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13. ABSTRACT *(Maximum 200 words)*

The highlights of this period are centered around the development of polymer nanolayer systems by a novel continuous coextrusion method. Nanolayers ranging in thickness between 5 nm to 500 nm have been manufactured using inexpensive polymeric materials such as polystyrene, polystryene acrylonitrile copolymers, polypropylene, polyethylene, polycarbonate and polymethylmethacrylate. Two and three component systems have been made from various combinations of these polymers.

In particular, the morphology of polypropylene has been drastically changed from a routine spherilitic α-form structure to a discoidal meso-form structure by just decreasing the layer thickness to nano dimensions. High density polyethylene has been totally changed to a "shish-kabab" structure due to the fact that the nano-layer thickness is less than the radius of gyration of the polymer macromolecule. When oriented, this novel crystalline morphology appeared as extended chain fibrillar crystals imbedded in polystyrene acting as the continuous phase in a nanocomposite structure.

Recently, we have started to develope nano-systems with anisotropic electrical and mechanical properties. Also, gradient and vertical layer structures are being considered. In the last few weeks we have actually succeeded in creating a vertical composite with highly anisotropic mechanical properties composed of polystyrene and a styrene-butadiene block copolymer.

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Enclosure 1

Standard Form 298 (Rev. 2-89)
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1. Publications:

S. Nazarenko, A.Hiltner, E. Baer, *Polymer Microlayer Structures with Anisotropic Conductivity*, J. Mater. Sci., **34**, 1461-1470 (1999).

T. Schuman, S. Nazarenko, E.V. Stepanov, S.N. Maganov, A. Hiltner, E. Baer, *Solid State Structure and Melting Behavior of Interdiffused Polyethylene in Microlayers*, Polymer **40**, 7373-7385 (1999).

J. Kerns, A. Hsieh, E. Baer, A. Hiltner, Mechanical Behavior of Polymer Microlayers, in <u>Mechanical Behavior of Polymeric Materials</u> (J. Kahovec, ed.), Macromol. Symp. 147-Wiley-VCH, pp. 15-25 (1999).

D. Jarus, E. Baer, A. Hiltner, Relationship of Hierarchical Structure to Mechanical Properties, in <u>Mechanical Behavior of Polymeric Materials</u> (J. Kahovec, ed.), Macromol. Symp. 147, Wiley-VCH, pp. 37-61 (1999).

S. Nazarenko, M. Dennison, T. Schuman, E.V. Stepanov, E. Baer, A. Hiltner, *Creating Layers of Concentrated Inorganic Particles by Interdiffusion of Polyethylene in Microlayers*, J. Appl. Polym. Sci., **73**, 2877-2885 (1999).

A. Hiltner, E. Baer, J. Kerns, Processing and Properties of Polymer Microlayered Systems, in <u>Structure Development during Polymer Processing</u> (A.M. da Cunha, ed.), Kluwer, The Netherlands (in press)

L. Flandin, E. Baer and A. Hiltner, *Interrelationships between Electrical and Mechanical Properties of a Carbon Black-Filled Ethylene-Octene Elastomer*, Polymer, (in press)

J. Kerns, A. Hsieh, E. Baer, A. Hiltner, *Comparison of Irreversible Deformation and Yielding in Microlayers of PC with PMMA and SAN*, J. Appl. Polym. Sci., (in press)

L. Flandin, A. Chang, S. Nazarenko, E. Baer, A. Hiltner, *Effect of Strain on the Properties of an Ethylene-Octene Elastomer with Conductive Carbon Fillers*, J. Appl. Polym. Sci., (in press)

L Flandin, A. Hiltner, E. Baer, *Interrelationships between Electrical and Mechanical Properties of a Carbon Black-Filled Ethylene-Octene Elastomer*, Polymer (submitted)

Oral Presentations:

New Polymer Microlayer Composites, invited lecture at NATO ASI Conference on Structure Development in Processing for Polymer Property Enhancement, Caminha, Portugal, June 17-28, 1999.

Microlayer Coextrusion Technology, plenary paper presented at SPE ANTEC '99, New York, May 2-9, 1999.

Invited lecturer on "Processing of Polymer Microlayered Systems," NATO-ASI Conference on Structure Development in Processing for Polymer Property Enhancement, Universidade do Minho-Azurem, Guimaraes, Portugal, May 17-28, 1999.

Invited lecturer on "Polymer Microlayer Coextrusion and Composites," XVIII Plastics Seminar, Grande Hotel de Luso, Lisbon, Portugal, May 28-29, 1999.

Invited lecturer on "New Topics in Microlayered Composites," International Paper, Cincinnati, OH, July 13, 1999.

Invited lecturer on "Microlayer Structures with Anisotropic Conductivity," Twenty-Second Asilomar Conference on Polymeric Materials," Pacific Grove, CA, February 14-17, 1999.

2. list of PI's, students, and postdocs supported under the grant

Undergraduate Students
S. Norek, A. Hasan, A. Shah, M. Dennison

Graduate Students
C. Mueller, T. Ebeling, T. Schuman, J.A. Kerns

Postdoctoral Research Associates
S. Nazarenko, E.V. Stepanov, L. Flandin

3. awards and honors from the past year

Michael Dennsion won the best poster prize at the 1999 National Engineers Week for his poster on *Microlayer Gradient Structures with Concentrated Filler Particles*.

4. description of interactions with ARL scientists during past year

   - Alex Hsieh - ballistics
   - Jo Ann Ratto - biodegradation

5. list of significant technology transfer activities with industry or Army labs during past year

6. short summary of most notable accomplishments, breakthroughs, and technology transfer events during the past year under the program

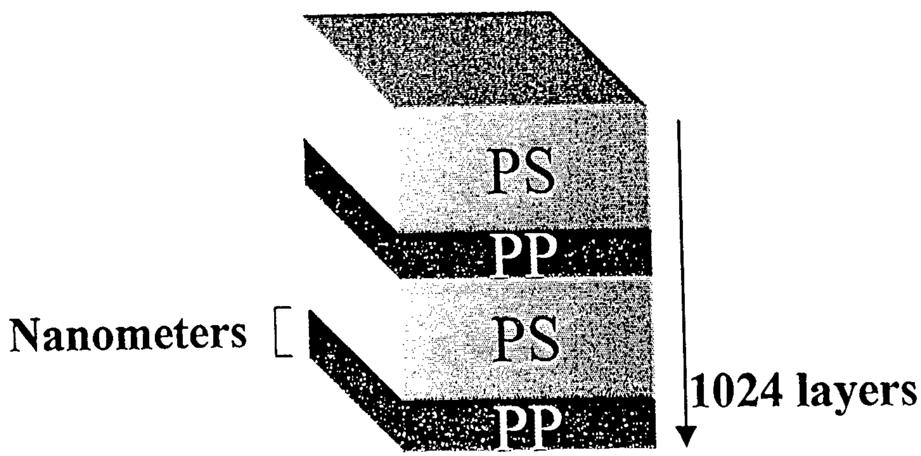
   See attached

7. 1-2 view graphs that highlight recent accomplishments (Powerpoint slides)

   See attached

Novel Nanolayered Films

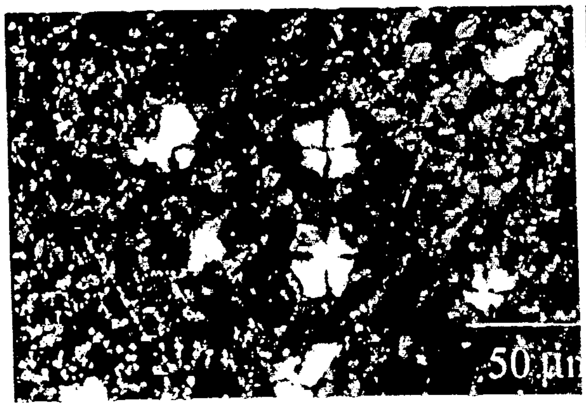
PP/PS Microlayered System

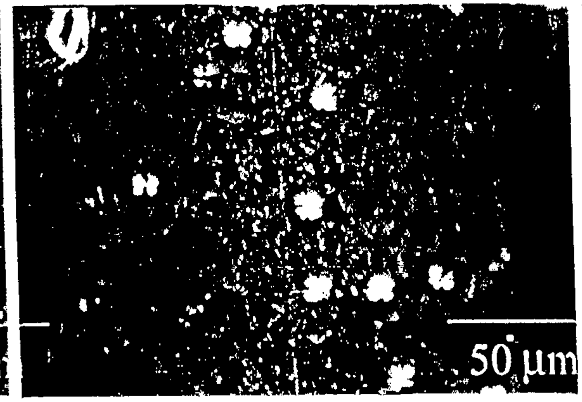


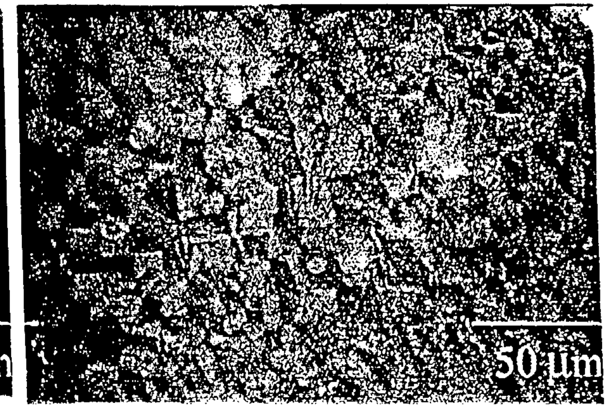
Composition PP/PS	Film Thickness (mils)		
	1	5	10
	Calculated PP Layer Thickness (nm)		
100/0	--	--	--
90/10	50	220	450
80/20	--	200	--
50/50	--	120	--
20/80	9	50	100
10/90	5	30	50

Microlayering is a unique method for achieving films where the layer thickness can be controlled from the micro to the nanoscale. As the film thickness is decreased, limitation on the crystal growth in the third dimension occurs at different hierarchical scales.

	PP/PS 90/10 10 mils	PP/PS 10/90 10 mils	PP/PS 10/90 1 mil





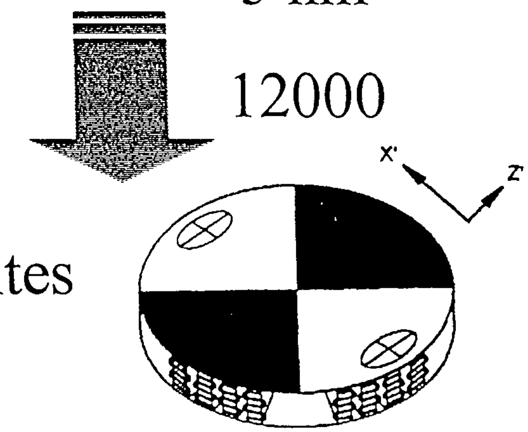


T	450 nm	50 nm	5 nm
D/T	60	640	12000

T* = *Calculated PP Layer Thickness

D* = *Discoid Diameter

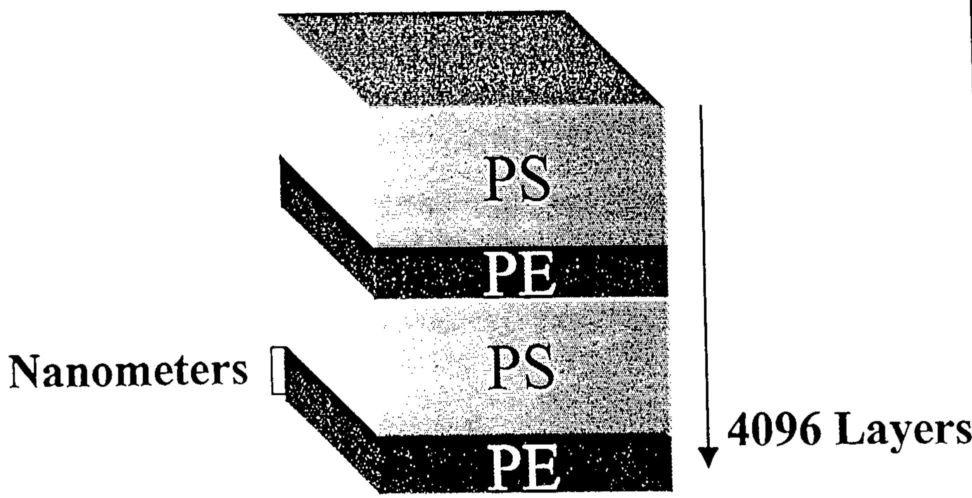
Discoid Spherulites



As PP layer thickness decreases, constraint on the spherulitic level occurs, and two-dimensional spherulites (discoids) are obtained. Orientation of this nanolayered film would decrease PP layer thickness an order of magnitude, causing mixing of the components on the molecular scale.

Novel Molecular Composite

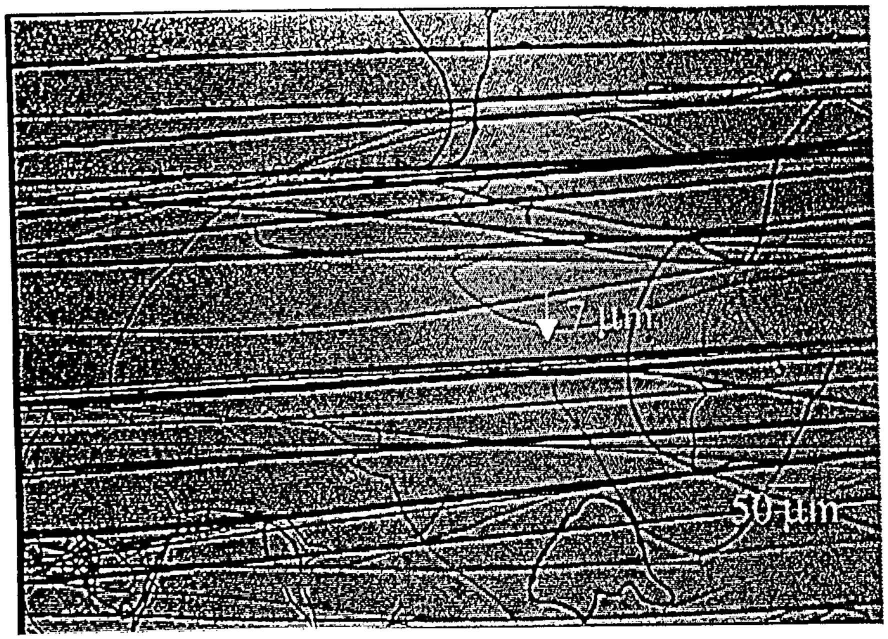
HDPE/PS Microlayered System

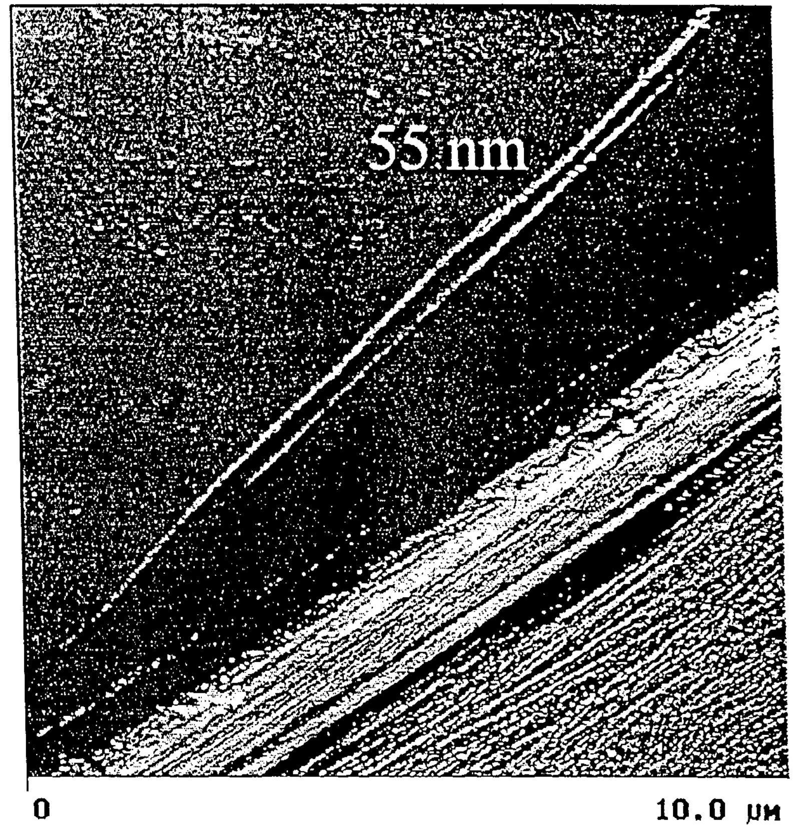


System	Nanolayer 4096 Layers		Microlayer 128 Layers	
Composition HDPE/PS	*Film Thickness (mils)*			
	10	2	10	2
	Calculated HDPE Layer Thickness			
	(nm)		(μm)	
100/0	--	--	--	--
30/70	37	7	1.2	0.20
20/80	25	5	1.30	0.16
10/90	12	3	0.40	0.08
5/95	6	1	0.20	0.04
0/100	--	--	--	--

There is great scientific interest in ultrathin layers, where the layer thickness is decreased to the scale of a few nanometers and is comparable with the radius of gyration of the polymer molecules.

Optical Microscope | *Atomic Force Microscope*

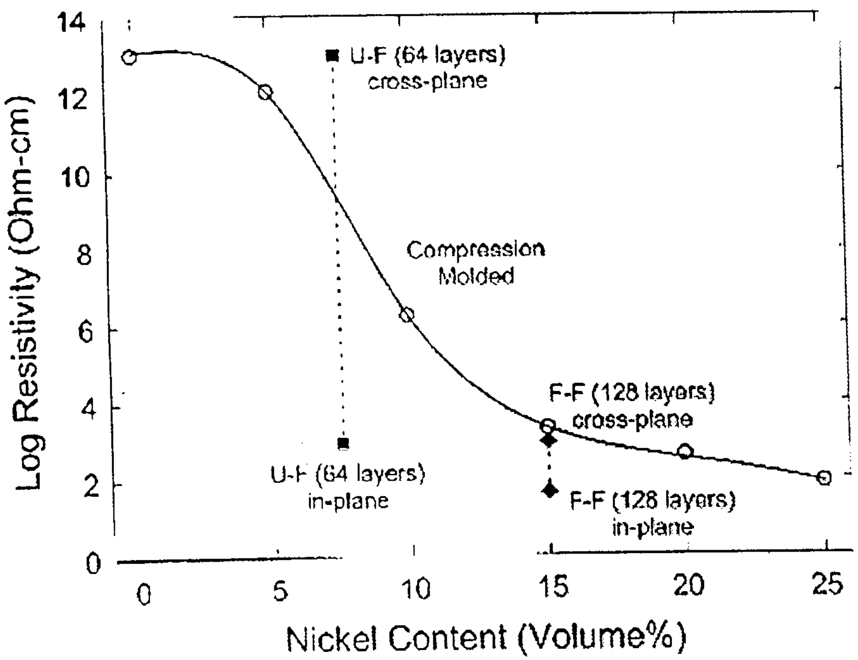




HDPE/PS, 5/95, 4096 Layers, 2 mil thick

This novel crystalline morphology of nanolayers appeared as extended-chain fibrillar crystals. Orientation of such system at high temperature will create a fiber reinforced molecular composite.

Anisotropic Electrical Properties

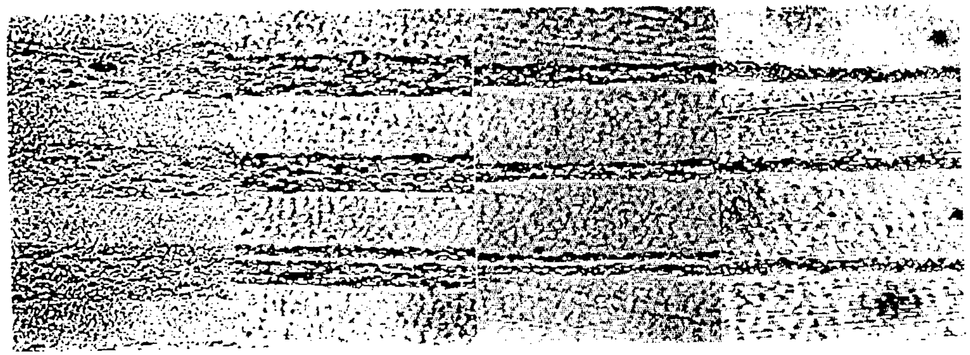


Microlayers having highly anisotropic electrical properties were created

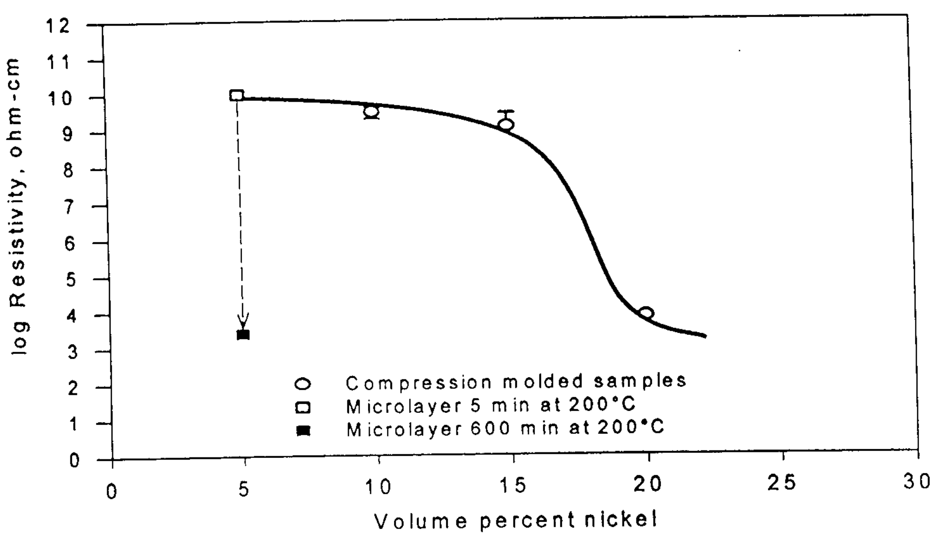
In-plane and cross-plane resistivity of the microlayers differed by ten orders of magnitude

- A non-conductive system of nickel in polyethylene was microlayered using a low amount of filler

- After annealing the samples in the melt, interdiffusion of the layers created a moving boundary, subsequently concentrating the particles to a point above the percolation threshold.



Optical micrographs of filled-unfilled PE microlayers annealed in the melt for 0, 5, 600, 3000, and 10000 minutes

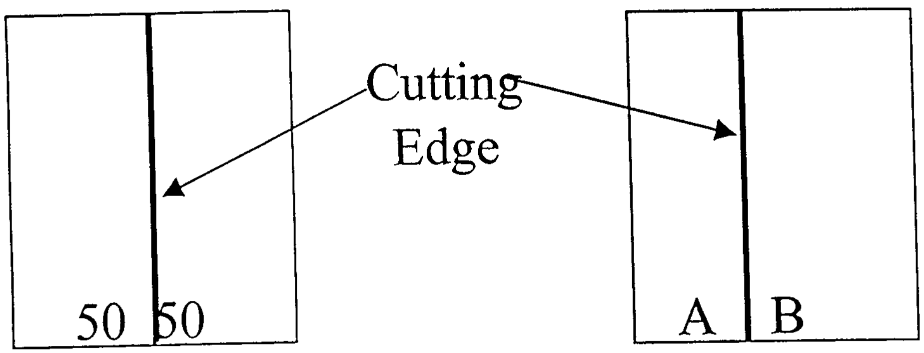


Electrical behavior of unfilled-filled and filled-filled microlayers superimposed on resistivity versus volume fraction for nickel platelets

- These anisotropic conductive systems have application in EMI shielding, electronic switching, solid-state batteries, and ESD protection.
- Concentrating systems can extend to a wide range of filler types, particularly those that exhibit poor processability at high loading.

Gradient Microlayer Structures

Microlayered films that exhibit a gradient in layer thickness can be achieved with new multiplier design



Current multiplier

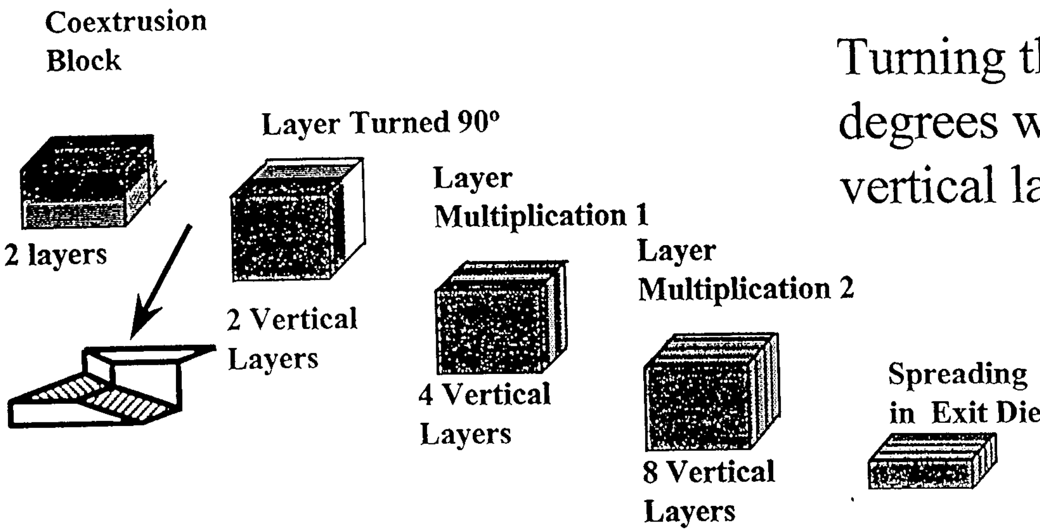
Gradient multiplier
$A \neq B$

This can be accomplished by increasing the B/A ratio in each subsequent multiplier, as illustrated.

With 6 multiplier die elements, layer thicknesses would differ by a factor of 50

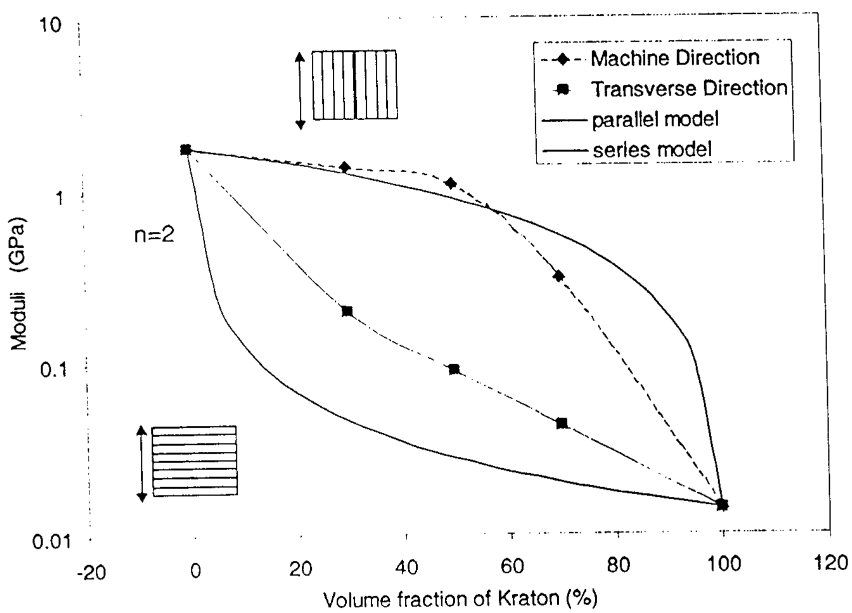
This geometry can be tailored to create films having novel transport properties, or unique optical, electrical, and mechanical properties

Vertical Microlayers



Turning the existing multipliers by 90 degrees will lead to the creation of vertical layers

Decreasing layer thicknesses to the nanoscale may lead to morphologies that emulate lamellar block copolymer systems



This structure can exhibit highly anisotropic mechanical properties, as exemplified in the PS/Kraton 512 layer system shown here.