby form and grow interactively to inherently promote morphology uniformity. The idea of organizing melt components into layers to controllably yield a variety of derivative morphologies constitutes a new approach for making structured materials.

Progressive morphology development due to the growth and interaction of holes has been studied computationally. Results from a LBM simulation are shown in Fig. 3 [18]. Beginning with a periodic array of holes in a periodic arrangement of layers resembling those in Fig. 2, distinct and important derivative morphologies are obtained in sequence. In

these simulations, the major component flowed into enlarging holes and caused their source layers to thin. Bulbous regions in

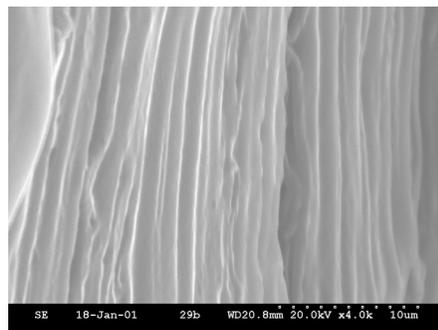


Fig. 2 Polymer melt streams can be controllably converted to numerous thin layers such as these in extruded 500 micron films composed of 20% by volume EPDM and PP.

the minor component enlarged and became closer. The minor component penetrated the thinning major component layer. An interpenetrating blend morphology resulted. Oriented fibers were finally obtained when neck-like regions pinched off by capillary instability. Either morphology can be captured in extrudates where chaotic advection is used to form shapes progressively. Fiber diameters are related to the initial layer thicknesses so that plastics can be produced with an abundance of internal reinforcements. Interpenetrating blends find application in electrically conducting plastics and tough plastic materials due to mechanical interlocking associated with dual phase continuity, among other uses. Results depend chiefly on volume composition and component viscosity ratio C . For $0.3 < C < 0.5$ and $1 < C < 10$, computations indicated that these morphology transitions are applicable. Outside these ranges, other morphologies can arise.

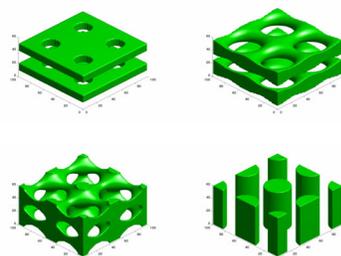


Fig. 3 Interactive hole growth in multiple layers leading to the formation of interpenetrating blends and fiber morphologies.

Interpenetrating blends and fibrous morphologies of LBM simulations such as shown in Fig. 3 have been observed in experiments [5,6,9,11,25]. An example of an interpenetrating blend is given in Fig. 4 where a polystyrene (PS) component has been removed by dissolution in a solvent to expose an interconnected structure in a low density polyethylene (LDPE) component. In Fig. 5, LDPE fibers are shown in PS. Commercially important blend morphologies with single phase continuity, encapsulated structures, thin platelets, and very small droplets have also been documented experimentally. LBM simulations have similarly elucidated how morphology

transitions for these occur. Their characteristic dimensions are directly related to the thicknesses of parent layers. As such, very fine-scale structures are producible where very thin layers can be formed. For example, where interfacial tension is small and viscosity ratio is about unity, instabilities leading to layer breakup occur only after layers become very thin. In such polymer combinations, the production of nanoscale shapes in blends is possible [24].

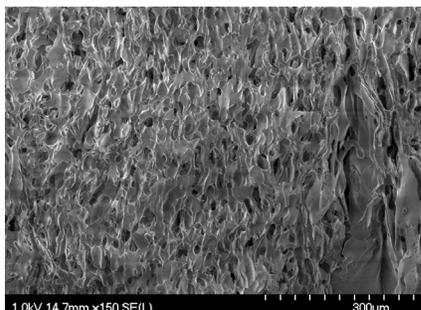


Fig. 4 Example of an interpenetrating blend resulting from interactive hole growth in multiple layers of polyethylene and polystyrene.

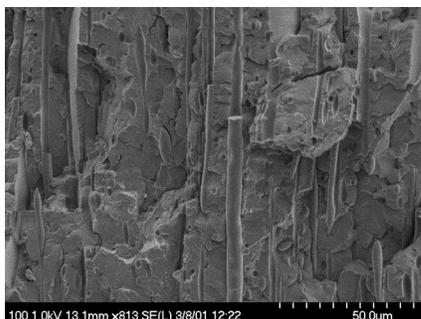


Fig. 5 Low density polyethylene fibers formed in polystyrene from a parent multi-layer morphology.

MOLECULAR- AND NANO-SCALE COMPOSITES

The multilayer morphology of Fig. 2 incorporates a very large interfacial area on the order of 10^6 cm^2/ml . Opportunities are available to organize additives onto the many internal interfaces to create molecular layers and supramolecular structures among molecules influenced by non-covalent interactions [24]. Although the extent of this potential awaits further study and can make use of specially synthesized molecules, an example is provided that has relation to current practice. In present-day compounding steps, co-polymers are sometimes added to reduce interfacial tension between polymer components and thereby allow smaller structures, most often droplets, to form. Interfaces are stabilized, for example, as an individual block seeks preferentially the polymer component in the melt for which it has greatest miscibility. As such, orientation along the interface occurs. This orientation mechanism can be promoted when melt domains are intermingled by chaotic advection such that numerous and expansive thin layers evolve as in Figs. 1 and 2. In effect and in contrast to common blending, the processing method and molecular characteristics act together to create spatially expansive structures with small internal dimensions. Both

molecular scale layers at interfaces and very thin layers of the melt components form so that multiple small scales exist.

This effect is shown in Fig. 6 [11] where blends of LDPE, ethylene vinyl hydroxide (EVOH), and maleic anhydride graft-polyethylene (MA) were organized into layers by smart blending and extruded into 500 micron-thick films. In the left panel of Fig. 6, a film with no MA is shown that consisted of numerous thin EVOH sheets and platelets with thicknesses ranging from about 0.5 to 2 microns. The unique folded morphology was reflective of the chaotic advection used to produce it. In the right panel of Fig. 6, the addition of MA at the EVOH – LDPE interface resulted in a much finer structure with EVOH layer thicknesses below 500 nm. Differential scanning calorimetry tests on EVOH/LDPE film samples indicated that the degree of crystallinity was larger in films containing thinner layers. Molecular orientation, as indicated by higher crystallinity, was promoted upon solidification by confining the melt components to multiple thin layers. Because permeants move more readily through amorphous regions, lower oxygen permeation rates were correlated with smaller layer thicknesses. Higher permeation rates were measured, however, for the EVOH/LDPE/MA films despite the reduced layer thicknesses. Although layer thicknesses were smaller, the intrusion of graft molecule chains into the adjacent thin EVOH layers may have hindered crystallization and increased intrinsic mass diffusivity in the EVOH. Results demonstrate that smart blending is an effective method for producing high barrier (i.e., low permeation) films without the complications inherent in co-extrusion now used.

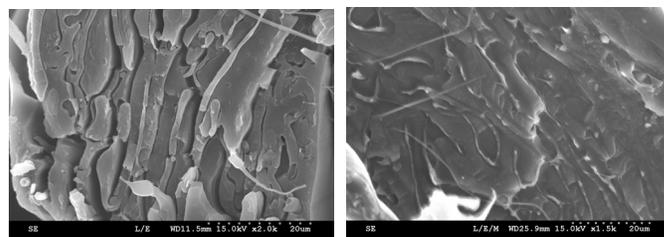


Fig. 6 Formation of thin layers by the placement and orientation of maleic anhydride graft polyethylene at EVOH/LDPE interfaces formed by smart blending.

Because of their very small size, it is impractical to directly manipulate large numbers of nanotubes or other nano-scale additives to produce functional structured distributions for commodity products. Smart blending offers a means to indirectly manipulate additives with nano-scale dimensions to form a variety of structures. An example is shown in Fig. 7(a) of single wall nanotubes (SWNTs) oriented in a PP matrix [24,26]. Internal arrangements among the SWNTs were revealed by fracturing specimens following immersion in liquid nitrogen. Samples were produced with a batch smart blending device [15] in lieu of a continuous smart blending device so that only small quantities of SWNTs were required. The SWNTs were initially concentrated within a cluster occupying a one-quarter sector of a 5 mm high by 5 cm diameter device cavity. Domains were stretched and folded as depicted in Fig. 1 to yield a layered morphology of PP and SWNT-rich PP. Their confinement within layers of decreasing thickness induced the orientation shown. More nanotube rows can be produced by

increasing the SWNT concentration. Although a subject of ongoing work, differences in affinities for polymer components may allow additional opportunities to localize nanotubes within the variety of shapes obtainable in blends.

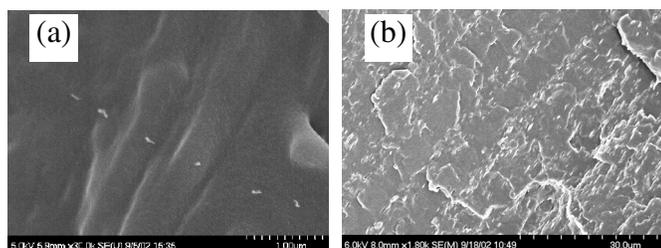


Fig. 7 Orientation of nano-scale solid additives in polypropylene: (a) exposed ends of single wall nanotubes aligned within a layer for matrix reinforcement; (b) clay platelets arranged into layers for low permeation films.

A relatively new and cost-effective method for producing packaging materials that have high barrier properties involves the addition of inorganic materials to plastics. Such materials can find application in food packaging and beverage containers. Clay is currently being investigated since it consists of very thin (~10 nm) platelets having high frontal area. It is currently dispersed in plastics by using screw extruders. Random distributions result that provide diffusion pathways around platelets. Barrier properties in such situations are only marginally improved at preferred small loading levels. In Fig. 7(b), clay platelets were concentrated by smart blending into layers so that distances between individual platelets were reduced and diffusion pathways were significantly impeded [27].

PERCOLATION AND ELECTRICALLY CONDUCTING PLASTICS

In conventional compounding methods, electrically conducting plastics are often produced via addition of a conducting powder consisting of carbon black or metallic particles. A conducting state is attained at a percolation threshold where the particle concentration is sufficiently high to give abundant contact points by random encounters among particles. In smart blending, percolating structures among particles are instead constructed in situ [12,13]. As such, conducting plastics can be produced with much smaller additive concentrations. This capability is quite important since additives increase costs, reduce processability by raising melt viscosity, and can degrade the desirable characteristics of the host plastics. Moreover, a variety of electrical properties can be deliberately imparted.

An example of the internal structure of a conducting plastic that was produced by smart blending is given in Fig. 8 where carbon black was used [28]. By concentrating the carbon black within one polymer melt stream (i.e., in a 'masterbatch') of Fig. 1, the initial positions of nearby carbon black particles diverged exponentially fast over time as an outcome of chaotic advection. The masterbatch was converted to long striations with the filamentary features in Fig. 9(a). Both the number of striations and their filamentary features in Fig. 9(b), or branches, increased in number and length depending on the

specified melt residence time and rod motions in the smart blending device (Fig. 1). Electrical current flow was provided along the striations and also between them via the branches. The formation of branches in striations is an outcome of sensitivity to initial conditions, or in this case, sensitivity to initial locations of particles in the masterbatch. Such behavior is a defining characteristic of the chaotic advection used to implement smart blending. The development of striations and the growth of filamentary features are controllable and repeatable features via selection of process parameters. As such, a variety of electrical properties can be more deliberately imparted to materials produced. Properties and structure characteristics are reproducible since chaotic advection for a particular set of process parameters provides a consistent template for structure formation. However, sensitivity to initial locations necessarily causes the precise particle locations among various extrudates to differ. Such differences have no practical importance since the overall characteristics of the resulting composites are identical.

CLOSING REMARKS

Chaotic advection and a growing understanding of multi-component flows provide a basis for reconsidering how blending is performed. It seems probable that smart blending devices will become available to intelligently agitate melts so that desired internal structures among material components can be more deliberately formed. With such devices, an ability to impart desired functionalities to manufactured products will be possible. Blend morphology will be selectable via a computer keyboard in lieu of the often present-day approach of trial-and-error. Smart blending devices may find application to any material that can be processed in a viscous, fluid-like state such that turbulence does not counter structure development. As suggested by examination of Fig. 1, multi-component flow modeling, rheology, instrumentation and control, machine design, polymer science, chemistry, heat transfer and many other topics are pertinent. Opportunities for investigators to make important contributions are manifold.

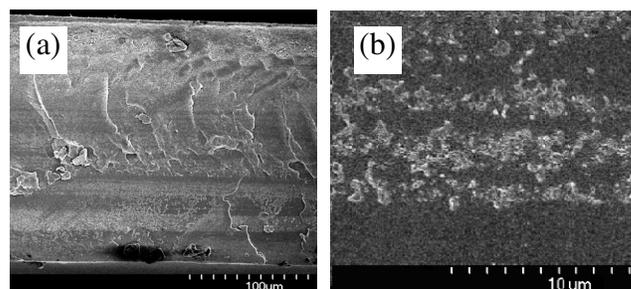


Fig. 9 Conducting networks formed in carbon black at a concentration of 3% by weight: (a) striations throughout film cross-section, (b) appearance of interconnections by branches between striations.

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