Chaotic Advection in Multi-component Melts for the Manufacture of Composite Materials

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by

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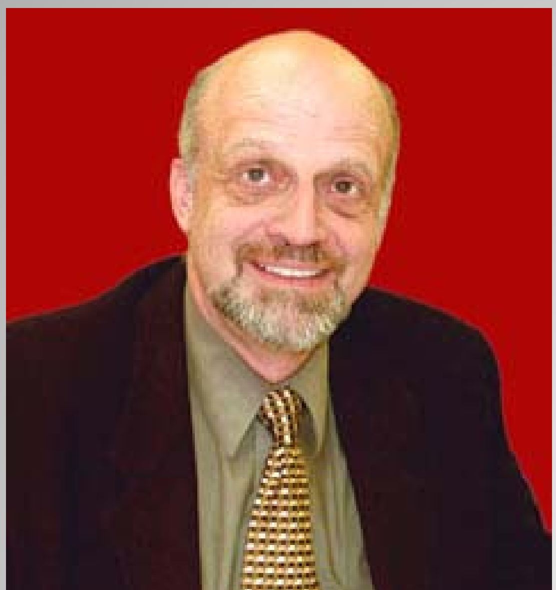
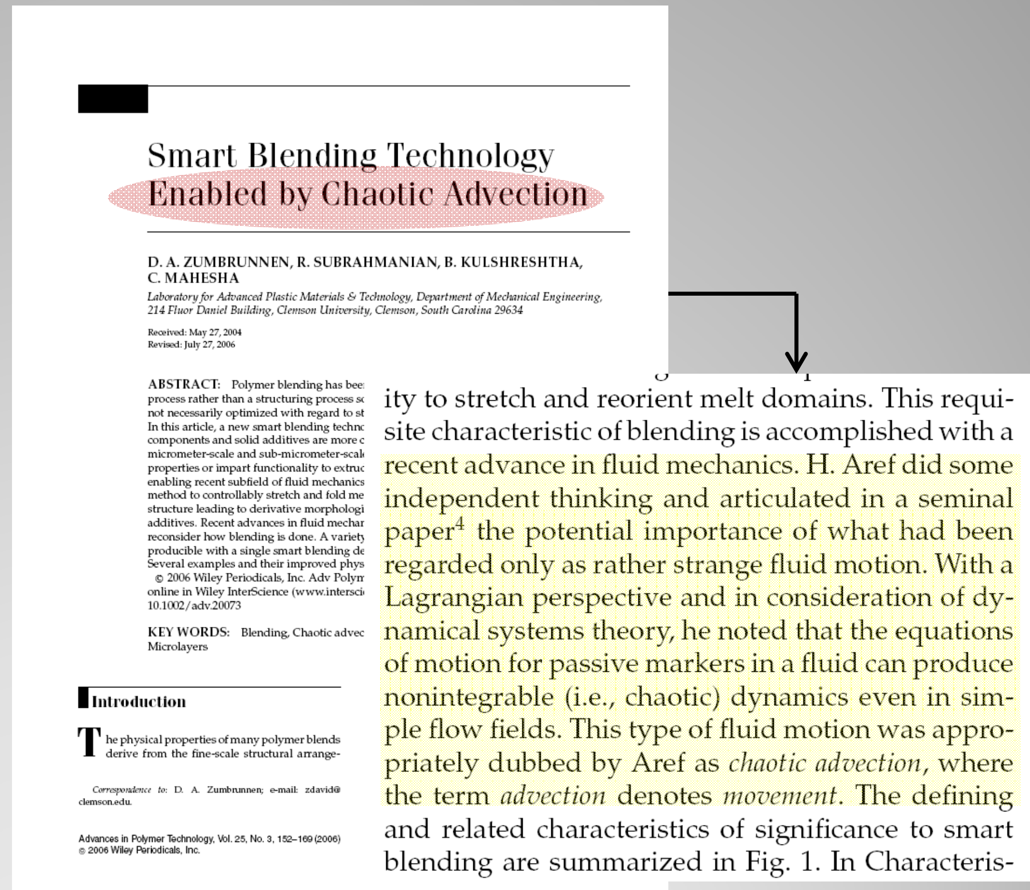
Dedication





Smart Blending Technology Enabled by Chaotic Advection

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ABSTRACT: Polymer blending has bee
process rather than a structuring process s
not necessarily optimized with regard to st
In this article, a new smart blending techn
components and solid additives are more c
micrometer-scale and sub-micrometer-scal
properties or impart functionality to extru
enabling recent subfield of fluid mechanics
method to controllably stretch and fold me
structure leading to derivative morphologi
additives. Recent advances in fluid mecha
reconsider how blending is done. A variety
producible with a single smart blending de
Several examples and their improved phys
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10.1002/adv.20073

KEY WORDS: Blending, Chaotic advec
Microlayers

Introduction

The physical properties of many polymer blends derive from the fine-scale structural arrange-

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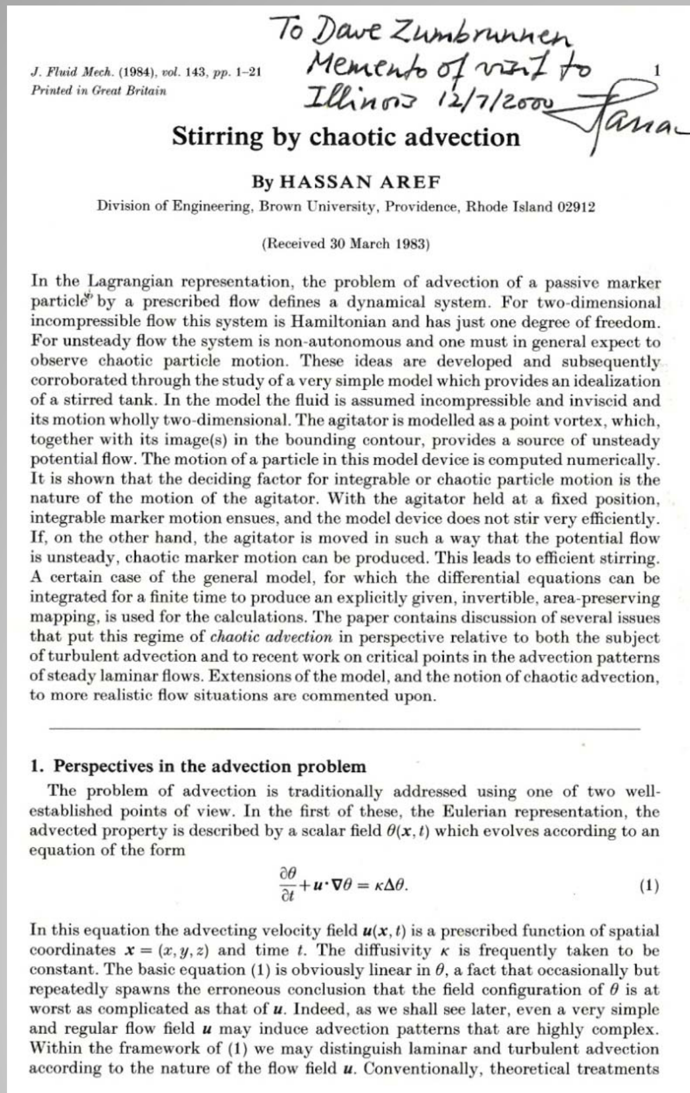
ity to stretch and reorient melt domains. This requisite characteristic of blending is accomplished with a recent advance in fluid mechanics. H. Aref did some independent thinking and articulated in a seminal paper[4] the potential importance of what had been regarded only as rather strange fluid motion. With a Lagrangian perspective 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 even in simple flow fields. This type of fluid motion was appropriately dubbed by Aref as *chaotic advection*, where the term *advection* denotes *movement*. The defining and related characteristics of significance to smart blending are summarized in Fig. 1. In Characteris-

Dr. Hassan Aref: The father of chaotic advection and the person who most profoundly influenced my research. Smart blending was truly *enabled* by chaotic advection.



To Dave Zumbrunnen
Memento of visit to
Illinois 12/7/2000
Hassan

J. Fluid Mech. (1984), vol. 143, pp. 1–21
Printed in Great Britain

Stirring by chaotic advection

By HASSAN AREF
Division of Engineering, Brown University, Providence, Rhode Island 02912

(Received 30 March 1983)

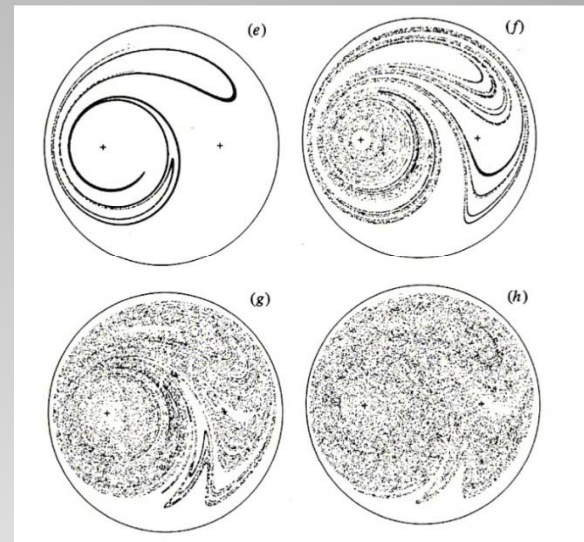
In the Lagrangian representation, the problem of advection of a passive marker particle by a prescribed flow defines a dynamical system. For two-dimensional incompressible flow this system is Hamiltonian and has just one degree of freedom. For unsteady flow the system is non-autonomous and one must in general expect to observe chaotic particle motion. These ideas are developed and subsequently corroborated through the study of a very simple model which provides an idealization of a stirred tank. In the model the fluid is assumed incompressible and inviscid and its motion wholly two-dimensional. The agitator is modelled as a point vortex, which, together with its image(s) in the bounding contour, provides a source of unsteady potential flow. The motion of a particle in this model device is computed numerically. It is shown that the deciding factor for integrable or chaotic particle motion is the nature of the motion of the agitator. With the agitator held at a fixed position, integrable marker motion ensues, and the model device does not stir very efficiently. If, on the other hand, the agitator is moved in such a way that the potential flow is unsteady, chaotic marker motion can be produced. This leads to efficient stirring. A certain case of the general model, for which the differential equations can be integrated for a finite time to produce an explicitly given, invertible, area-preserving mapping, is used for the calculations. The paper contains discussion of several issues that put this regime of *chaotic advection* in perspective relative to both the subject of turbulent advection and to recent work on critical points in the advection patterns of steady laminar flows. Extensions of the model, and the notion of chaotic advection, to more realistic flow situations are commented upon.

1. Perspectives in the advection problem

The problem of advection is traditionally addressed using one of two well-established points of view. In the first of these, the Eulerian representation, the advected property is described by a scalar field $\theta(\boldsymbol{x}, t)$ which evolves according to an equation of the form

$$\frac{\partial \theta}{\partial t} + \boldsymbol{u} \cdot \nabla \theta = \kappa \Delta \theta. \tag{1}$$

In this equation the advecting velocity field $\boldsymbol{u}(\boldsymbol{x}, t)$ is a prescribed function of spatial coordinates $\boldsymbol{x} = (x, y, z)$ and time t. The diffusivity κ is frequently taken to be constant. The basic equation (1) is obviously linear in θ, a fact that occasionally but repeatedly spawns the erroneous conclusion that the field configuration of θ is at worst as complicated as that of $\boldsymbol{u}$. Indeed, as we shall see later, even a very simple and regular flow field $\boldsymbol{u}$ may induce advection patterns that are highly complex. Within the framework of (1) we may distinguish laminar and turbulent advection according to the nature of the flow field $\boldsymbol{u}$. Conventionally, theoretical treatments



Aref's blinking vortex model

Particles were tracked to give 1-d striations. I saw layers. I had an interest in *layer* stability as well as chaos. I wondered about *multilayer* stability in a melt and *structural outcomes*.

Contents of this seminar

- Chaotic advection and its application to controllable in situ structure formation (smart blending)
- Computational modeling and physics of in situ structure formation
- Physical properties of some novel plastic materials produced
  - ❑ Toughness
  - ❑ Electrical conductivity
  - ❑ Permeation reduction (barrier)
  - ❑ Controlled release
  - ❑ Solvent resistance
  - ❑ Patterning (wood grains)

  Not covered
- Other applications (manufacturing and rheology)
- Suggested areas for further study
- Discussion

Acknowledgements

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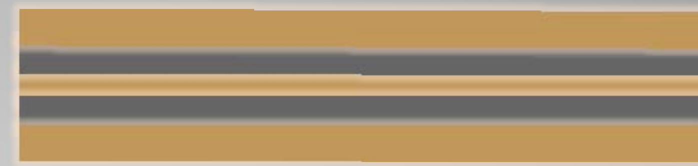
Research assistants: V. Chougule, C. Chhibber, R. Danescu , A. Dhoble, S. Inamdar, B. Gomillion, A. Joshi,* Y. Liu, C. Mahesha, K. Miles, B. Nagarajan, Y. Parulekar, P. Keener, P. Verma, W. Wright, D. Zhang

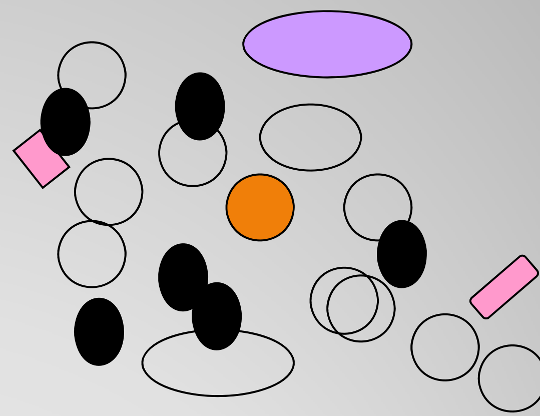
*Lattice Boltzmann modeling that is presented in this talk was performed by Abhijit Joshi in conjunction with his doctoral studies.

Post-doctoral research associates: R. Danescu, O. Kwon, B. Kulshreshtha, X. Jin

Co-extrusion: To put together only in one manner.



Mixing: To put together indiscriminately or confusedly (Ref: American College Dictionary).



<u>Observation</u>**:** Plastics that combine different polymer types or polymers and solids are either co-extruded or mixed. Structural outcomes are limited and are not necessarily associated with optimal results.

Progressive structure (morphology) development

Processing conditions where fine-scale shapes among melt components or arrangements among solid additives are formed progressively in situ. A variety of polymer blend morphologies are obtained via sequential morphology transitions.

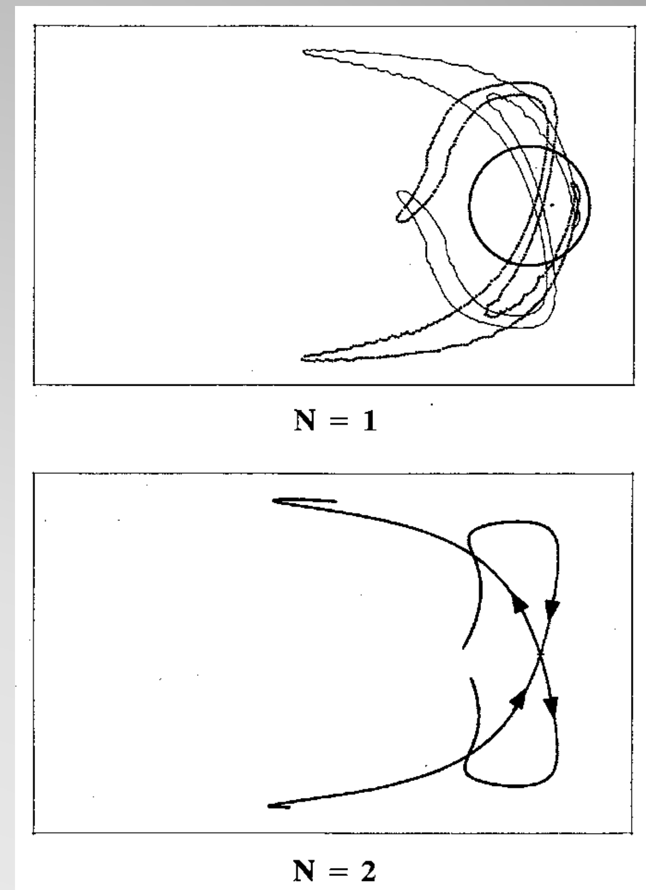
Chaotic advection is enabling to progressive structure development and thereby smart blending.

Chaotic advection: What is it?

Chaotic motion of passive particles in a fluid.

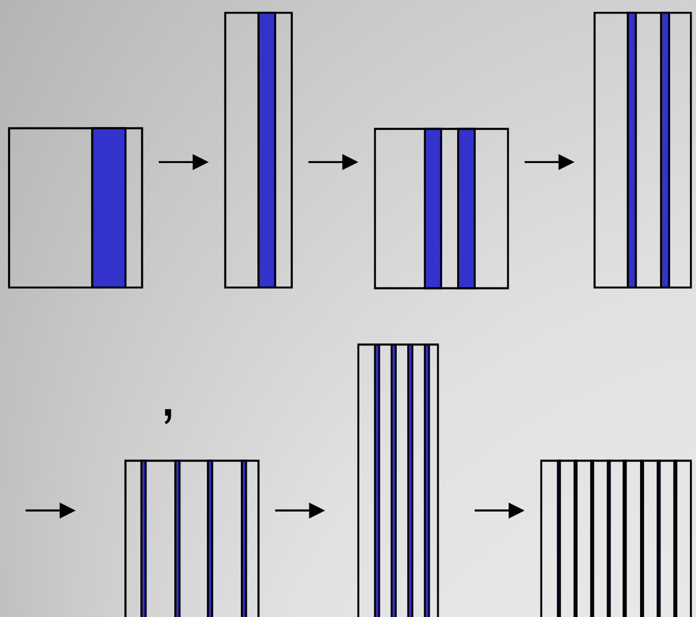
What is its relevance to smart blending?

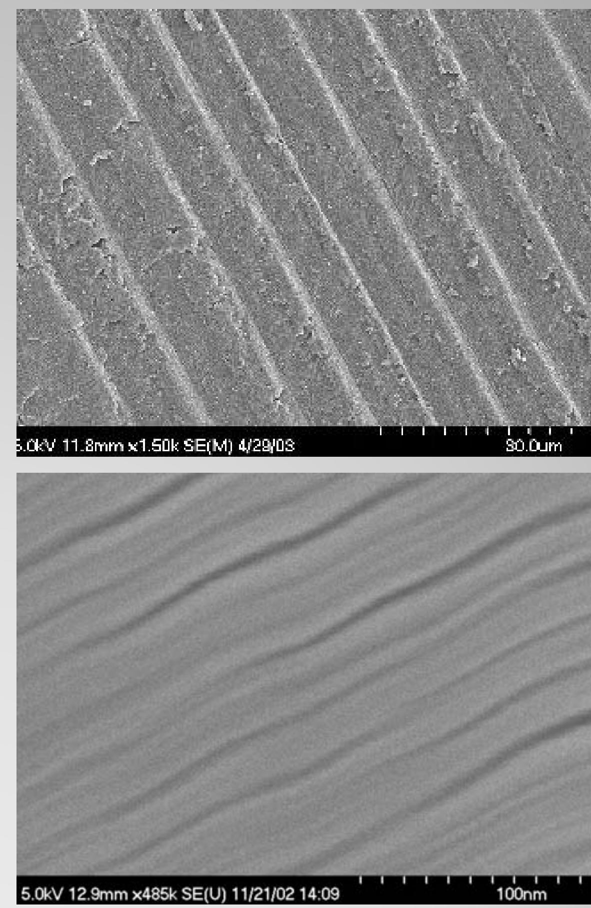
The collective chaotic motions of melt domains cause successive shear deformations and reorientations. A layered morphology first arises that may lead to other morphologies. Morphology development can be controlled.



Characteristics of chaotic advection

1: Stretching and folding

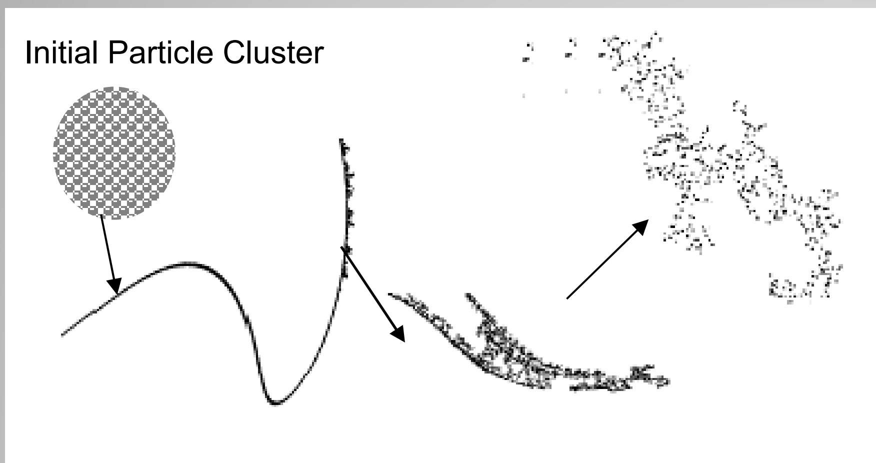


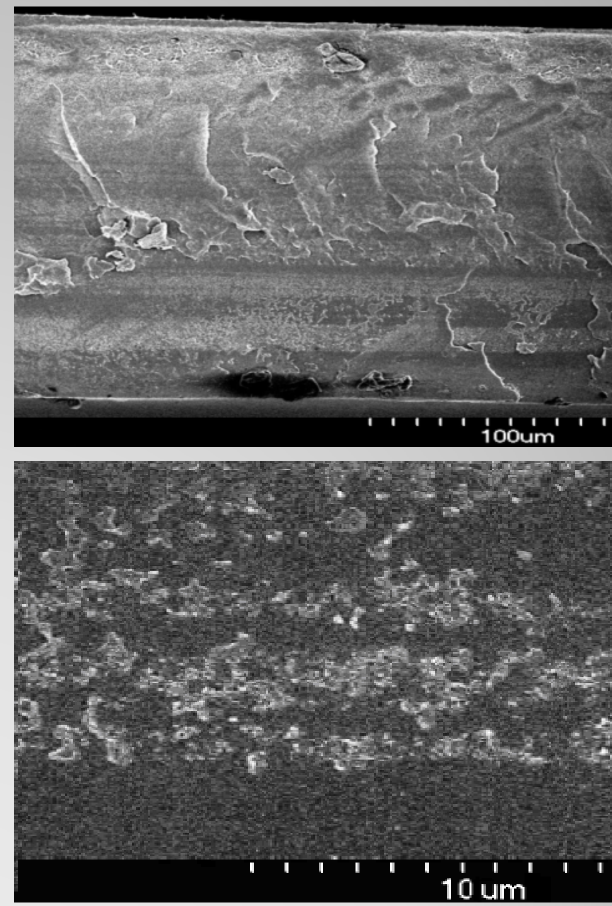


Multilayers in plastics

Characteristics of chaotic advection

2: Sensitivity to initial conditions



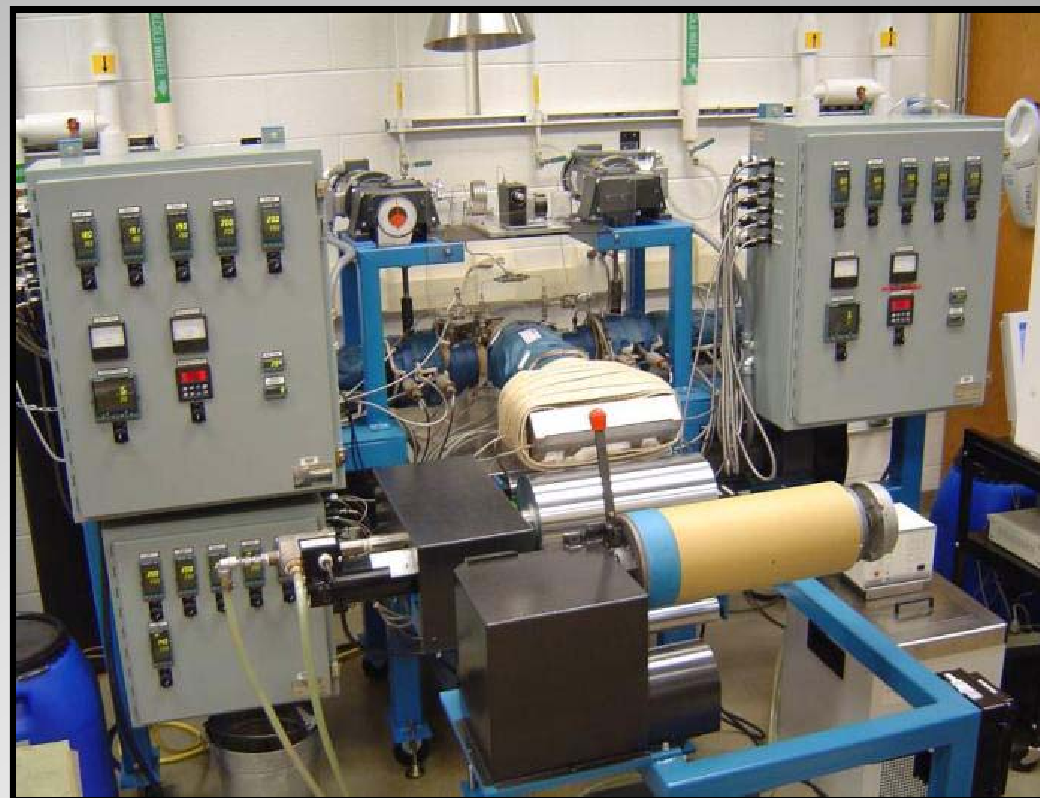


Electrically conducting plastics

PE layer in PS

Early example using batch chaotic advection blender of incipient development of a PE layer in a PS matrix due to stretching and folding of both melt components about one another.

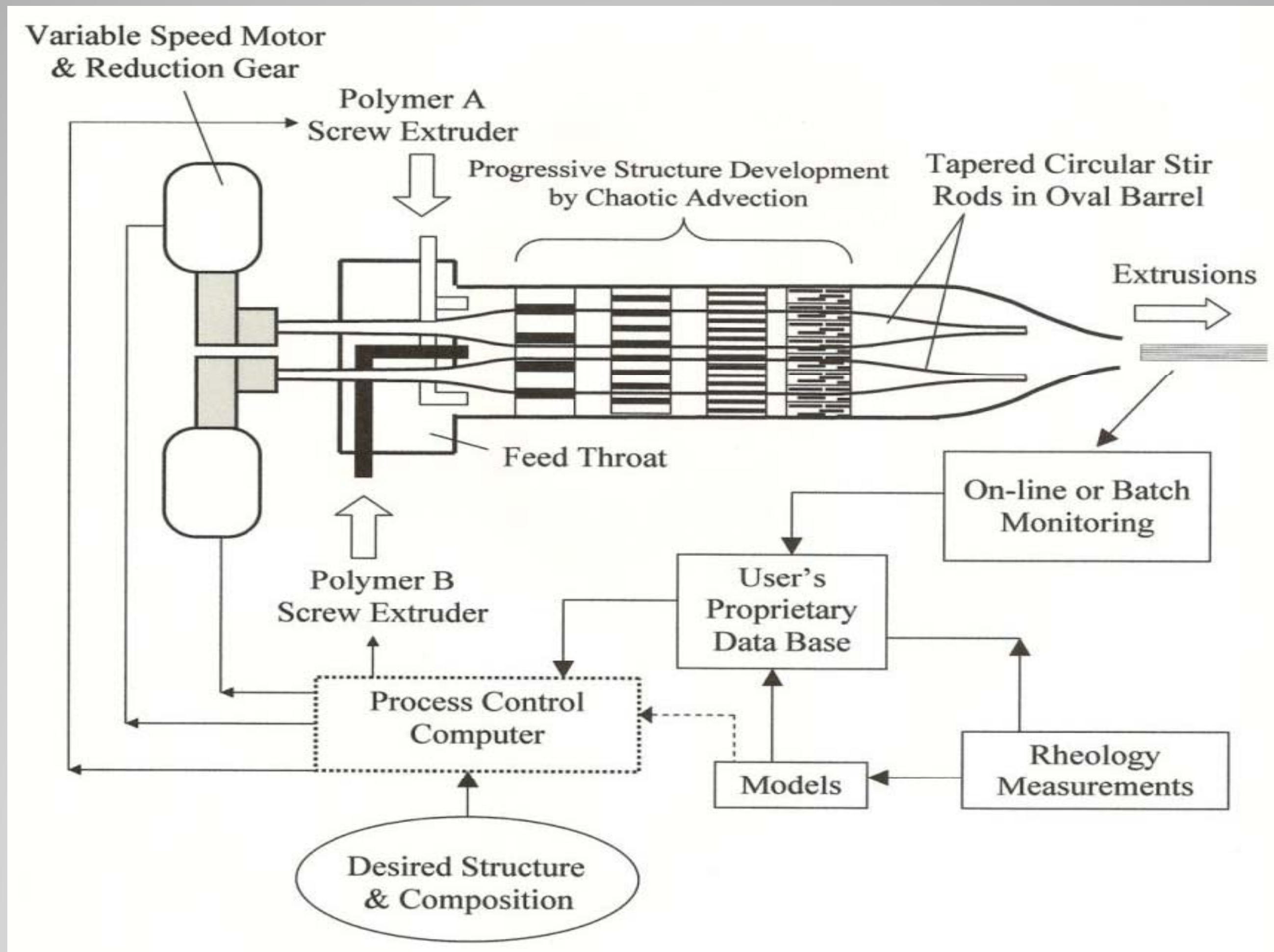
Laboratory smart blender test bed



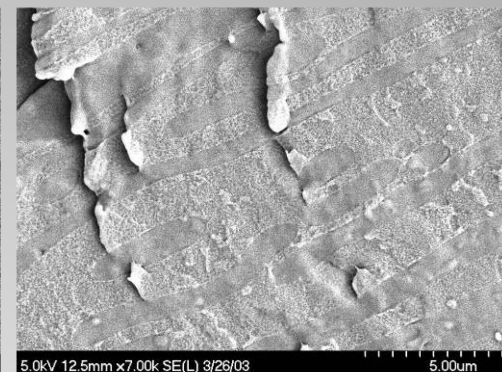
Various dies can be installed to produce structured materials of essentially any shape.

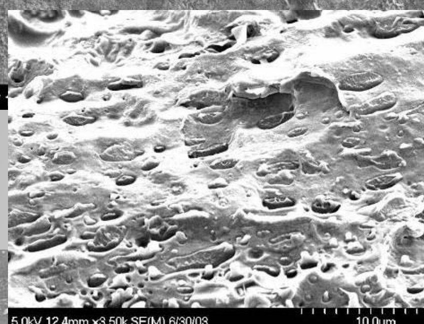
Smart blender operation

On-line control of in situ structure formation

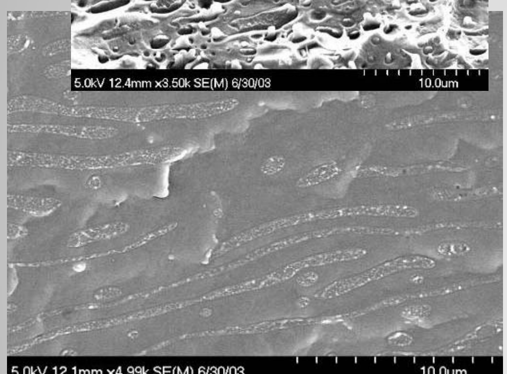


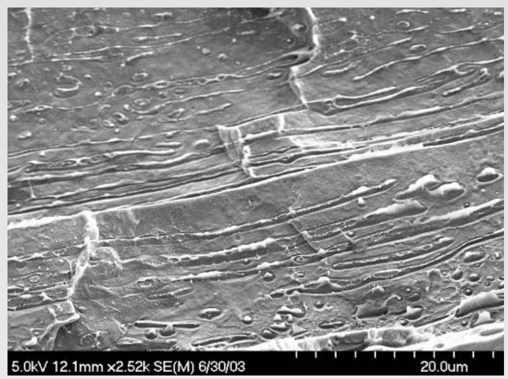
Progressive structure development in PP/LDPE 70/30% blends

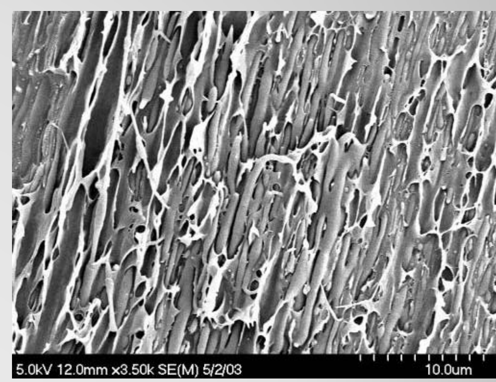




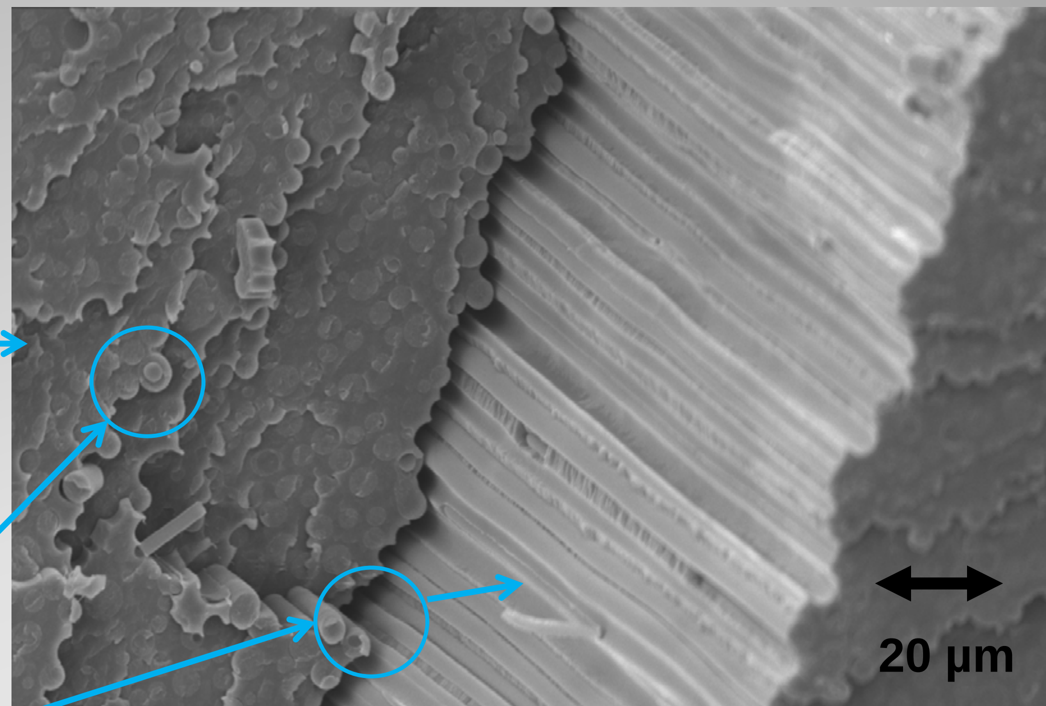
Droplets finally result such as obtaining by conventional processing.







Structured fibers (Structure in extruded fibers is tunable on-line.)



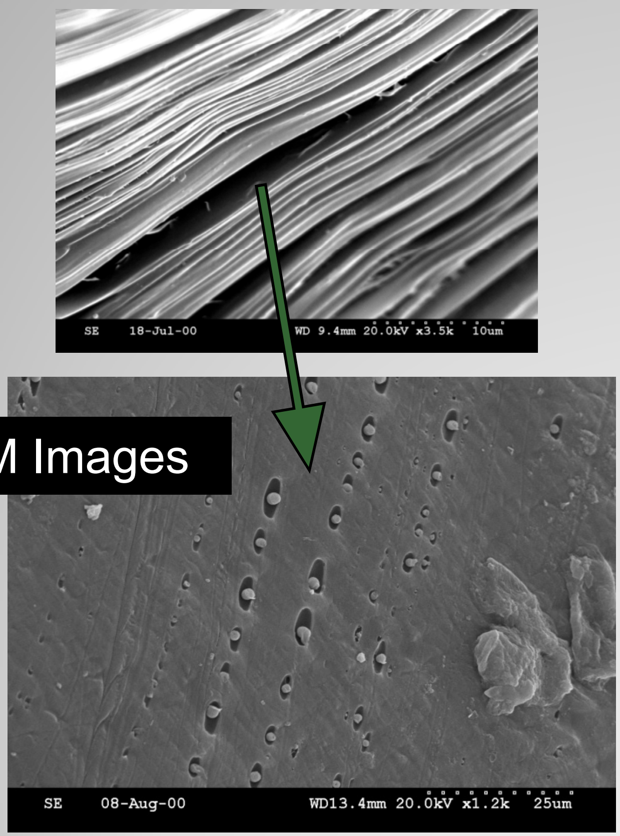
Internal fiber in fiber

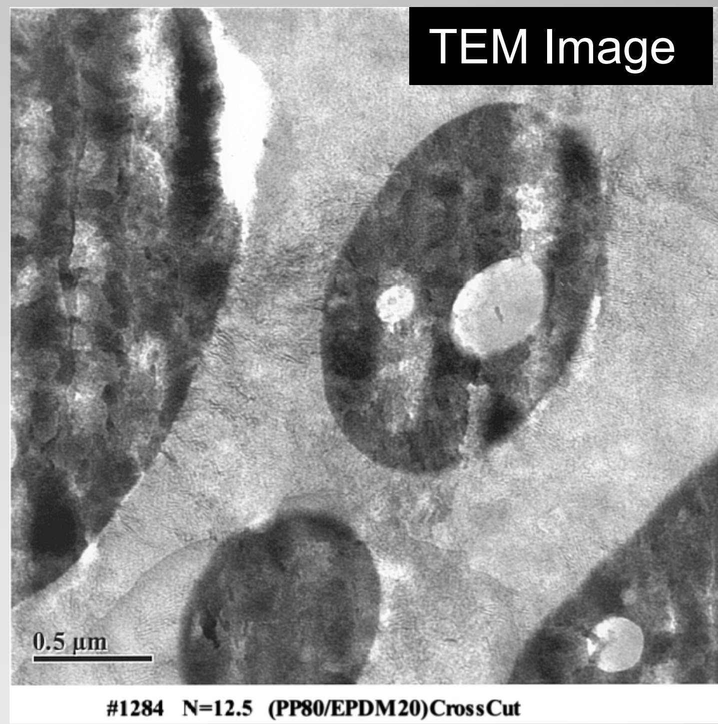
Internal fiber and fiber imprints in matrix revealed upon fracture

Cryogenic fracture of monofilament exposing internal fibers having internal fibers (novel hierarchical structure)

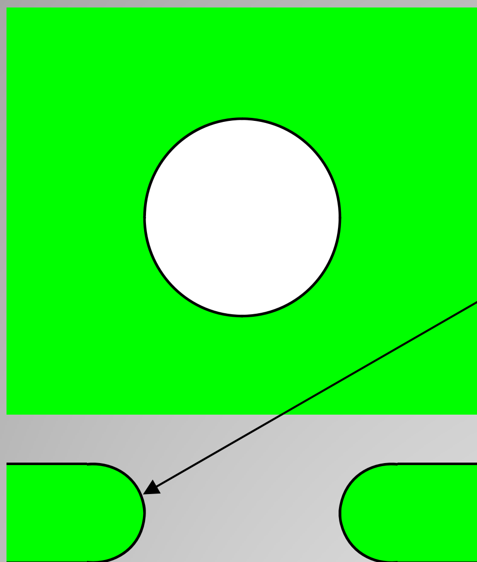
Experimental examinations have pointed to the central importance of rupture formation and growth in multi-layers to structural changes.

SEM Images



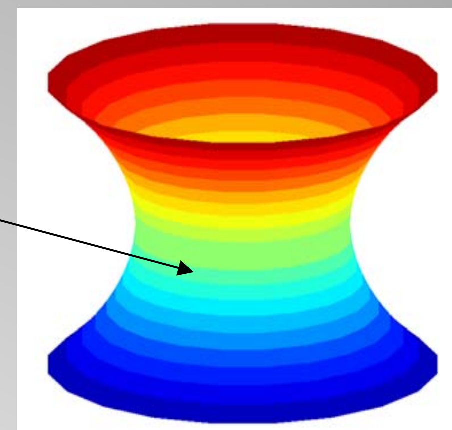


PP/ 20% EPDM, smart blender



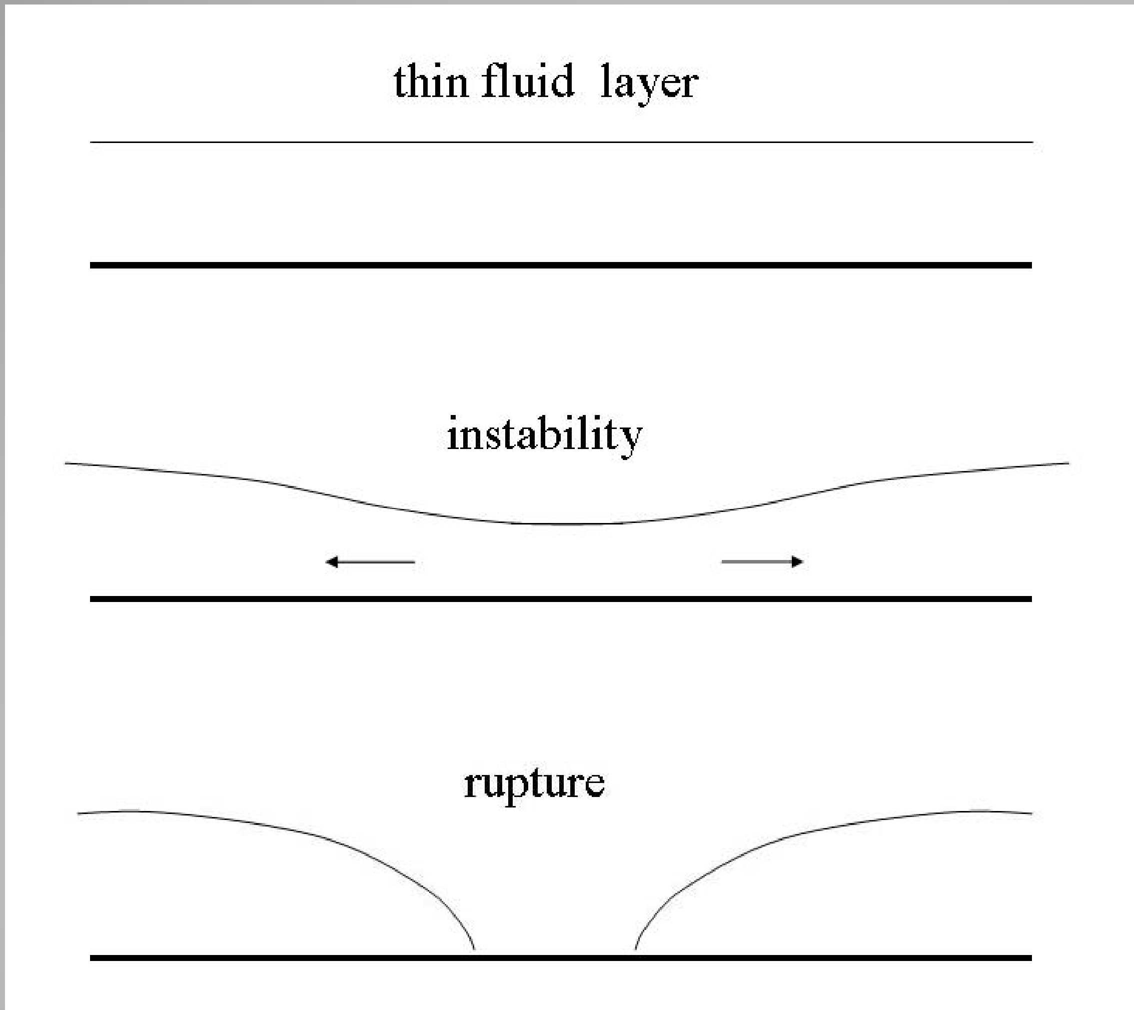
Hole in a fluid layer

Shape of the hole interface resembles the stable catenoid shape, but <u>does not have fixed edges</u>.



Soap film between two rings forms a stable catenoid surface under certain conditions

- A single hole formed in a fluid layer can <u>NEVER BE IN STABLE EQUILIBRIUM</u>.
- The hole either grows or shrinks.
- How and why do holes form in thin layers ?



$$P = \frac{A}{h^3}$$

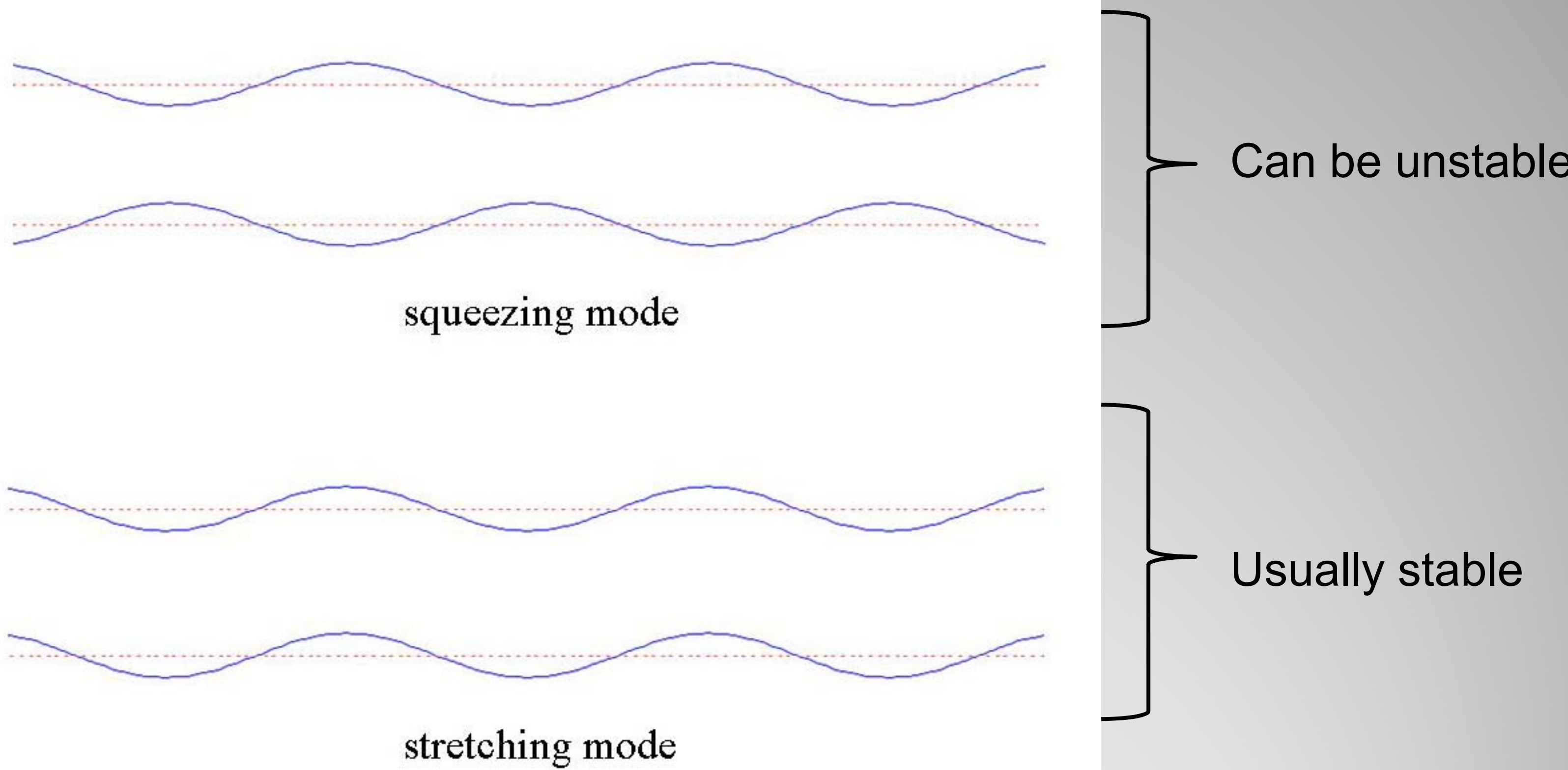
P = conjoining pressure

h = layer thickness

A = Hamaker constant

Conjoining pressure causes instability (Kheshgi & Scriven, 1991)

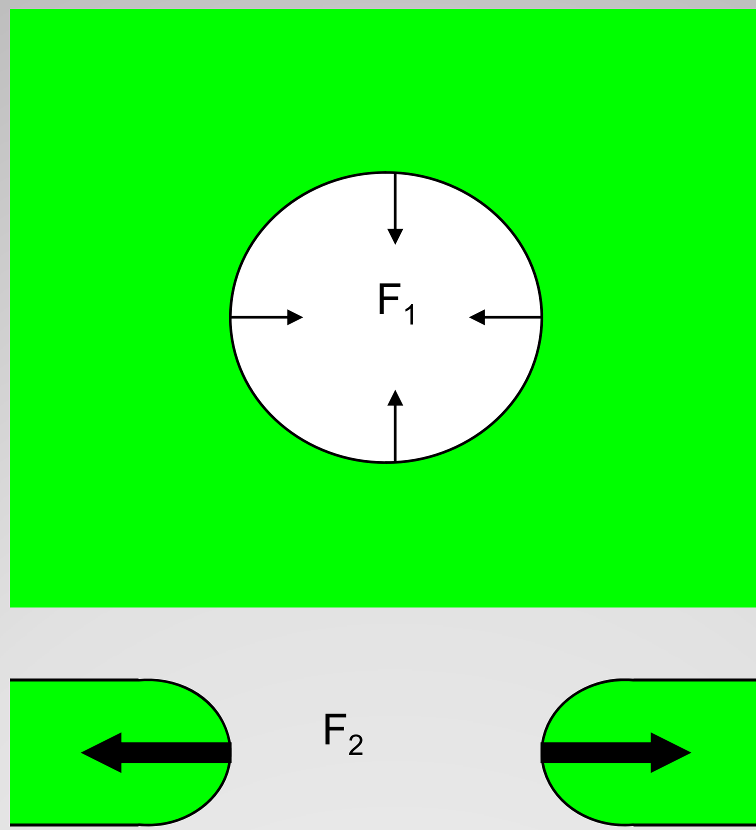
Instabilities in freely standing fluid layers



Interfacial tension is a restoring force and promotes flatness.

Van der Waals force is the destabilizing agent and can lead to rupture.

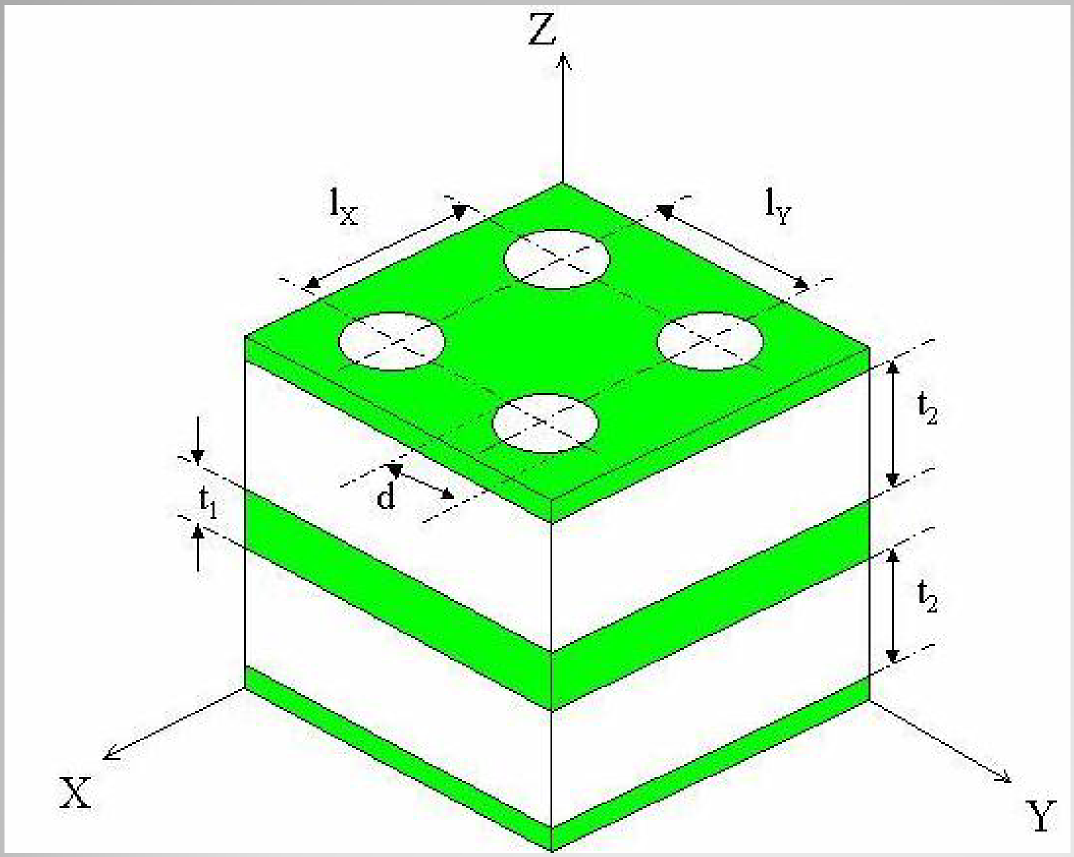
Local modeling by Lattice Boltzmann Method (LBM)



*

A single hole can grow if the hole diameter d is greater than twice the layer thickness h_1. Interfacial force F_2 dominates F_1 under this condition.

Local modeling by Lattice Boltzmann Method (LBM)



3D analog to more familiar dewetting of a surface by a liquid layer

❖ Growth in ruptures of multi-layers occurs in tandem with melt redistribution and morphology changes.

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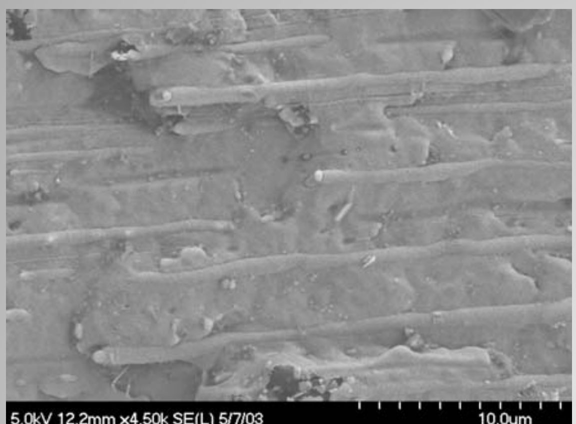
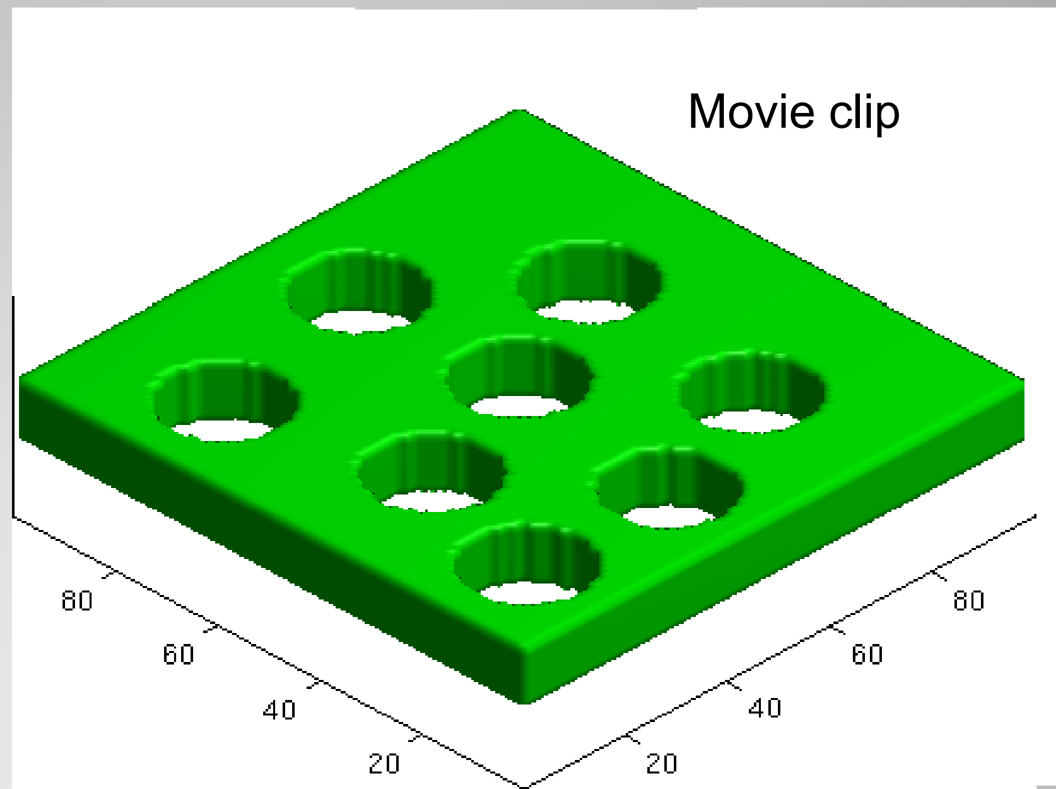
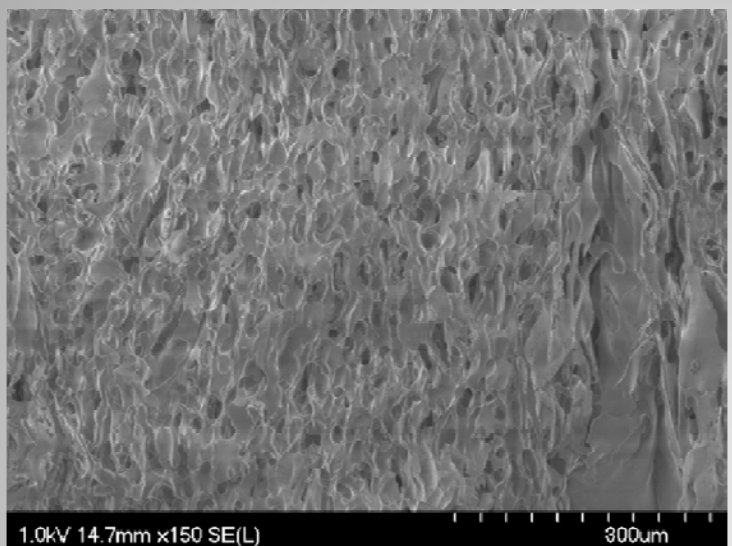
Fiber formation at low minor component compositions (single component continuity)

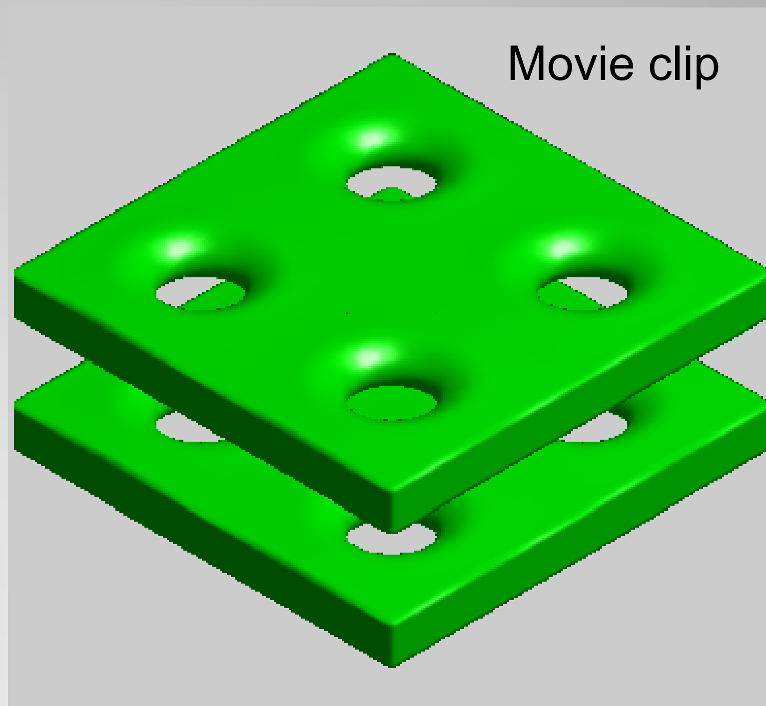


At low compositions, little layer interaction occurs and fibers emerge from rupture growth and coalescence.



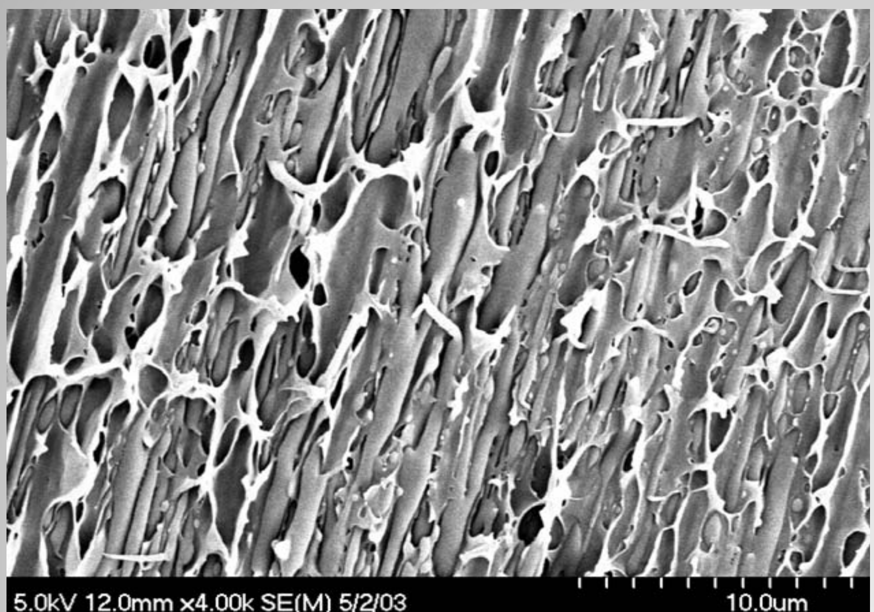
Formation of interpenetrating blend morphology (dual component continuity)

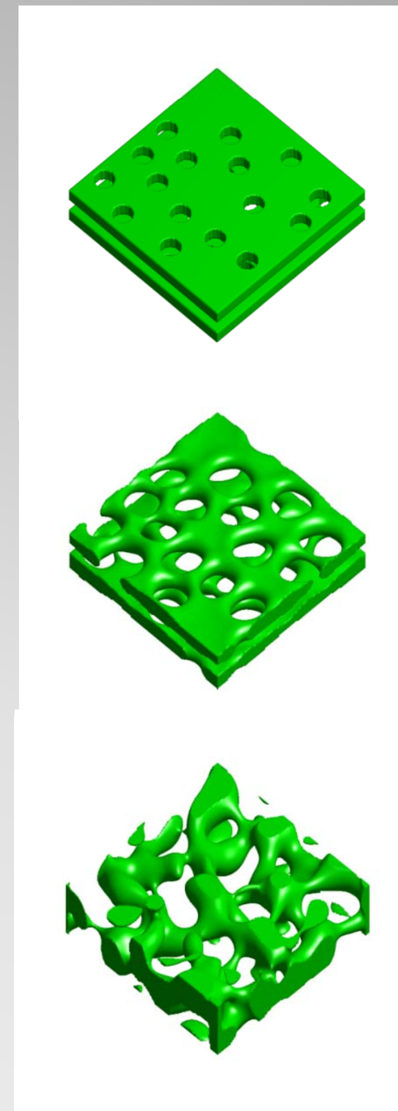




At intermediate compositions, layer interaction occurs as ruptures grow to give sponge-like blend morphologies.

Formation of interpenetrating blend morphology with initial random rupture locations





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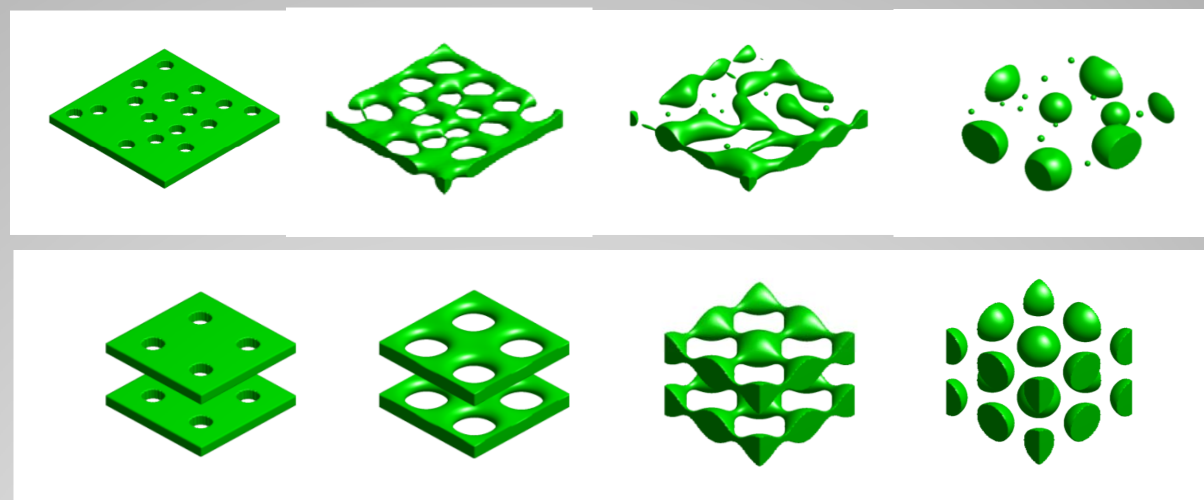
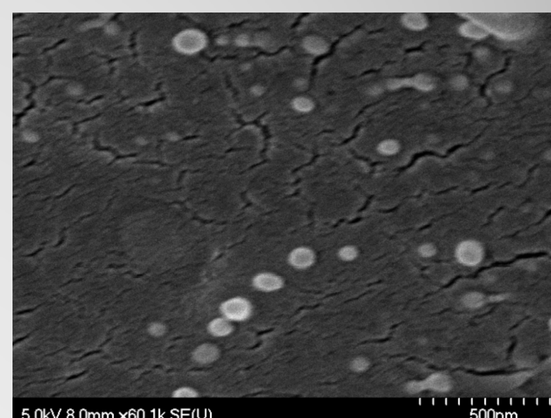
Formation of sieve-like structures and small droplets

Random holes

Organized holes

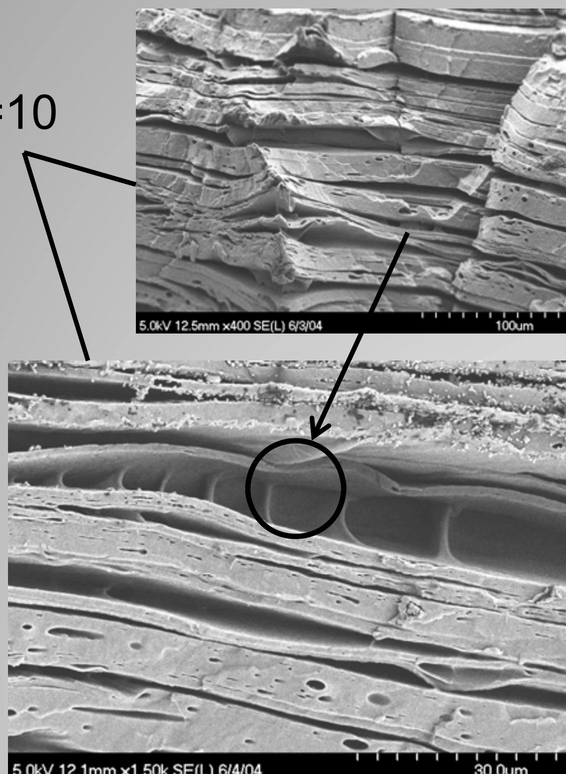


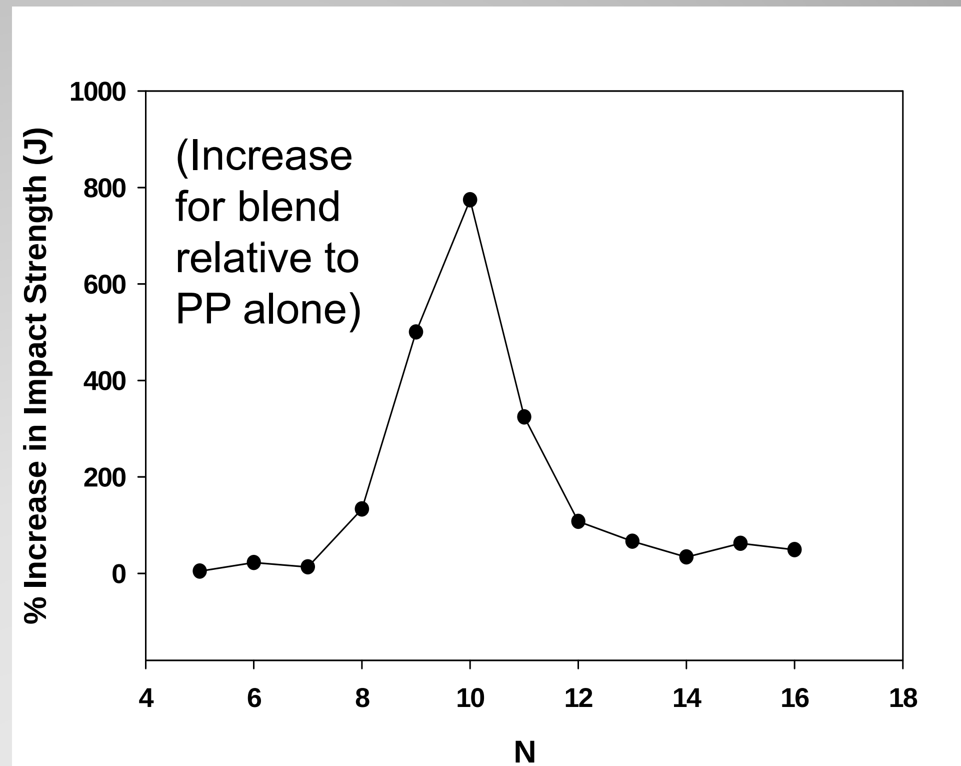
Droplet diameter is related to the parent layer thicknesses so very small diameters can result.



Impact toughness improvements in PP/EPDM 80/20 blends

N=10





Interconnected multilayer morphology is shown subsequent to cryogenic fracture and solvent removal of EPDM. Coalesced layers via ruptures increase toughness.

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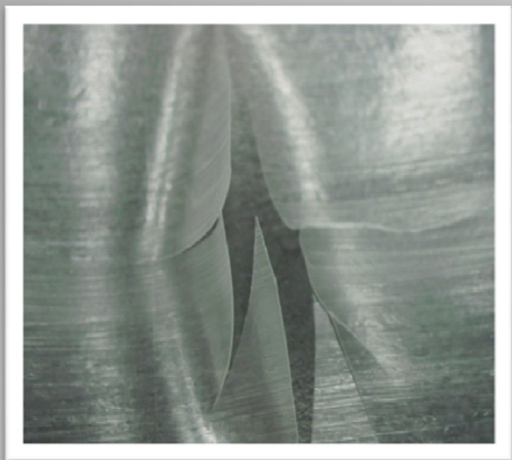
Impact toughness improvements in polypropylene



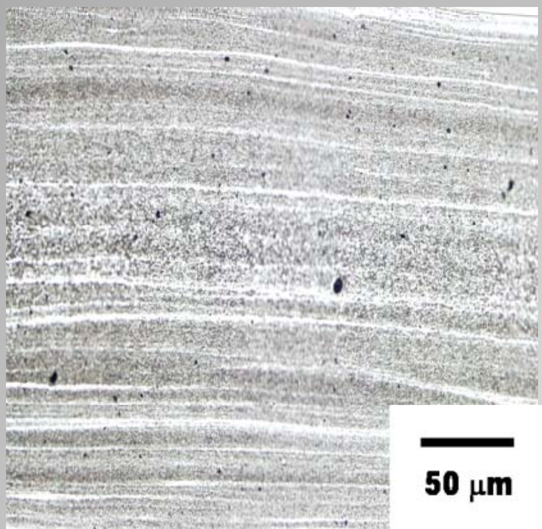
Multilayer, N=8

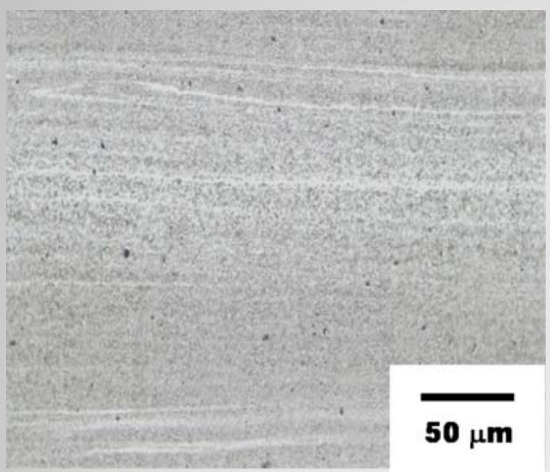
Thin, interconnected layers, N=10

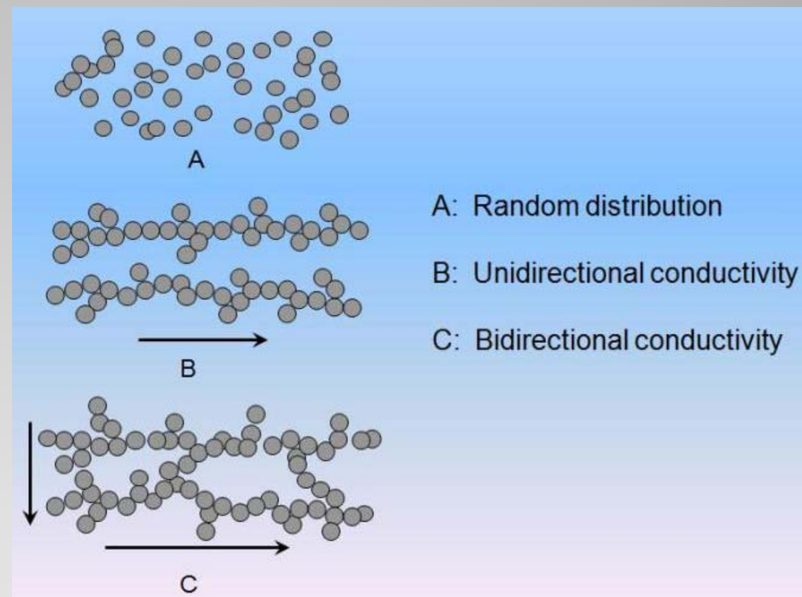
Droplet, N=16

In addition to toughness increases, the impact failure of PP-EPDM films was *qualitatively* changed by blend morphology. Crack propagation was suppressed.

Electrically conducting films with addition of carbon black powder

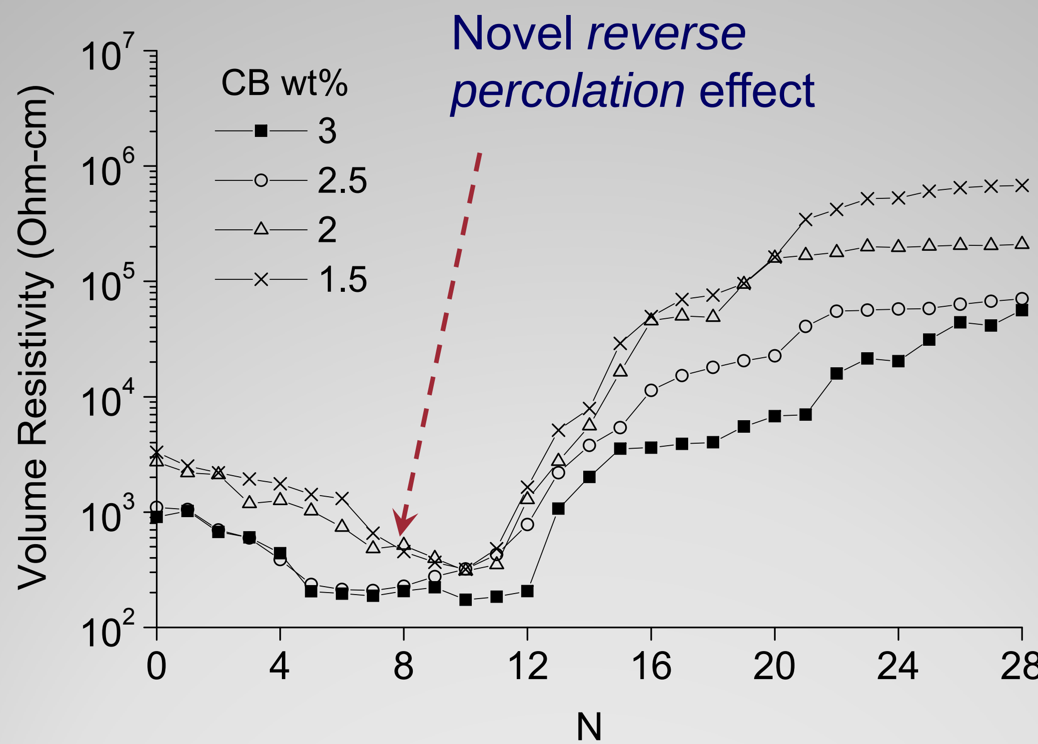






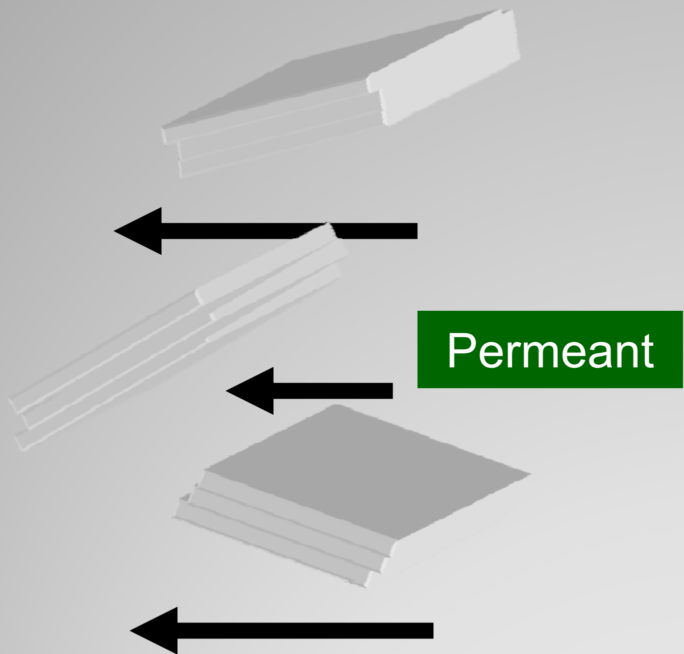
Optical micrographs of translucent sub-micron thick sections taken from extruded films with addition of 3% by weight carbon black. Interconnectivity of carbon black is controllable to impart distinct electrical properties.

Electrically conducting films with addition of carbon black powder

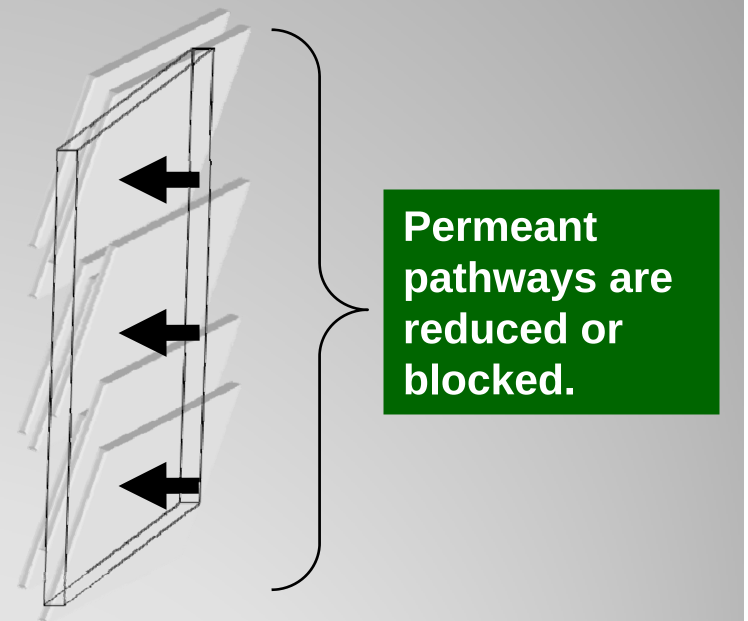


Resistivites pertain to the extrusion (or machine) direction for various overall carbon black compositions. Electrical properties can be selected or *tuned* via on-line process control.

Multilayer nanocomposites with silica platelets



Inefficient structure: unoriented and randomly located platelets obtained by conventional blending.



Effective placement and alignment of platelets in multi-layers.

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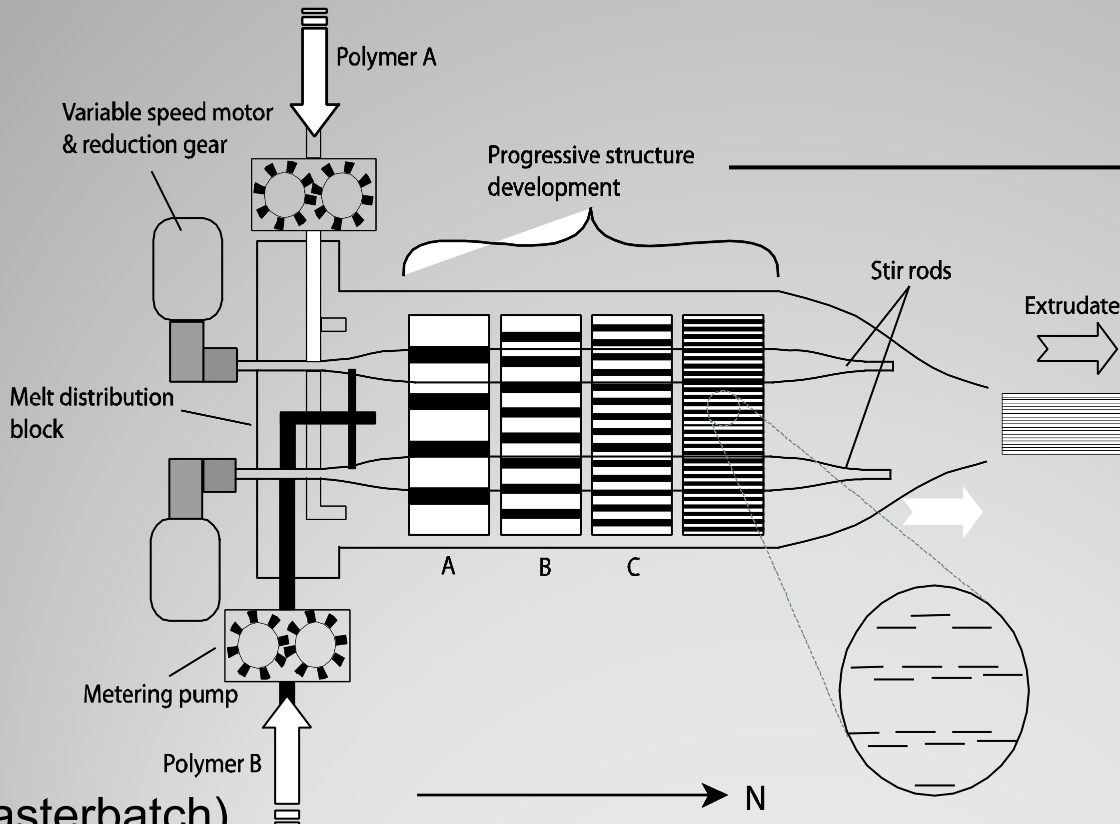
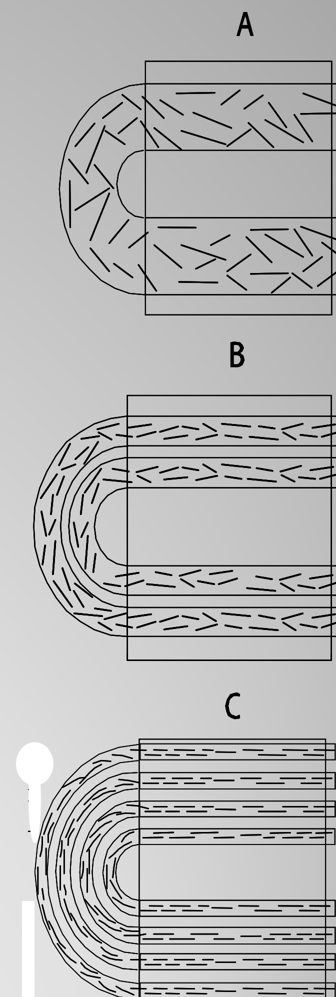
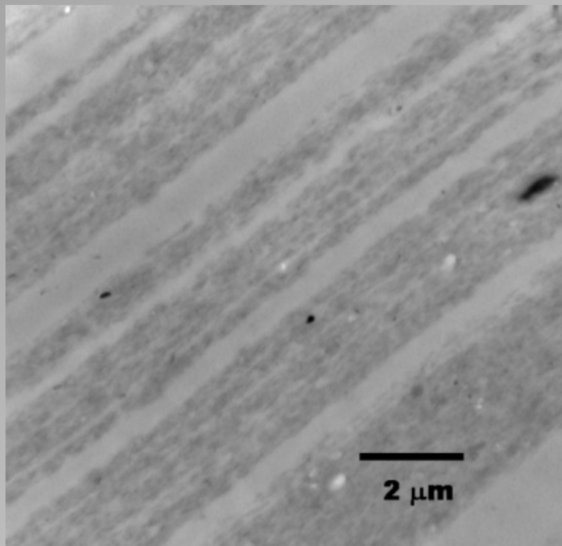
Multilayer nanocomposites with silica platelets

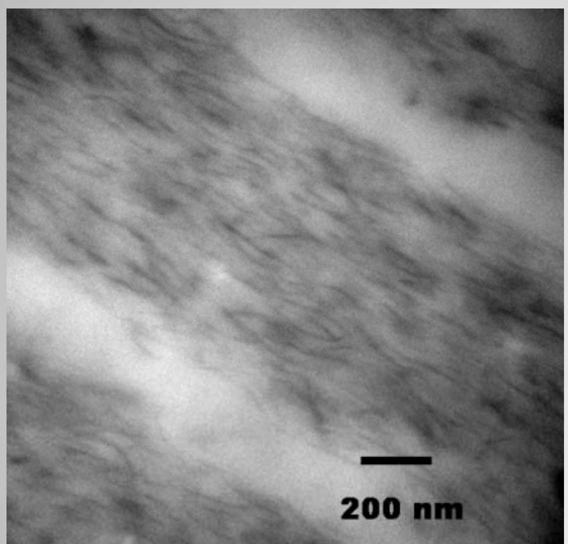




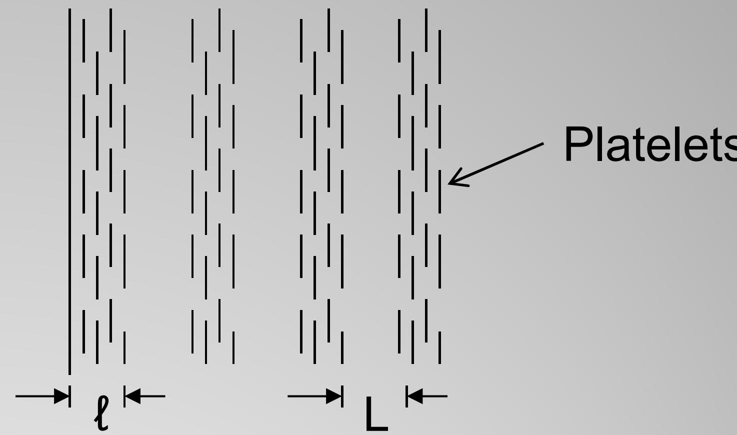
(Masterbatch)

Recursive horseshoe mappings (or baker's transformations), platelets become oriented within the layers that contain them which also decrease in thickness to nano-scales.





Novel structured nanocomposites

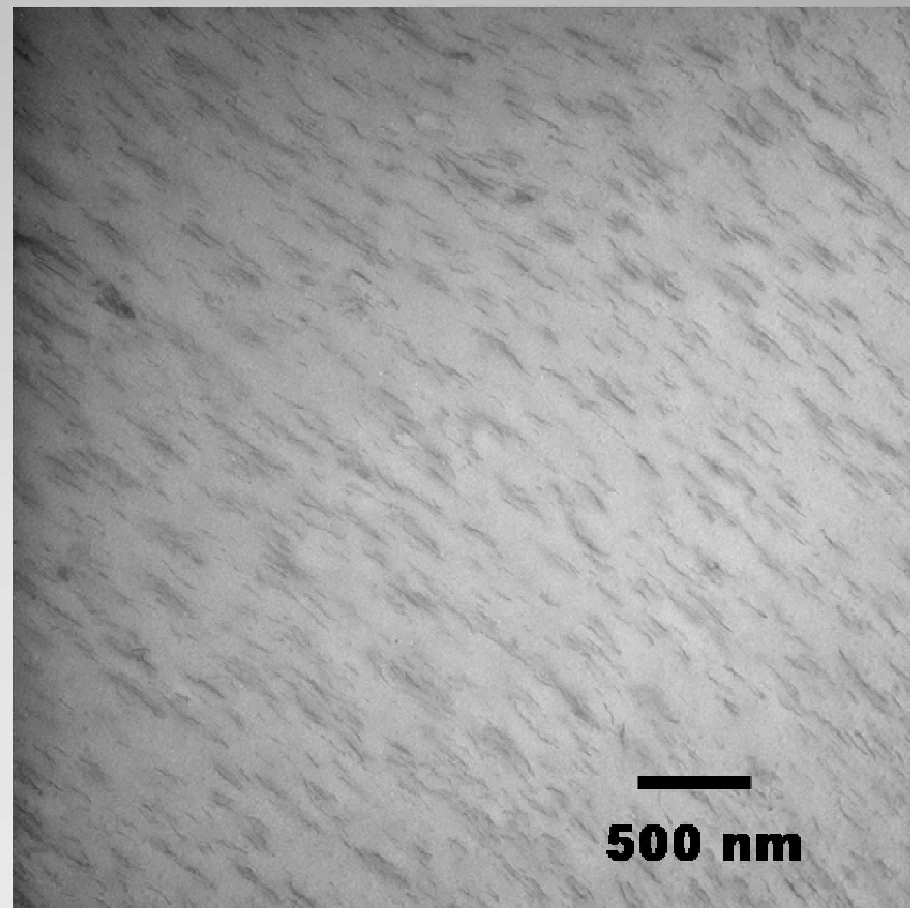


- Oriented platelets
- Platelets localized in numerous layers
- Platelet-rich and virgin polymer layers have nano-scale thicknesses ℓ and L.
- Hierarchical structure
- Structure can be tailored for outcome.

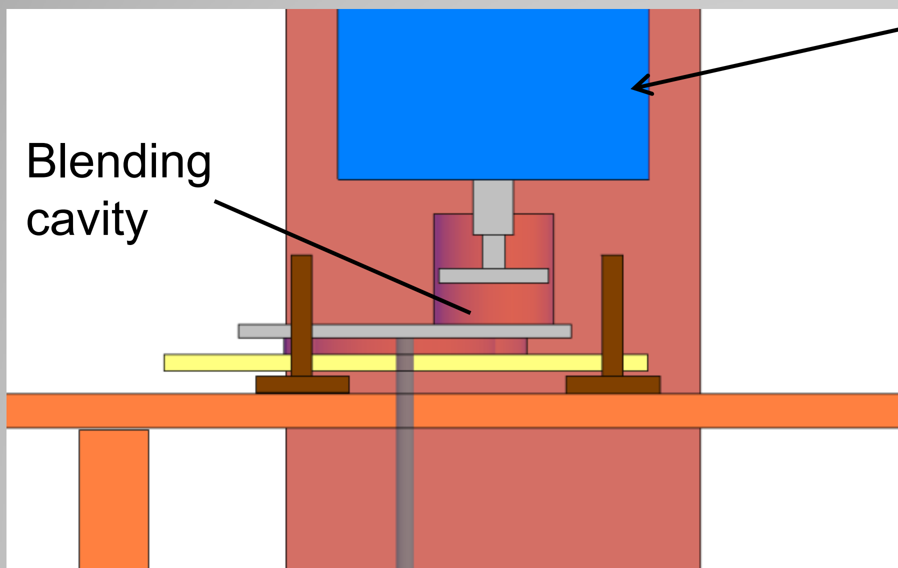
“Ultra-dispersion” of nano-platelets (TEM image)

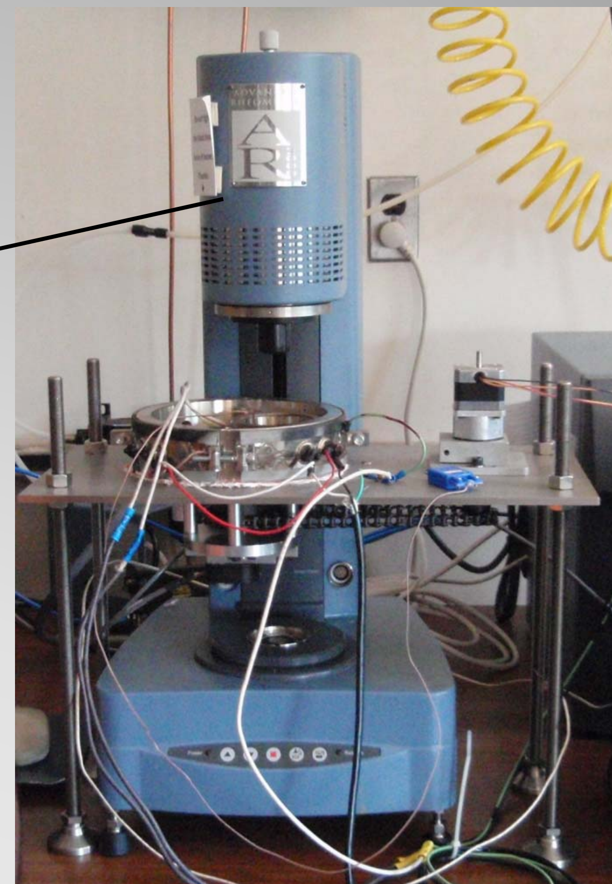
Chaotic advection can be continued until layer thicknesses are thinner than the nano-platelet dimensions. The result is an ultra-dispersion where the nano-platelets are shown obliquely.

Can you improve on this dispersion by moving a nano-platelet?



In situ structuring rheometer
(Chaotic advection applied to rheology)

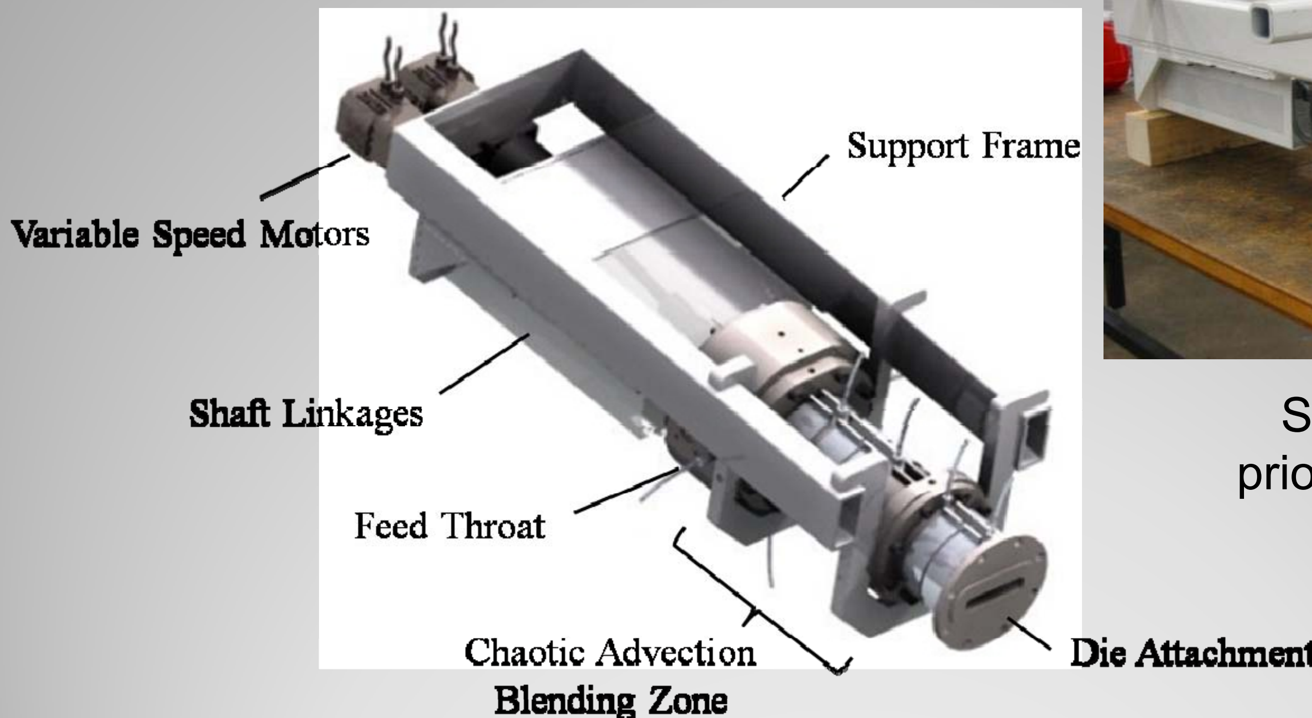


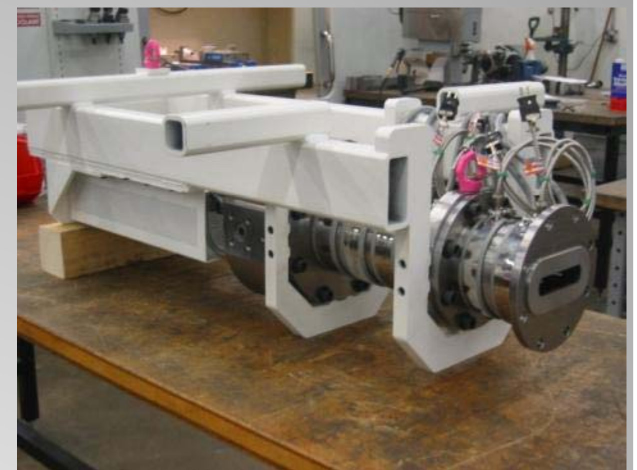


Applications: Rheological properties of polymer blends, nanocomposites, mixtures, biological fluids, percolating networks in melts……..

Industrial smart blenders

(Cast film or sheet, general purpose)





Smart blender
prior to installation

Research has resulted in industrial smart blenders that expand greatly the variety and properties of plastic products producible. Various dies can be attached.

Additional information:

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Suggested areas of further study:

1. Chaotic advection in multicomponent flows with interfacial effects
2. Multiscale (i.e., time and size) models of in situ structure formation
3. Mechanisms for hole *formation* and *interactive* growth in multilayer melts
4. Further clarifications of progressive structure development and morphology transitions
5. Viscoelastic and shear thinning effects on progressive structure development and chaotic advection
6. Morphology changes in extrusion steps
7. Properties of *structured* nanocomposites
8. Utilization as a rheological tool

Thank you!