

Chaotic Advection as a Means to Develop Nanoscale Structures in Viscous Melts

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ABSTRACT

Nanoscale materials are typically produced either by breaking down larger structures or by assembling them directly from their smaller constituents. Another approach is to establish processing conditions where initially large component domains in the melt intermingle via intelligent agitations in accordance with continuum mechanics, refine progressively, and eventually give nanoscale materials where molecular interactions may induce further orientation. In this paper, the potential of chaotic advection to develop in situ nanoscale structures is specifically described in polymer melts. Due to induced chaotic motions, melt domains stretch and fold recursively. Structure is evolved in lieu of being broken down as occurs typically in common blending. Moreover, the extent of structure development is controllable so that a variety of distinct material arrangements can be formed.

Introduction. In recent years, new methods for organizing matter have emerged separately that if brought together may yield important new processes and materials. At the molecular scale, self-assembly provides a means to organize large numbers of molecules to modify surface properties.¹ Molecules are being designed and synthesized such that noncovalent interactions among them lead to the formation of supramolecules.² At the continuum scale, chaotic advection has emerged as a recognized subfield of fluid mechanics. Even absent inertial forces that characterize turbulent flows, it has been demonstrated that fluid particles can be advected along complex paths in response to simple periodic motions of bounding surfaces. Particle motion over time can be chaotic.³ Fluid domains become stretched and folded and the rate of progression can be controlled. In studies focused on mixing, vivid photographs have shown refinement in pigmented fluid domains.⁴ Although chaotic advection has been implemented primarily to gain an understanding of mixing in general, it has also been implemented to create structured materials where one or more thermally compatible components can exist in a liquid state.⁵

Given the interest in molecular organization and a focus on synthesizing molecules capable of forming extended structures, this paper addresses a need to develop new blending methods capable of promoting the development of fine-scale structures in contrast to existing processes that typically focus on breaking down structure and randomizing

to achieve a mixed condition. In this regard, it is more fruitful to regard blending as a structuring process rather than a mixing process, as is common practice. Chaotic advection is employed to organize initially large components into several types of arrangements with nanoscale features and where molecular interactions may induce further orientation. Internal structures, as defined by interfaces among components, can become physically expansive while allowing very small scale features to develop, such as numerous very thin internal layers, molecular films, interpenetrating structures, holes in layers, fibers, droplets, and oriented microscale and nanoscale solid additives. Polymer melts are utilized to demonstrate concepts, although other viscous melts are also pertinent. Melt viscosities must be sufficiently high such that structure development is not mitigated by turbulence effects.

Although sometimes seemingly contradictory to persons not familiar with the mathematical science of chaos, chaotic advection offers new opportunities to develop processes where structure development among material components can be better controlled. It may be a basis for new “smart blending” devices. Such devices allow the formation of specified morphologies by dictating the motions of stir rods to agitate melts intelligently, for example. Unlike random motion, chaotic advection has two defining and related characteristics of significance here. In characteristic 1, the region of space enclosing an initial minor component body becomes stretched and folded. In characteristic 2, the positions of individual parts of an initial minor component body diverge exponentially fast over time. The influences

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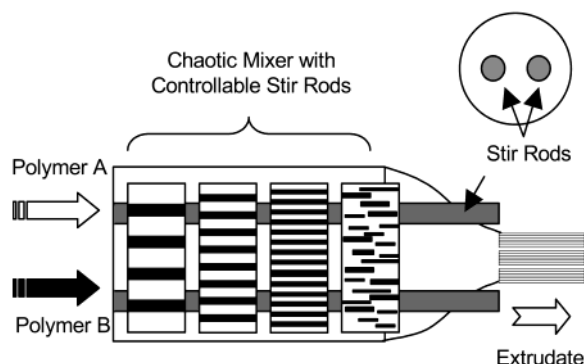


Figure 1. Polymer melt streams are converted to a layered configuration within a continuous flow chaotic mixer. Stretching and folding of melt domains is a characteristic of chaotic advection.

of both characteristics can be made to progress to a desired degree and are evident in materials produced. Eventually, as length scales reduce, structure development can be eventually dictated by molecular interactions in lieu of continuum mechanics. These interactions can offer further opportunities for achieving structure development on smaller scales.

Like any blending method, chaotic advection involves deformation and reorientation steps. However, unlike common blending, it can be implemented in devices of relatively simple construction. An example of a continuous flow chaotic mixer is depicted in Figure 1. This device consists simply of a cylindrical barrel and two internal rods. It has been used in prior mixing studies in a batch configuration⁶ and was adapted here to develop a continuous flow device to produce structured materials that could be extruded in uninterrupted lengths. Chaotic advection was induced by rotating each rod separately and periodically. Careful selection of the rotational displacements and rod positions is necessary for effective performance. It should be noted that many alternate configurations are possible, such as those incorporating multiple rods. Instead of small flow clearances associated with present-day blending devices, comparatively large spaces exist in which physically expansive structures with small scale features can evolve. For example, both polymer melt stream A and polymer melt stream B in Figure 1 are stretched and folded (characteristic 1) within a cylindrical barrel as the melt stream moves toward an extrusion point. A multilayer structure forms with layers that are expansive within their individual planes but can be very thin and numerous. The number and thickness of individual layers is selectable by controlling the rod rotations.

If perhaps polymer melt stream B in Figure 1 contained particulate additives, filaments would appear as shown in Figure 2. When used in this manner, chaotic advection offers a means to indirectly manipulate within melts solid additives such as nanotubes, clay platelets, and carbon black to yield composite materials with a variety of functional structured distributions. Upon close inspection, the filaments, if composed of particles, contain subfilaments and branches due to characteristic 2. The number of filaments, subfilaments, and branches would increase nearer to the extrudate point as chaotic advection acted for longer times. Electrically

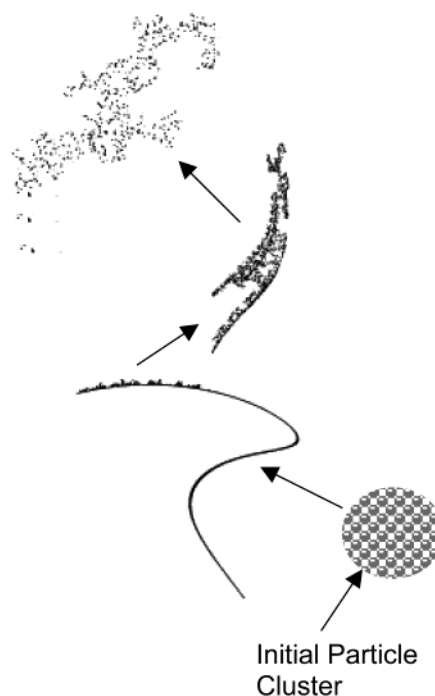


Figure 2. Particles that are initially assembled into a small cluster can be formed into striations or layers. Sensitivity to initial locations causes the path of each particle to differ so that striations or layers are actually composed of finer-scale filamentary structures.

conducting plastics have been made with reduced carbon black concentrations using this approach.^{7,8} It is interesting to note that composite materials produced in this manner can have nanoscale features both in regard to the sizes of the solid additive and the features evolved by chaotic advection, such as the thicknesses of thin films in which the additives reside.

Although a new processing device, the continuous flow chaotic mixer of Figure 1 has an association with present-day equipment. The formation of melts with a very large number of component layers can also be accomplished using layer multiplication dies in which an initial melt flow that may comprise two layers is divided and stacked within stages.⁹ If two layers are initially formed in these devices, the subsequent number of layers is constrained by 2^n , where n is the number of multiplication stages. Because a variety of morphologies can be obtained from the breakup of multilayer blends,^{10,11} such devices inherently lack process control attributes that allow desired structures in melts to be captured in extrudates. In effect, continuous flow chaotic mixers are similar to layer multiplication dies but utilize moving surfaces in lieu of fixed surfaces so that process control is improved.

Methods. The processing concept is depicted in Figure 1. A minor component polymer A melt (dark band) and a major component polymer B melt entered a 5.3 cm diameter cylindrical chaotic mixer. Either or both melts can contain solid additives such as nanotubes, clay platelets, or carbon black. The initial polymer streams were converted to an increasingly fine-scale layered and spatially distributed structure by recursive stretching and folding that characterizes chaotic advection. This layered blend morphology was

directed to either a linear tapered circular die or a slot die where additional refinement occurred and an extrudate emerged as a 2.5 mm filament or 500 micron film. To instill chaotic advection, two internal stir rods (see inset) were alternately rotating. The rods were both of 1.91 cm diameter and extended the 75 cm length of the chaotic mixer. The rods were offset by 1.5 cm from the cylinder axis. Each rod was rotated separately four complete turns by an automated drive system. The same rotational direction was used. The automated drive system was identical to ones used with batch mixers and has been described in earlier studies.⁵ The amount of melt structuring depended on the number N of pairs of rod motions. For example, for $N=5$, the rods were rotated in sequence four complete rotations for a total of five times for each rod.

Polymer A and Polymer B melt streams were provided by separate metering pumps fed in turn by a 2.54 cm single screw extruder and a 3.18 cm single screw extruder. The extruders and metering pumps served only to provide steady and separate melt flows to the chaotic mixer. The minor component polymer was injected through a single, 0.95 cm diameter port and the major component polymer was injected through six, 0.51 cm diameter ports. External heating elements maintained a uniform melt temperature within the chaotic mixer section. The resulting extrudates were cooled by ambient quiescent air and were not subjected to drawing.

The steady shear viscosities of polymer components were measured at the processing temperatures with a cone and plate rheometer (Rheometric Scientific, ARES, Piscataway, NJ). Internal structures in extrudates of filament or film form were exposed by fracturing samples after immersion in liquid nitrogen. They were subsequently examined by scanning electron microscopy (Hitachi, model 3700, Tokyo, Japan). The effect of layer refinement on crystallinity was assessed by modulated differential scanning calorimetry using a heating rate of 5 °C/min with a modulation of ± 1.0 °C. Oxygen transmission tests were performed with a permeability tester (Mocon, Inc., Ox-Tran 10/50 A, Minneapolis, MN) on 50 cm² samples in accordance with ASTM 3985–95. Tests were performed at least three times at 23 ± 0.3 °C after sample conditioning for at least 10 h and the average value was used.

Results and Discussion. As depicted in Figure 1, recursive stretching and folding of polymer melt streams initially yielded a layered morphology that refined progressively as the melt moved along the chaotic mixer toward an extrusion point. Polymer components in bulk streams became confined within very thin alternating layers. The degree of refinement was controllable by selecting the manner in which the rods rotated while the melt was resident in the mixer. An example is shown in Figure 3 of very thin and numerous layers in an extruded 500 micron-thick film composed of 20 vol % ethylene-propylene-diene terpolymer (EPDM: semicrystalline, Nordel IP NDR 3720P) and polypropylene (PP: isotactic, Montel PH723). Individual layer thicknesses were about 100 to 200 nm, and several thousand layers were present. Similar layered morphologies have also been formed in extruded 2.5 mm monofilaments.¹² The similar morphol-

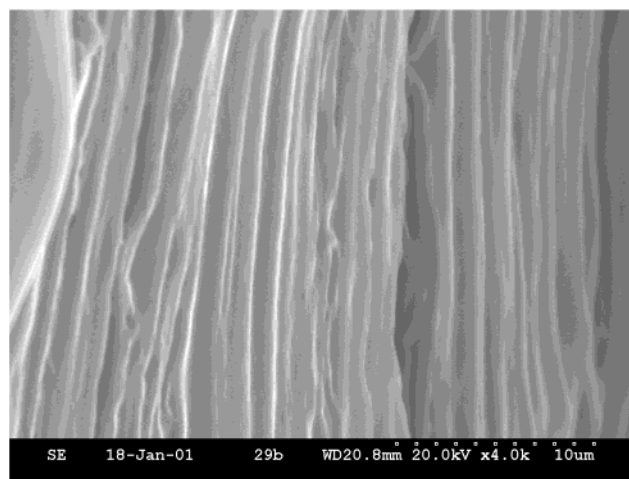


Figure 3. Polymer melt streams can be controllably converted by stretching and folding of chaotic advection to numerous internal thin layers such as these in extruded 500 micron films composed of 20% EPDM and PP ($N = 10$).

ogy demonstrates that very thin and numerous layers can be formed into different shapes during extrusion steps. The viscosity ratio (EPDM/PP) at the processing temperature of 235 °C ranged from 4 to 8 for shear rates during chaotic mixing from 0.2/s to 2/s. Because of the propylene monomer unit in EPDM, interfacial tension with PP was small (1.07 dyn/cm).¹³ Interfacial instabilities proceed slowly for melts with a viscosity ratio greater than unity and small interfacial tension so multiple unbroken layers formed readily.¹⁴ Combining a polymer with a block copolymer by this method, for example, may yield extremely thin layers and promote a lamellar molecular orientation. The attainable degree of layer refinement was less for polymer combinations having high interfacial tension and small viscosity ratios.

The multilayer morphology of Figure 3 incorporated very large interfacial area on the order of 10^6 to 10^7 cm²/ml. Opportunities are available to organize additives onto the many internal interfaces to create molecular films. Interfacial area growth as chaotic advection proceeds is accompanied by reduced distances between additives and interfaces. Additionally, as will be discussed, long chain molecules that are initially randomly oriented in bulk melts can become more oriented as melt domains are progressively converted to multiple thin films. Instabilities that seek to reduce interfacial area can also give rise to a variety of derivative morphologies. These can initially retain the very small dimensions of the parent layer thickness. The derivative morphologies depend on the dominance of a particular breakup mode.

As has been reported for single sheets thinned by shear flows,¹⁵ holes eventually formed as the multiple layers refined. The aforementioned ability to control structure formation allowed capture of the holes while they were still very small. Analytically, it has been shown that a hole in an isolated layer can grow due to interfacial tension forces only when the hole diameter is larger than the layer thickness.¹⁶ The formation of nanoscale holes (e.g., < 200 nm diameter) thereby required that layers be very thin. Internal holes in a



Figure 4. Upon refinement due to continued processing, very small holes eventually formed for $N = 12.5$ in the layers of Figure 3. Chaotic advection offers a means to capture these holes in extrudates.

20% EPDM and PP extruded film that was produced under the same conditions as the film in Figure 3 are shown in Figure 4 where the internal layers were exposed by cryogenic fracture. Because very many alternating layers were present, hole formation in layers of one polymer component yielded a novel structure with single-phase continuity. The polymer from the adjacent layers that had flowed in the melt through the incipient holes and coalesced appeared as small circular domains within each hole. In this specimen, it is interesting to note that the polymer components were organized by continuum scale interactions (i.e., fluid mechanics and chaotic advection) into layers with thicknesses below about 100–200 nm such that molecular-scale interactions (e.g., incipient hole formation by van der Waal interactions and coalescence) became influential and caused morphology changes on very small scales. Although hole formation is usually associated with thicknesses below 10 nm, hole formation in single films with larger thicknesses on substrates has been attributed to greater van der Waal interactions at locations where thickness was thinned due to gravitational drainage or surface tension gradients.¹⁷ Similarly, differing stretching and folding rates that are inherent in chaotic advection and thermal fluctuations in the multiple surfaces of the multilayer film structure may be responsible for local thickness variations that promoted hole formation in layers with larger average thicknesses.¹¹ Thickness variations can also promote the transition from a multilayer morphology to a morphology with dual phase continuity and a spongelike morphology when hole formation occurs simultaneously and interactively in layers of both components.¹⁰ The manufacture of plastics with selective permeability, electrical conductivity, or enhanced toughness are possible applications.

If chaotic advection was continued after hole formation, hole growth yielded small bodies with one or more characteristic dimension similar to the thicknesses of the parent layers. In the common case of capillary instabilities, for

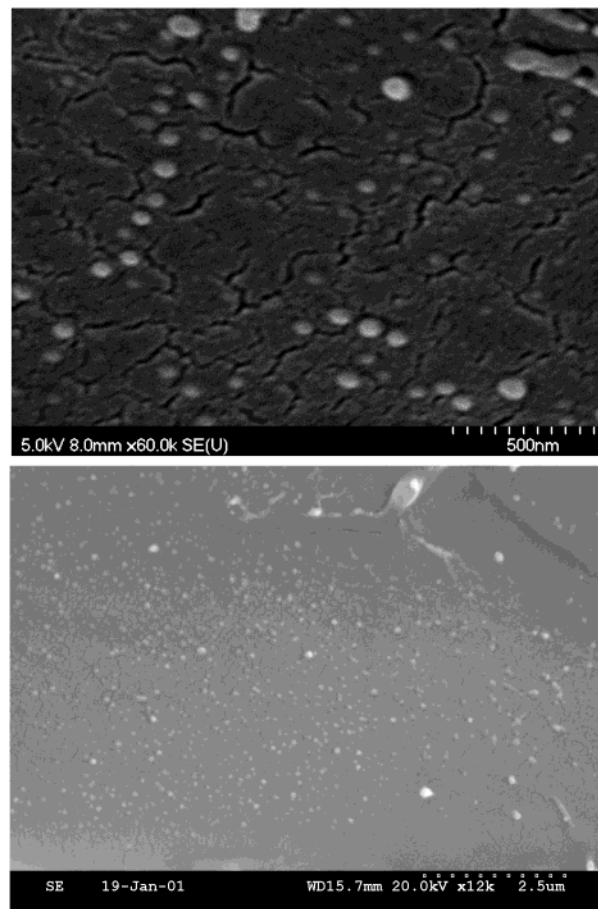


Figure 5. Layer breakup can yield a variety of useful shapes such as very small diameter droplets (upper: $N = 25$; lower: $N = 40$).

example, droplets have diameters that approximate the parent fibers. In Figure 5 of an internal layer in an extruded 500 micron-thick film for $N = 25$, EPDM droplets of about 50 nm are evident within PP. The droplets emerged from the breakup of thin threads formed among enlarging holes and also from the breakup of cylindrical shapes filling interconnecting holes. The orientation of some droplets in Figure 5 was thereby reflective of the parent layered morphology. It is noteworthy that the droplet diameters were smaller than the calculated critical droplet diameters for minor component fluids subjected to shear flows.¹⁸ A comparison of critical droplet diameter to the diameters of droplets produced by chaotic advection is given in Figure 6. In Figure 6, the triangular points correspond to measurements at specific shear rates of the component viscosities. The smaller droplet diameters were possible because the droplets emerged from the very thin layers of Figure 3 in lieu of the deformation and breakup of circular blobs arising in conventional mixing processes. In this sense, the droplets were not in equilibrium with the imposed shear fields so that coalescence over time would cause coarsening. However, at the 20% EPDM concentration, coarsening occurred slowly. Droplet diameters in Figure 5 for $N = 40$ were not appreciably larger than those for $N = 25$, even though processing time was nearly 60% longer. Polymer engineers often attempt to decrease droplet size by operating compounding equipment at higher

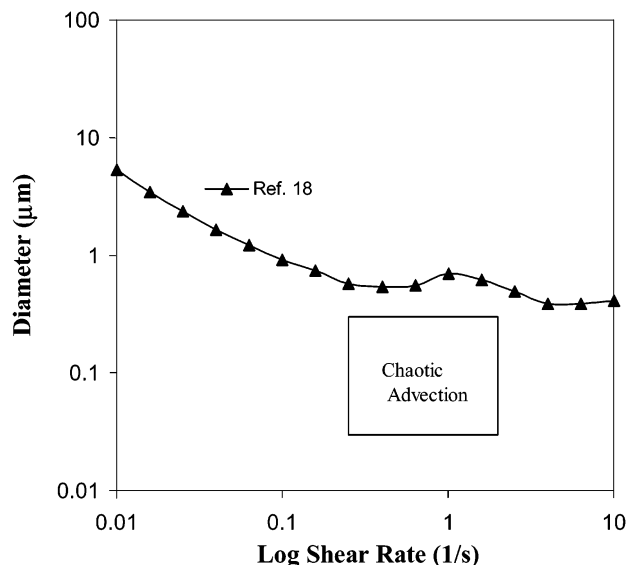


Figure 6. Comparison of droplet diameters obtainable by conventional methods and those obtained by chaotic advection for the range of shear rates present.

imposed shear rates. Unfortunately, the reduction in droplet size can be small since deformation becomes more difficult as the viscosity of the major component decreases (i.e., shear thinning behavior). Where droplet diameters of tens of nanometers are the goal, the formation of thin layers appears to be a desirable if not necessary route.

The prior examples have shown how nanoscale shapes can be formed among components in the melt. It was proposed above that similar methods can be applied to organize molecules specifically designed and synthesized to develop molecular films and supramolecular structures. Although the extent of this potential awaits further study, an example is provided that has relation to current practice. In present-day compounding steps, copolymers 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 process can be promoted when melt domains are intermingled by chaotic advection such that numerous and expansive thin layers evolve as in Figures 1 and 3. 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. When introduced into the chaotic mixer of Figure 1 as three distinct melt components, an alternating structure is formed such that the copolymer is ideally situated between the other components. 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 Figure 7 where blends of low density polyethylene (LDPE: Affinity PL 1840, Dow Chemical Company, Midland, Michigan), ethylene vinyl hydroxide (EVOH: EVAL GC156B, EVALCA, Lisle, Illinois), and maleic anhydride graft-polyethylene (MA: Tymor 1203, Morton International, Inc., Chicago, Illinois) were used to

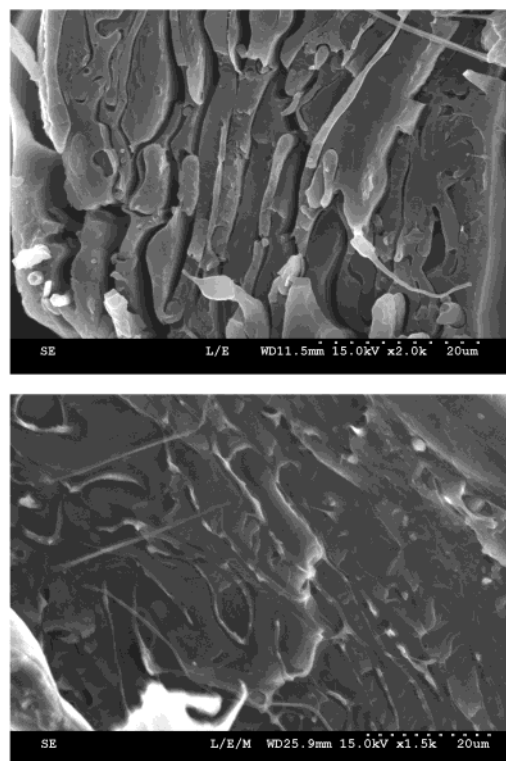


Figure 7. Formation of thin layers by the placement and orientation of maleic anhydride graft polyethylene at EVOH/LDPE interfaces formed by chaotic advection ($N = 3$).

extrude 500 micron-thick films. Maleic anhydride is often used in LDPE/EVOH plastics to improve interfacial adhesion or stabilize blend morphology. Numerous distinct films were produced for different processing times so that the effect of layer refinement on molecular orientation and oxygen barrier properties could be assessed. In the upper portion of Figure 7, 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 folded morphology was reflective of the chaotic advection used to produce it. In the lower portion of Figure 7, the addition of MA 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 was promoted upon solidification by confining the melt components to multiple thin layers. Because permeants diffused more easily through amorphous regions, lower oxygen permeation rates were correlated with smaller layer thicknesses. Higher permeation rates were measured for the EVOH/LDPE/MA films despite the reduced layer thicknesses. Although layer thicknesses were smaller and further study is required, the intrusion of graft chains into the adjacent thin EVOH layers may have hindered crystallization.

Because of their very small size, it is impractical to directly manipulate large numbers of nanotubes or other nanoscale additives, such as exfoliated clay platelets or carbon black, to produce functional structured distributions for commodity products. Chaotic advection offers a means to indirectly

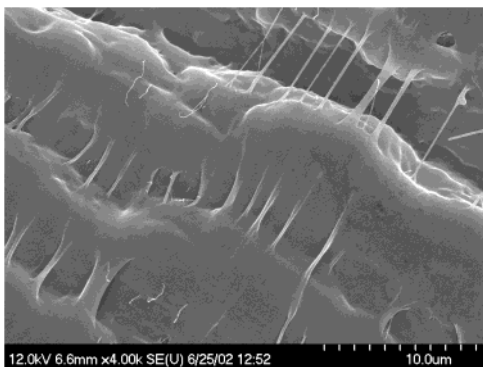


Figure 8. Single wall nanotubes distributed and oriented by chaotic advection in polypropylene.

manipulate additives with nanoscale dimensions to form a variety of structures. An example is shown in Figure 8 of single wall nanotubes (SWNTs) oriented in a PP matrix. Internal arrangements among the SWNTs were revealed by fracturing specimens following immersion in liquid nitrogen. Some ductile failure in the PP occurred due to a low glass transition temperature. Samples were produced with a batch chaotic mixer⁸ in lieu of a continuous flow chaotic mixer so that only small quantities of SWNTs were required. In accordance with the procedure in Figure 2, the SWNTs were initially concentrated within a cluster occupying a one-quarter sector of the 5 mm high by 5 cm diameter chaotic mixer cavity. Domains were stretched and folded as depicted in Figure 1 to yield a layered morphology of PP and SWNT-rich PP. Their confinement within layers of decreasing thickness induced the orientation shown in Figure 8. Although a subject of ongoing work, differences in affinities for polymer components may allow additional opportunities to localize nanotubes within specific shapes, such as a matrix with holes as in Figure 4 or the droplets of Figure 5.

Closing Remarks. Where material constituents are synthesized to assemble into nanoscale and molecular-scale structures, it is appropriate that devices and processes also be available that promote in situ structure development.

Results demonstrate that chaotic advection can be an enabling science for such devices. If processable in a fluidic state, initially large component domains can be controllably converted to numerous thin layers in and on which molecular orientation can arise. Solid additives can be indirectly manipulated to give functional orientations so that the manufacture of large quantities of nanocomposite materials is practical. The availability in the future of engineered batch and continuous flow chaotic mixers for materials research and manufacture may heighten the potential of newly synthesized molecules while also providing avenues to make better use of existing ones.

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