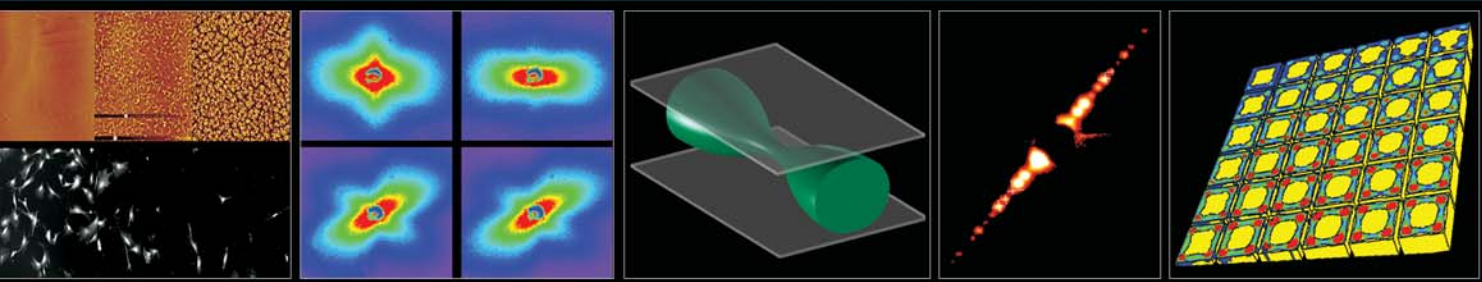


# POLYMERS Division



## MATERIALS SCIENCE AND ENGINEERING LABORATORY

## FY 2002 PROGRAMS AND ACCOMPLISHMENTS

**NIST**

National Institute of  
Standards and Technology

Technology Administration

U.S. Department of  
Commerce

NISTIR 6906

September 2002

## **On the Cover:**

From the front cover and continuing on to the back, the images shown are, respectively: (1) a finite element simulation of interfacial debonding of a combinatorial test library; (2) a synchrotron x-ray scattering pattern of a nanostructured thin film for electronic applications; (3) a lattice Boltzmann simulation of the breakup of a stationary string under simple shear flow in a polymer emulsion between parallel plates; (4) polarized light scattering patterns from multiwalled carbon nanotubes dispersed in a polymer matrix under shear; (5) atomic force (top) and fluorescence microscopy (bottom) images of poly(l-lactic acid) annealed over a temperature range and the cell growth on it after uniform seeding; and (6) a series of Gel Permeation Chromatography (GPC) curves on six polyethylene Standard Reference Material (SRM) fractions. More information about each of these topics can be found within this report.

**National Institute of  
Standards and Technology**  
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**Technology  
Administration**  
Phillip J. Bond  
Undersecretary of  
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**U.S. Department  
of Commerce**  
Donald L. Evans  
Secretary



## MATERIALS SCIENCE AND ENGINEERING LABORATORY

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## FY 2002 PROGRAMS AND ACCOMPLISHMENTS

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# POLYMERS DIVISION

Eric J. Amis, Chief

Bruno M. Fanconi, Deputy

Chad R. Snyder, Deputy

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September 2002

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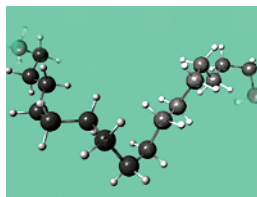
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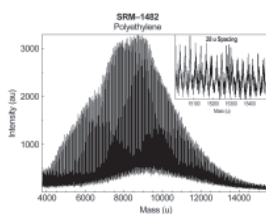
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## Executive Summary



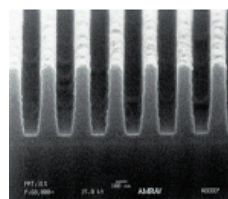
The advent of controlled polymerization, advanced electronics, biomimetic materials, nanostructured systems, and a range of other new avenues for polymeric materials has raised the bar for measurements and standards research. This report of the 2002 activities and accomplishments describes many of the projects designed by the scientists in the Polymers Division at NIST to creatively meet this ongoing challenge. As usual, our research encompasses a range of topics and only a selection can be presented in this summary, and we are also able to discuss only a fraction of the many interactions with complementary teams throughout NIST, with our industrial partners, and with the larger scientific community. I encourage you to consult our website at [www.nist.gov/polymers](http://www.nist.gov/polymers) for more information.



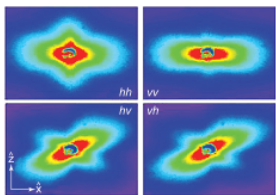
As the “everyman” polymers, polyolefins have seen a resurgence of interest and importance with the development of new catalysts with more precise molecular control. The Polymers Division is pioneering measurements of absolute molecular mass distribution of these polymers through the laser vaporization and ionization methods of mass spectrometry. A mainstay of analysis for organic molecules and biological macromolecules, mass spectrometry is particularly challenging for some common polymers such as polyethylene because of their simple molecular structure. Nevertheless, this year we have produced intact gas phase polyethylene single chains with over six times greater mass than previously reported by any researchers. This is one example of how the Polymers Division provides critical measurement methods, standards, and fundamental concepts to enable polymer-based technologies.



The projects in our Division are selected by evaluating current and future needs of industries through workshops, industry roadmaps, visits to companies and other research organizations, and a variety of other means. In addition, much of our research is performed in collaboration with customers. To further enhance these types of collaboration and to increase the success of technology transfer, a NIST-wide effort centered in the Polymers Division, the NIST Combinatorial Methods Center (NCMC), was formally established in January 2002. The Center provides a portal for demonstrating our cutting edge combinatorial materials research effort. Examples of recent NCMC research efforts include new methods for rapidly quantifying over a range of conditions, the mechanical properties of thin films, adhesion and failure mechanisms, and crystallization kinetics.

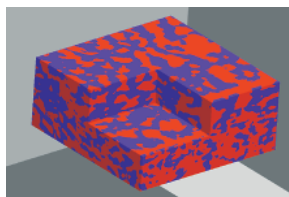


As part of our ongoing assessment of current and future needs, the Polymers Division, and NIST as a whole, have identified nanotechnology and health care as two critical areas for investment. While nanotechnology is not an industry per se, the technology it represents is at the heart of many growing industries. Key to enabling the practical applications of nanotechnology will be the ability to reliably manufacture nanoscale structures. Due to the ever-pressing drive of Moore’s Law, the semiconductor electronics industry is at the forefront of this technology. As size scales shrink, the associated tolerances also shrink. Electronics are rapidly approaching the point at which sub-100 nm structures are needed. Control of the photolithographic process at this size-scale is painfully exquisite with dimensional tolerances on the order of the size of the polymer molecules. Headed by a recent winner of the Presidential Early Career Award for Scientists and Engineers (PECASE) and in collaboration with key industrial partners, our Electronics Materials Group is developing experimental methods needed to characterize chemical transport and materials science phenomena over nanometer length scales. Another project supporting the semiconductor electronics industry has developed a solvent porosimetry technique using x-ray reflectivity to calculate the pore-size distribution in “low-k” nanoporous materials being developed for the next generation of integrated circuits.



Another class of nanostructured materials is the broad range of nanocomposites that have potential uses ranging from materials for wireless communication, to gas barrier materials, to

structural composites. Despite their intriguing potential, there remain several fundamental problems in reaching practical success. One such problem is the dispersion and alignment within the polymer matrix of nanoparticles and nanotubes. In Division projects, work has begun to relate online optical measurements of carbon nanotube composites and dielectric measurements of nanoclay composites with a full suite of characterizations by transmission electron microscopy, x-ray scattering, and small-angle neutron scattering measurements. The goal is to provide predictive measurement tools to relate processing parameters to the microstructure of nanocomposite materials. Our recent success in developing broadband dielectric metrology extending into the GHz region complements this work by allowing similar quantification in composites formed with ferroelectric ceramics.



For over 70 years, NIST has had a successful collaboration with the American Dental Association (ADA). Today, our efforts in dental materials are focused on determining how monomer structure,

composition, and initiator affect the ultimate dental composite properties. At the same time, we are vigorously extending this work, more broadly, to address critical issues at the interface of materials science with biology. We are using our expertise in combinatorial methods for rapid quantification of cell interactions with synthetic biomaterials. Complementing this work, we are developing *in vitro* tests for cell infiltration, mechanical properties, and inflammatory response of polymer scaffolds for tissue engineering. Successful tests of this sort would lower R&D costs by reducing the need for *in vivo* animal model tests. To characterize the response of cell attachment and proliferation, we are developing visualization by multimodal microscopies and optical tomography. Currently, we have demonstrated a combination of three hybrid techniques based on optical coherence tomography for imaging of fluorescent markers as well as structure within tissue scaffold materials.

In 2002, the Polymers Division has continued to extend its work into new areas and strengthen projects within our core programs. From health care to manufacturing, we see many challenges for polymer technology. The creativity of our researchers is assuring that our research remains at the cutting edge of polymer science, and our pervasive commitment to NIST's mission guides our choices from among the many exciting opportunities for advances in soft materials research.

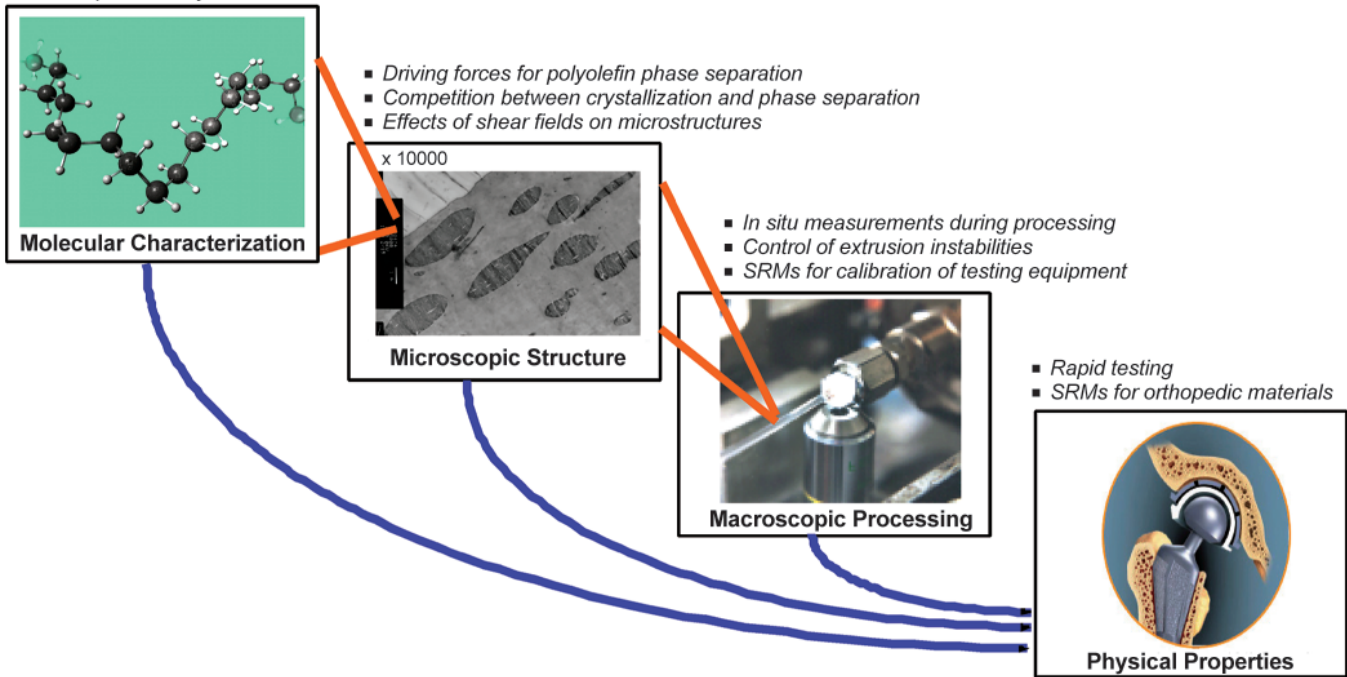
As always, I welcome your comments on our programs.

**Eric J. Amis**  
*Chief, Polymers Division*



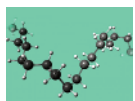
# Polyolefins: Serving the Largest Market

- Standard Reference Materials (SRMs) for calibration of Gel Permeation Chromatography (GPC)
- Mass Spectrometry for absolute mass distribution and molecular structure



*Polyolefins, primarily polyethylene and polypropylene, comprise the largest share of the U.S. market for polymers. Demand for the newer metallocene polyolefins is expected to grow 20 percent per year through 2006. The Polymers Division develops a variety of measurement tools and concepts to meet the broad needs of this diverse industry. Below, the program is broken down into four interrelated components: molecular characterization, microscopic structure, processing, and physical properties. Each component addresses the needs of different industrial segments, but together they provide a backbone for continued growth. While each component has focused on polyolefins, there is a broader applicability of the research.*

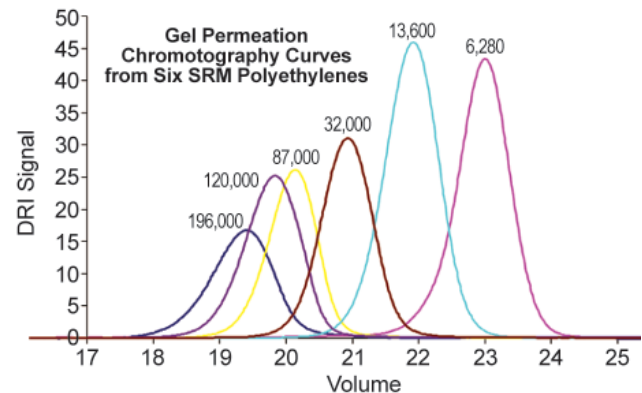
Materials Science and Engineering Laboratory research and services in molecular characterization provide industry with the tools to properly ascertain molecular mass and distribution. Calibration of instruments with National Institute of Standards and Technology standard materials allows suppliers and processors to trade with confidence. Research into next generation calibration techniques ensures that U.S. industry will maintain its competitiveness as increasingly stringent demands are placed upon materials producers.



## Molecular Characterization

The increasing number of distinct polyolefin molecules that have entered the marketplace, and the larger number that can now be synthesized in the laboratory, drive the need for characterization techniques; in particular with respect to molecular mass and distribution. These quantities determine the processability as well as the final properties of the material.

## SRMs for Molecular Characterization

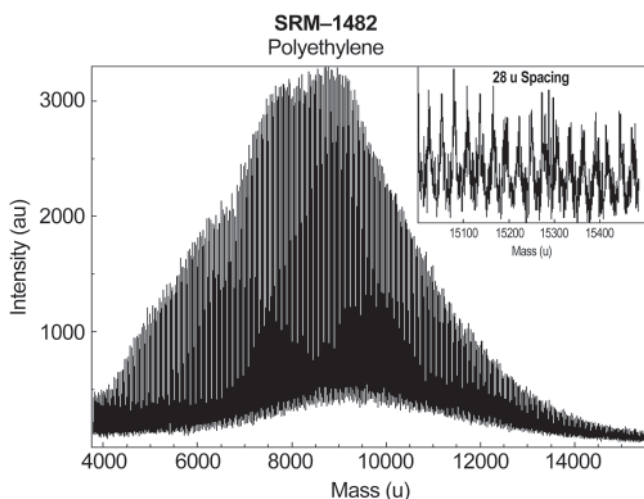


**Figure 1:** Six narrow polyethylene fractions, with the molecular mass moments obtained by absolute methods, are used for calibration of instrumentation and for research. Plotted is the differential refractive index (DRI) versus elution volume in mL.

### Mass Spectrometry of Polyethylene

Polyethylene is not amenable to analysis by the usual mass spectrometric methods owing to the lack of chemical functionality to yield intact macromolecular ions.

In the last year, the polyolefin mass spectrometry team produced intact, gas-phase polyethylene single chains more than six times greater in mass than previously reported by any research group. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) and the covalent cationization method, developed last year in the Polymers Division, were each optimized by a multidisciplinary team of Division scientists. A palette of spectroscopic techniques was used to find the optimal conditions for the necessary conversion of polyethylene into its ionizable phosphonium salt.



**Figure 2:** Mass spectrum of SRM 1482 obtained by the covalent cationization method. The insert shows details of the spectrum above 15,000 g/mol showing that the technique sees higher molecular mass species but not in the correct proportion. Plotted is signal intensity in arbitrary units (au) versus mass in u.

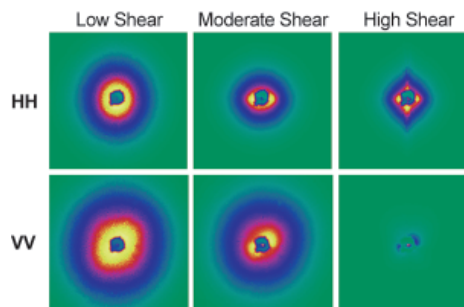
The molecular mass moments determined from mass spectrometry are about two-thirds as large as those found classically. This discrepancy may be due, in part, to the highly crystalline nature of the polyethylenes examined that may reject the MALDI matrix during target preparation. In order to prevent this occurrence, a heated sample stage will be fitted to a TOF mass spectrometer allowing experiments to be performed above the melting temperature of polyethylene. In addition, experiments on the covalent cationization of atactic polystyrene are being undertaken in order to rule out effects solely derived from the ionization process. This project enjoys keen interest from industrial producers who have offered to synthesize specialized materials to further the Division's work.



### Microscopic Structure

Complex microscopic structures due to crystallization, phase separation, and particulate dispersion directly determine physical properties such as permeability, impact strength, and toughness. The various microstructures are developed during processing operations and reflect the molecular characteristics of the polyolefin such as monomer regularity and chain branching.

During the past year, extensive experimental work has been carried out to understand the effect of blending and thermal history on structure development in polyolefin blends. This represents the first comprehensive investigation of blends that exhibits both liquid phase separation and crystallization. Among many interesting findings, we mention just two. First, an abnormally large effect of co-crystallization in this blend, which is not expected if truly random copolymerization, is assumed. Second, the effect of simple shear flow on crystal suspensions in polyolefin blends has been investigated using light scattering (see figure below) and microscopy. The rich complexity of structure that we observed demonstrates the potential for directed control of microstructure through thermal and shear history.



**Figure 3:** Structural information regarding polymer blends under shear flow is obtained via in situ light scattering, where HH indicates horizontal incident and scattered light polarization, and VV is vertical light polarization.

### Influence of Monomer Structure on Polymer Blend

Many commercially important polymer materials are "alloys" of polymers having different monomer structures. Flory-Huggins theory has provided the main theoretical framework for describing the miscibility, phase separation and scattering properties of polymer blends, but this theory completely neglects the dissimilarity of monomer structure. This fundamental issue was taken up in collaboration with the University of Chicago. A generalization of the Flory-Huggins theory, accounting for monomer structure for high molecular weight (incompressible) blends, indicates that monomer structure has profound effects on blend properties and miscibility. We discovered a new classification scheme, featuring four distinct classes of blends. A re-analysis of earlier experimental studies from the Polymers Division provides strong evidence for this new theoretical framework.



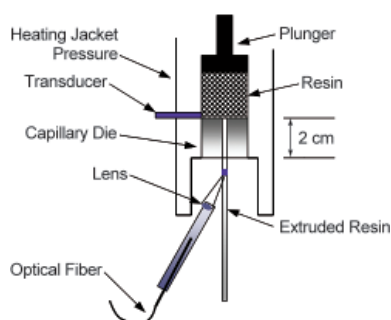
## Macroscopic Processing

One primary reason for the size of the polyolefin market is that numerous processing techniques have been developed which provide the bridge between the raw polymer and the final product. Processing considerations force strong constraints upon new polymer development, for example, frequently a new polymer molecule or formulation must be processable with existing equipment in order to succeed in the market. We frequently work closely with the polyolefin industry on well-focused topics or ensure the commercial relevance of our work.

One frequent concern in the processing of polyethylene is its susceptibility to “sharkskin melt fracture” during extrusion. We have utilized and developed instrumentation to conduct precise measurements of the cause and location of this processing defect. Current work includes the construction of a Total Internal Reflection Coating Instrument, which will be able to quantitate the buildup of fluoropolymer additives, which is one strategy to eliminate sharkskin.

A second critical issue in polyolefin processing is the shear induced temperature excursions which can significantly alter the viscosity and hence the processing. Previously, we have developed fluorescent-based techniques to conduct *in situ* measurements of polymer temperature during extrusion. Recently, we have utilized this methodology to carry out simultaneous measurements of polyethylene rheology and temperature (see Figure 4). We find that during a standard ASTM test method, the resin temperature can increase uncontrollably by 20°C, meaning that great care must be taken in the application of the generated data.

A third area concerns molecular orientation during polypropylene film production. Using fluorescent probes that can orient with the extensional flow, we make fiber optic-based sensors which determine the anisotropy of the material.



**Figure 4:** Instrumentation takes simultaneous measurements of polyethylene rheology and temperature.

## SRMs for Processing

Virtually all polyolefins are specified by their melt flow index (MFI). NIST produces melt flow rate standards that are used for checking an ASTM method (ASTM D1238) commonly used to determine processability of polyethylenes.



## Physical Properties

Physical properties are a result of molecular structure, microstructure and processing history. Here we describe two activities intended to improve the final properties.

### Flammability of Polypropylene-Nanotube Composites

There is much current interest in the enhancement of physical properties of polymeric materials by incorporation of nano-scale additives, such as carbon nanotubes and clay. In conjunction with the Fire Research Division, we have recently shown that carbon nanotubes can significantly reduce the heat release rate of polypropylene under controlled burning conditions. This work was carried out with multi-walled nanotubes that were well dispersed at a 1% volume fraction, *without* the addition of compatibilizers or organic treatments of the nanotubes. Preliminary measurements indicate that the fire suppression effectiveness is better than achieved for clay filler nanocomposites at much higher loadings (order 10% to 20% volume fraction), where surfactant is required for effective clay dispersal. The rapidly decreasing cost of the multi-walled carbon nanotubes and the advantages of these composites for recycling make this approach to fire suppression potentially attractive for commercial development in the future. Fire suppression in polyolefin materials, in particular, is a problem of crucial importance to society because of the widespread use of these materials and the pollution associated with existing fire retardant agents.

### SRMs for Orthopedic Implants

Concerns about long-term durability of polyethylene hip implants have created a need for a standard material to test the properties of implant materials. In response, the first reference biomaterial, an orthopedic grade ultrahigh molecular weight polyethylene, UHMWPE, was issued for use in development of improved test methods for wear and as a benchmark for development of improved materials. Properties reported are the Tensile Young's Modulus, Yield Strength, Ultimate Strength, and Elongation to Failure. In anticipation of continuing need for reference material UHMWPE for radiation studies, NIST issues orthopedic grade UHMWPE cubes for radiation cross-linking tests and analysis.

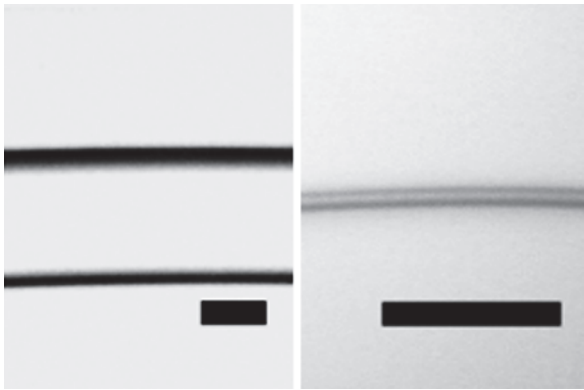
### For More Information on this Topic

*Molecular Characterization:* B. Fanconi, C. Guttman, W. Wallace; *Microscopic Structure:* J. Douglas, C. Han, H. Wang; *Macroscopic Processing:* A. Bur, K. Migler; *Physical Properties:* J. Douglas, J. Tesk

## Micro-Confined Blends

*Microscale processing is an emerging technology with unique challenges and applications in polymer processing and microfluidics industries, but the physics of processing emulsions when the drop size is comparable to a sample dimension is poorly understood. We are developing predictive models as we measure the effect of confinement and flow on the distribution and morphology of one component in another.*

Fluid strings, which can be observed during typical polymer processing operations, develop prominence in confined systems (Figure 1). The formation and stability of strings is being understood through unique observations of micro-confined polymer blends.

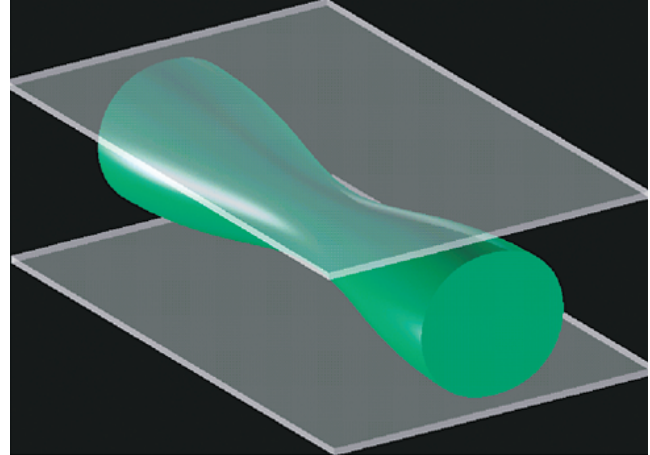


**Figure 1:** Strings in a flowing emulsion: a larger confinement stabilized string is shown at left, and a smaller string that is stabilized by shear alone is shown at right. The scale bars represent the gap spacing between the flow cell boundaries, 36  $\mu\text{m}$  and 100  $\mu\text{m}$ , respectively. After stopping shear, the string at right breaks on timescales on the order of 10 s, whereas breakup of the confinement stabilized string requires timescales on the order of 1000 s.

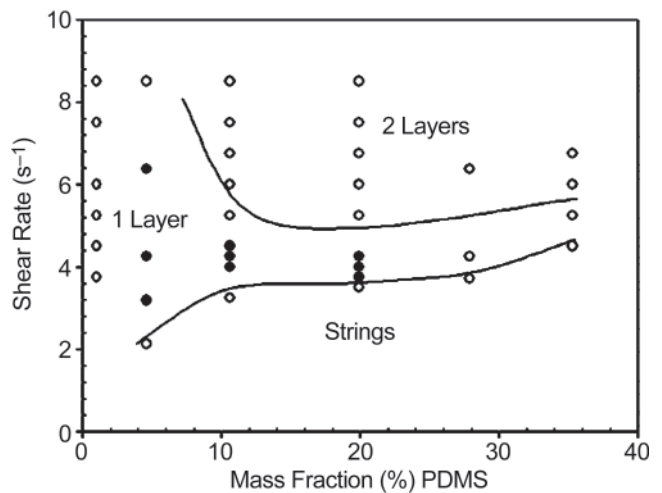
Their stability arises from the effects of shear and confinement. We are exploring the stability of bulk, unconfined strings, as we directly test a recent theory that predicts a new regime of processing conditions wherein strings are stable. Confinement greatly promotes the stability of strings, because the relaxation and breakup rate is suppressed several fold due to hydrodynamic interactions between the string and the wall (Figure 2).

In addition, we are also making direct observations of the mechanism of breakup of bulk strings (classical Rayleigh–Tomotika instability and end pinching) in simple shear flow. Direct comparisons will be made between our experimental data and predictions of hydrodynamic theories on quantities such as the time taken to break up by a string and the size of the final

droplets produced. Direct observation of this phenomenon in simple shear flow has not been reported thus far.

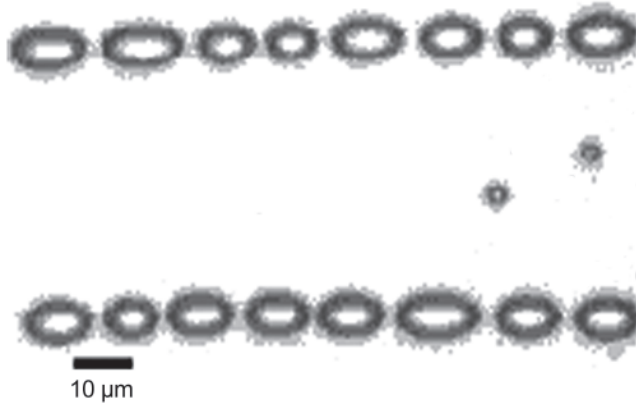


**Figure 2:** Lattice Boltzmann simulation of the breakup of a stationary string confined between parallel plates. Simulation results agree in detail with experimental observations of the string shape and breakup rate. Notice the ellipsoidal cross section of the string.



**Figure 3:** Morphology diagram describing microstructure in confined PDMS/PIB (polydimethylsiloxane/polyisobutylene) emulsions in the parameter space of mass fraction and shear rate, for a uniform gap-width (36  $\mu\text{m}$ ) and a fixed viscosity ratio ( $\lambda = 1$ ). Points denote shear rates where experimental data were obtained, and smooth curves are guides to the eye drawn by the authors to demarcate regions of different microstructure. Shaded points denote experimental observation of ordered pearl-necklace chains of droplets.

In confined blends, the formation of strings is facilitated by migration of drops away from the walls, which leads to enhanced concentration and coalescence



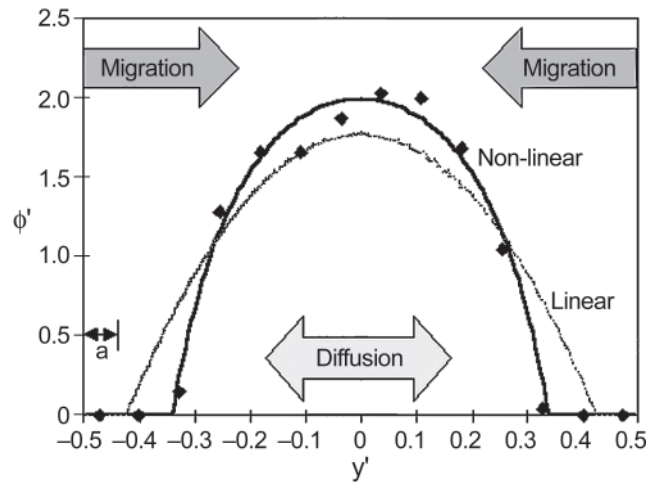
**Figure 4:** Pearl necklace arrangement of PDMS drops in a confined 5% mass fraction PDMS/PIB emulsion flowing in the horizontal direction at a shear rate of  $4.25 \text{ s}^{-1}$ , viewed normal to the confining planes, which are spaced  $36 \mu\text{m}$  apart.

of drops in the center of the flow channel. When coalescence is inhibited either by increasing the flow rate or by decreasing the total concentration of drops, interesting new arrangements of drops are discovered (Figure 3). At low drop concentration, pearl necklace structures form (Figure 4). At higher shear rates, the drops arrange into two layers that slide by one another. Although the drop migration effect pushes drops toward the center plane between the confining boundaries, collisions between drops push them apart so that separate layers are maintained.

As the drops become smaller at still higher rates due to breakup, collisions become more numerous and random, inducing random diffusive motion of the droplets transverse to the flow. The spatial distribution of drops under such conditions results from the interplay of this diffusive motion and migration away from the walls (Figure 5). By integrating the non-linear convective-diffusion drop-transport equation, an analytical expression is obtained for the steady state droplet concentration. The degree to which the drops are concentrated to the center depends on the dimensionless parameter  $Pe$ . At steady state, we derive the following volume fraction profile:

$$\phi'(y') = \phi_c' + Pe \left( 1 - \frac{y'^2}{2} - \frac{1}{1-4y'^2} \right)$$

$Pe = Ca (a/h) (4\alpha / (f_{gy} f\phi_0))$ , where  $Ca$  is the capillary number,  $a$  is the average drop radius,  $h$  is the spacing between plates,  $\alpha$  is a function of viscosity ratio,  $f_{gy}$  is the dimensionless diffusivity,  $y$  is a dimensionless position, and  $\phi_0$  is the nominal volume fraction of dispersed phase (Figure 5).



**Figure 5:** Dispersed phase concentration as a function of dimensionless position across the gap in which the emulsion flows, shown here for  $Pe = 2.4$ . Results of theory (curve) and experiment (symbols) are in good agreement. Near the walls, the emulsion is denuded of drops, having important implications for materials properties, including the surface finish of extruded polymer materials. A recently published linearized theory (gray curve) is not nearly as accurate.

As implied above, interfacial properties and coalescence phenomena have a large influence over the morphology that develops in microscale processing. Coalescence rates are measured through observation of the evolution of the drop size distribution following a step down in shear rate. Governing dimensionless parameters and the effect of associated material parameters are determined. In experiments involving weakly adsorbed surfactant, we find that, at small capillary number, the coalescence rate is limited by diffusion-limited sorption, and at high capillary number, when collision causes slight drop deformation, coalescence is arrested by drop interface immobilization.

These measurements and observations demonstrate that a remarkable variety of phenomena occur in micro-confined blends. We plan to develop new tools, based in part on these phenomena, to investigate interfacial properties. These phenomena are also relevant for micro- and nano-fabrication and for microreactors, because multiphase flow can also be used for separation and encapsulation of desired products. The development of such reactors requires the aid of polymer materials science, which will yield optimal fluids, substrates, surface treatment, and active devices.

### For More Information on this Topic

S.D. Hudson, K.B. Migler, J. Pathak, J.F. Douglas, J.G. Hagedorn (ITL); N. Martyts (BFRL)

## Pore Size Distributions in Low-k Dielectric Thin Films from X-ray Porosimetry

*NIST is working to provide the semiconductor industry with detailed information on the nanoscopic pore size distribution of porous thin films destined as low-k dielectric materials for the next generation of integrated circuits. The electronics industry has chosen the introduction of nanometer scale pores into interlayer dielectric films as the method of lowering the effective dielectric constant. While these modifications change the dielectric constant favorably, other important parameters such as physical strength and barrier properties will also change, often in an unfavorable way. A new method has been developed to calculate the pore size distribution from x-ray reflectivity measurements on thin films in a controlled environment of solvent vapor.*

The rapid and sustained advances in ultra-large-scale integrated circuit performance have been driven, to a large extent, by miniaturization of the circuitry. At these nanoscopic sizes, interlayers with extremely low dielectric constants (low-k) are imperative to reduce cross-talk and to increase processor speed. While the candidate materials differ in their base chemistries, a common theme emerges in the push to develop low-k dielectric materials: nano-scale porosity must be introduced in a controlled manner to further reduce the dielectric constant. Techniques are needed to accurately and non-invasively characterize the porosity in these films while attached on a silicon substrate.

Capillary porosimetry is a prime candidate to measure the pore size distribution (PSD) of the nanoporous films. Bulk materials have been characterized in this manner by measurement of the mass gain of the material when exposed to a controlled pressure of solvent vapor. As the pressure of the probe solvent increases, pores become filled hierarchically by size as is described by the appropriate thermodynamic analysis such as the Kelvin equation:

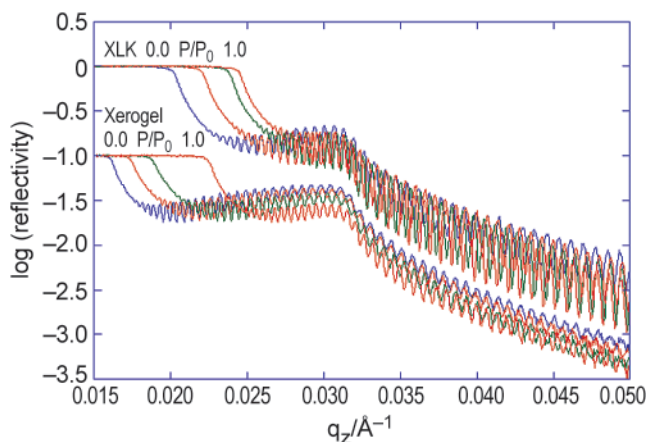
$$r = \frac{-2V_m\gamma}{RT \ln(P/P_0)}$$

where the pore radius,  $r$ , can be calculated from the partial solvent vapor pressure,  $P/P_0$ , known thermodynamic properties of the solvent such as surface tension,  $\gamma$ , and molar volume,  $V_m$ , temperature,  $T$ , and gas constant,  $R$ .

X-ray reflectivity (XR) has been extensively used in the Polymers Division to measure the thickness and density of  $1 \mu\text{m}$  nanoporous thin films. A method of x-ray porosimetry (XRP) has been developed to create a controlled solvent environment around the thin film so

that an equilibrium amount of adsorption occurs. The value of  $P/P_0$  can be varied either by mixing volumes of solvent saturated and dry air at a constant temperature, or by blanketing the sample in air that has reached solvent saturation at a low temperature and increasing the temperature of the thin film. Under such conditions, a standard XR scan gives accurate values of the total density that is a combination of wall density and solvent filled pores. The mass uptake as a function of partial pressure is calculated from these results.

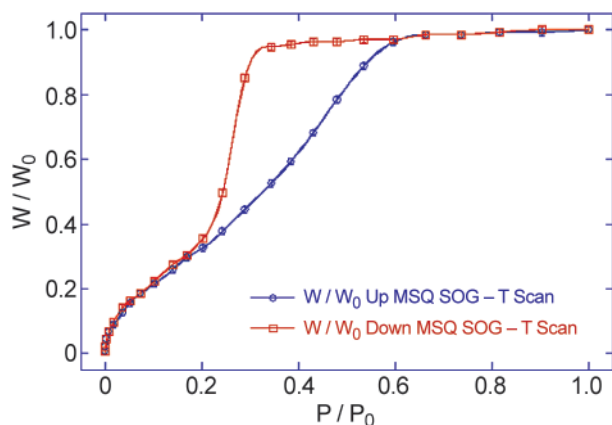
As an example, the reflectivity data from the porous hydrogen silsesquioxane (HSQ) and the silica xerogel films are shown in Figure 1. Each of the two samples has several data sets plotted together to show the effect of solvent adsorption. A critical edge is clearly visible at low  $q_z$  values as the sharp drop in  $\log(\text{Reflectivity})$  from the initially flat reflectivity curve. In Figure 1, four curves are shown for each sample, varying from the sample exposed to dry air (left most curve) to sample in saturated toluene vapor (right most curve). There is a progression of the critical edge to higher  $q_z$  as the vapor pressure increases, due to the increased electron density of the film as the smaller pores become saturated with liquid toluene.



**Figure 1:** XR curves of a porous organosilsesquioxane (XLK™) and xerogel films under controlled partial toluene vapor pressure.

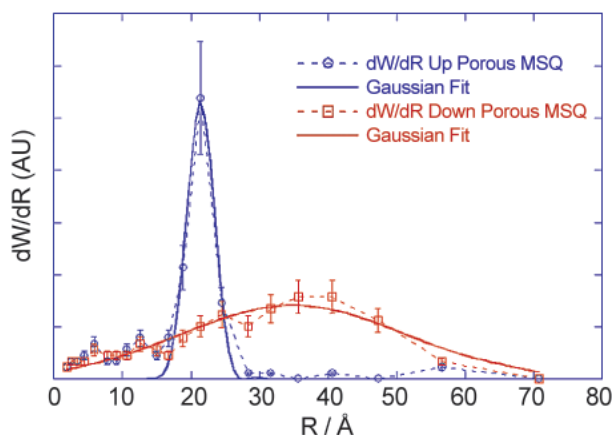
At  $P/P_0 = 1$ , toluene will condense in all of the accessible pores or open pores by definition, so the uptake at saturation,  $W_0$ , is a measure of the porosity. It should be emphasized that this porosity only reflects those pores that the toluene can infiltrate. There may also be closed pores not accessible to toluene vapor and therefore not reflected in the XR porosity. Therefore, a matrix density that is a combination of dense wall material and inaccessible closed pores can be calculated.

Figure 2 presents the adsorption/desorption data for a porous methyl silsesquioxane (MSQ) spin-on glass (SOG) film in which  $P/P_0$  is varied through the substrate temperature. The solid lines are cubic spline fits through the data and accurately mimic the shape of the curves. The data points have considerably less scatter than the data in which the isothermal technique is employed. The hysteresis loop is very well defined with data outside of the loop coinciding accurately. If the principle of temperature–pressure equivalency is valid, the temperature control method clearly increases the accuracy of the measurement.



**Figure 2:** XR toluene vapor adsorption data from MSQ SOG films by varying the substrate temperature.

The pore size distribution can be calculated by use of the Kelvin equation and other thermodynamic considerations from a point-by-point differentiation, as shown in Figure 3.



**Figure 3:** PSD of MSQ SOG films by varying the substrate temperature (where AU = arbitrary units).

There are several advantages of XRP over other techniques to determine pore size in ultrathin films. Some methods require that the film be deposited on

a special substrate, such as the piezoelectric surfaces required for both the quartz crystal microbalance and surface acoustic waves techniques. XRP can be done on any smooth substrate, including the Si wafers used in the semiconductor industry. In many ways, XRP is similar and complimentary to optical methods such as ellipsometric porosimetry (EP). However, the EP analysis requires knowledge of the optical constants, for both the matrix and the adsorbate. With EP it is also necessary to invoke the additional assumption that the polarizabilities are additive. XRP does not require these additional assumptions.

Another potential advantage of XRP is the ability to quantify not only the average film density, but also the density profile normal to the film surface. X-ray reflectivity has been used to extract non-uniform density profiles in a series of low-k films. It may be possible to use XRP to extract pore size distributions as a function of depth into film. To prevent dielectric breakdown, it is desirable to have low porosity or very small pores near the surfaces with the majority of the porosity localized in the center of the thin film. XRP could prove to be very useful for characterizing these types of structures.

*“The SANS/SXR measurements have become a key metric in our low-k dielectric materials characterization and screening process.”*

**Dr. Jeffrey Wetzel**

Manager  
Low-k Materials Technology  
International SEMATECH

*“The NIST x-ray reflectivity program is useful, perhaps even critical, to the industry.”*

**Dr. Abner Bello**

Technical Staff Member  
Defect and Thin Film Characterization  
Laboratory Applied Materials, Inc.

### For More Information on this Topic

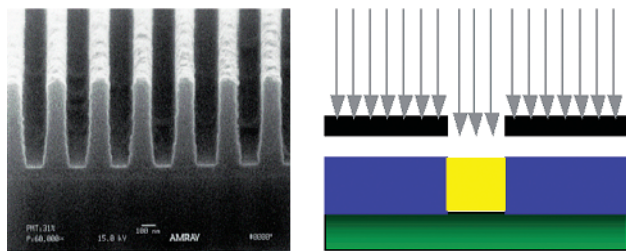
B.J. Bauer, W.L. Wu (Polymers Division, NIST)

Hae-Jeong Lee, Christopher L. Soles, Da-wei Liu, Barry J. Bauer and Wen-li Wu, “Pore size distributions in low-k dielectric thin films from X-ray porosimetry,” *Journal of Polymer Science, Polymer Physics Edition*, (in press).

## Direct Measurement of the Reaction Front in Chemically Amplified Photoresists

The continual device performance increases by the semiconductor industry has been largely driven by the fabrication of smaller structures with lithography. As feature sizes approach sub-100 nm, the photolithographic process must be controlled with tolerances of (2 to 5) nm, dimensions comparable to the molecular size of the polymer chains in the photoresist imaging material. New experimental methods are needed to measure transport and materials science phenomena over nanometer length scales to provide critically needed data for the understanding, design, and control of new lithographic materials and processes. In collaboration with IBM and the University of Texas, we directly measured the spatial evolution of a reaction front, within a photoresist, with nanometer resolution using neutron and x-ray reflectometry and a deuterium-labeled photoresist polymer.

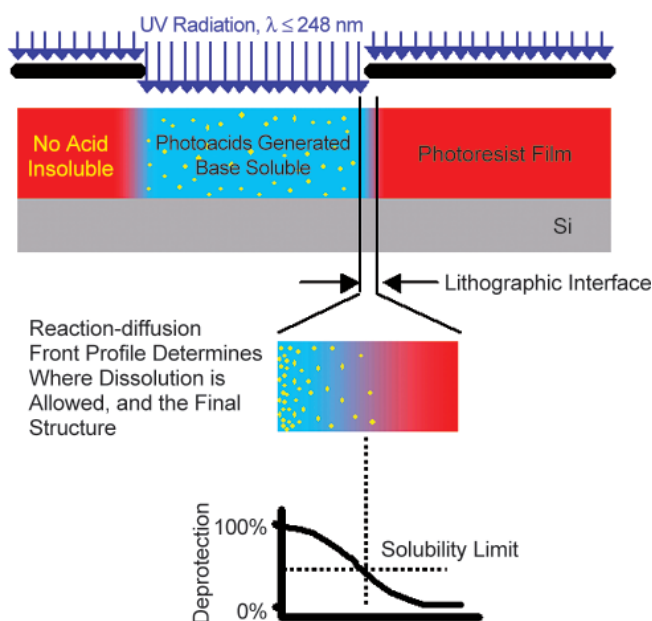
The semiconductor industry is rapidly approaching the need to fabricate sub-100 nm structures to continue performance increases in integrated circuits. Photolithography remains the enabling technology for the fabrication of integrated circuit patterns. Although industry is able to commercially produce 130 nm features, lithographic materials and processes are not fully available for the production of sub-100 nm structures. New materials must be able to produce structures with dimensional tolerances of (2 to 5) nm, dimensions near the size of the polymer chain molecules in the imaging layer.



**Figure 1:** At left, SEM image of a lithographically fabricated structure with a nominal critical dimension of 150 nm and 300 nm pitch. At right, schematic illustration of patterning through a mask to create the structure.

Current imaging layers, chemically amplified photoresists, are multi-component materials consisting of a polymer resin initially insoluble in an aqueous base developer solution, a photoacid generator (PAG), and other additives. A schematic diagram of the fabrication process and an example structure are shown in Figures

1 and 2. The patterns are generated in the resist by exposure to UV radiation through a mask. In the exposed areas, the PAG decomposes forming an acid species. Upon baking, the acid diffuses and catalyzes a deprotection reaction rendering the insoluble resist soluble in a developer. The soluble regions are then removed with the aqueous base developer. Control over this process is dominated by the events in the transitional region between exposed and unexposed areas of the photoresist.

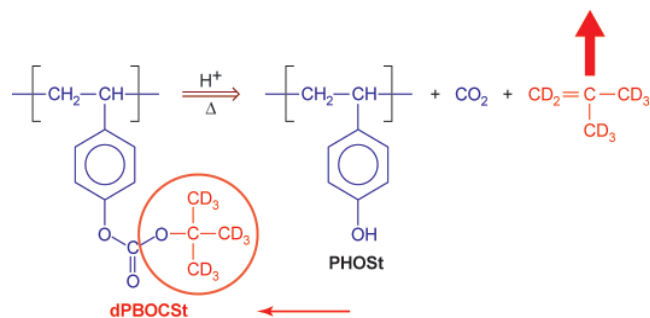


**Figure 2:** Schematic diagram of the reaction-diffusion process in chemically amplified photoresists. The transitional region between exposed and unexposed regions is particularly important for critical dimension and roughness control.

The initial development of chemically amplified photoresists was a key technological breakthrough furthering the continued use of optical photolithography for the fabrication of sub-micrometer features. The importance of chemically amplified photoresist concepts is illustrated by the industry-wide use of these materials in the fabrication of state-of-the-art devices today and into the foreseeable future. With the imminent need for sub-100 nm feature sizes, nanometer level control over the spatial evolution of the deprotection reaction front and the subsequent development steps is needed. The current level of understanding of the acid-catalyzed reaction-diffusion process is not sufficiently detailed to achieve this goal.



To meet the need for spatially detailed data, we have developed, in collaboration with the IBM T.J. Watson Research Center and the University of Texas at Austin, an experimental methodology to measure directly the spatial evolution of the deprotection reaction front through each processing step. By using model photoresist polymers with a deuterated protection group, neutron and x-ray reflectivity (NR, XR) measurements are able to follow the compositional and density profiles of the reaction-diffusion process in an idealized transitional region in a bilayer film stack. Neutron contrast with the reaction is possible because the reaction products involving the deuterated protection group are volatile as illustrated in Figure 3.

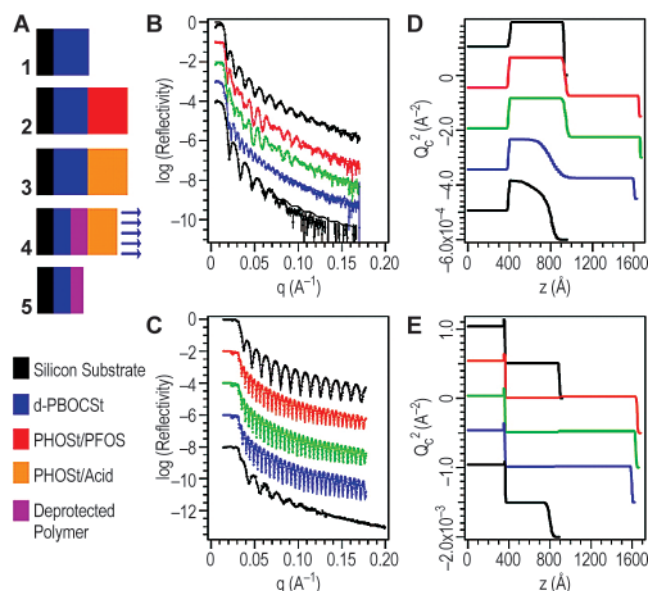


**Figure 3:** General deprotection reaction in a chemically amplified photoresist. Deuterated molecular parts with strong contrast to neutrons are shown in red. PHOSt = polyhydroxystyrene, PBOCSt = poly *p*-tert-butoxycarboxystyrene.

The NR and XR results from a series of bilayer samples are shown in Figure 4. NR and XR measurements were taken after each processing step from the spin-coating of each film layer through exposure and bake to the dissolution of the upper layer and any deprotected polymer. The data show that the deprotection reaction front broadens with time within the photoresist. The initial interfacial width was approximately 4 nm wide whereas the reaction front was nearly 20 nm wide. Upon development, the data show that the developed film remained sharply defined with a surface roughness of approximately 4 nm as well. Although the reaction front was much wider than the final interfacial width, the selectivity of the dissolution process allows for the fabrication of well-defined nanostructures with diffusive transport mechanisms.

The spatial detail afforded by the developed methodology can play an important role in not only the qualitative description of the reaction-diffusion process, but also with the quantitative determination of physical parameters and changes in any physical or chemical properties over the nanometer length scales required for

control over the fabrication of sub-100 nm structures. In addition, the strategy developed here is general and can be adapted for the study of candidate photoresist materials being developed for future applications.



**Figure 4:** A) schematic diagram of the processing steps including the application of each film layer, exposure to UV radiation, a post-exposure bake (PEB) and development. B) and D) show the NR data and compositional depth profile and C) and E) show the XR data and density depth profiles from each step.

“[This work] opens a window of opportunity to construct structure-property relationships between chemical transport mechanisms and ultimate resist resolution. It may also lead to insights into the ultimate, intrinsic resolution limits and critical dimension control of polymer-based imaging materials.”

**E. Reichmanis and O. Nalamasu**  
Bell Labs, Lucent Technologies,  
*Science*, 297, 349, (2002)

### For More Information on this Topic

E.K. Lin, C.L. Soles, R.L. Jones, J.L. Lenhart, W.L. Wu (Polymers Division, NIST); S.K. Satija (NCNR, NIST)

E.K. Lin, C.L. Soles, D.L. Goldfarb, B.C. Trinqué, S.D. Burns, R.L. Jones, J.L. Lenhart, M. Angelopoulos, C.G. Willson, S.K. Satija, and W.L. Wu, “Direct Measurement of the Reaction Front in Chemically Amplified Photoresists,” *Science*, 297, 372, (2002).

# Metrologies for Tissue Engineering

*Tissue engineering represents a new paradigm in medicine by seeking to regenerate missing or damaged tissue. Developing, manufacturing, and regulating tissue-engineered medical products requires proving the safety and efficacy of these complex devices. This presents a significant measurement challenge involving qualification of materials, cells, and delivery methods.*

Tissue engineering is a rapidly growing field that presents a host of new measurement problems for producers and regulators. Tissue engineered medical products are typically hybrid devices that incorporate materials and cells in order to regenerate damaged tissue. The safety and efficacy of both materials and cells, as well as their interactions, must be qualified in order for these to gain acceptance, and we are developing a host of *in vitro* tests to assist in this process.

Events at the cell–material interface determine the performance of these devices, but the complexity of the interactions has prevented development of a more rational approach to tissue engineering. In the Polymers Division, we are extending the established program in combinatorial methods to biomaterial interfaces. This will permit rapid screening of material variables and evaluation of their effects on cells.

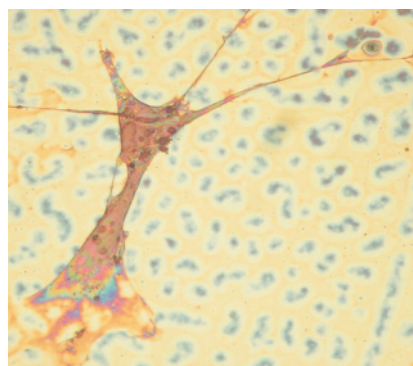
The extracellular matrix (ECM) to which cells adhere can initiate healing, direct cell migration, control cell cycle progression, and determine cell differentiation. The scientific community is just beginning to understand intracellular signaling networks, but it is clear that external stimuli participate in the cycle of cell activity. The challenge of tissue engineering is to control cellular behavior through the rational design of materials and culturing conditions. The industry is years away from meeting this challenge due, in part, to a void in the measurement infrastructure at the cell-biomaterial interface. Efforts within the Polymers Division to fill this void fall under three general topics: developing material libraries, expanding imaging capabilities, and managing and analyzing data.

## Developing Material Libraries

We are developing a three-tiered material library for investigating cell-material interactions; each tier represents an increased level of complexity. The first tier comprises polymeric material surfaces designed to mimic bulk material interfaces currently found in industrial applications. The second tier contains material surfaces designed to mimic the ECM through incorporation of cell-signaling molecules such as peptides and oligosaccharides. While the first two

tiers describe pseudo-two-dimensional phenomena, the third tier includes three-dimensional materials.

Current industrial applications, and those of the near future, rely on relatively simple materials such as poly(lactic acid) and poly(dimethylsiloxane). Even so, variables such as composition and processing conditions can drastically affect physical properties. Particular properties of interest include: nanometer- and micrometer-scale topography, hydrophilicity, charge, and mechanical rigidity. The Polymers Division has established methods for preparing gradient material surfaces encompassing this parameter space. As these methods are transferred to biomaterial systems, the first tier of our library will develop. From this tier, we will identify and develop SRMs that will assist industry in developing products, assessing quality control, and gaining regulatory approval.



**Figure 1:** Cell adhesion to a polymer blend.

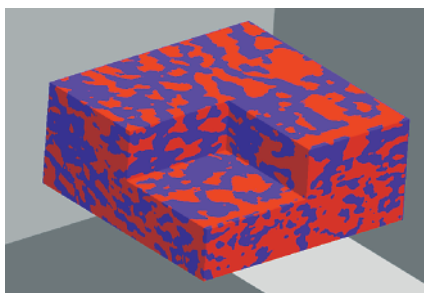
The next generation of tissue engineered medical products will incorporate cell-signaling molecules such as peptides and oligosaccharides. These materials will be engineered to interact with specific receptors and elicit selective cellular responses. Doing so requires fine-tuning the stimuli offered to cells by presenting appropriate combinations of signaling molecules. The cells then receive signals capable of initiating more complex cascades ultimately leading to the desired cellular response. This chain of events would emulate that which occurs during natural tissue formation. A high-throughput approach is uniquely qualified to characterize this complex, multi-dimensional space of ECM cues and cellular responses. As methods for preparing such materials are developed, the second tier of our library will emerge. From this tier, we will contribute to the general understanding of intracellular signaling networks, groundwork necessary for the development of new tissue engineered medical products.

Real tissues are inherently three-dimensional and realistic measurement tools will need to be as well. We are currently developing three-dimensional materials and

associated measurement methods to begin a metrology system complementary to the two-dimensional systems. Similar material issues will be faced with the added complication of three-dimensional architecture and its influence on cellular response. Such is the scope of the third tier of our library. In addition, other issues related to tissue engineered medical products will be investigated with a goal of creating necessary measurement capabilities. The devices being developed by tissue engineering companies have multiple requirements in order for them to be safe and effective. They have stringent mechanical requirements which depend on the tissue being engineered; they must allow infiltration by the necessary cells; and the inflammatory responses they evoke must be minimized. Toward this end, we are developing *in vitro* testing protocols for these performance requirements that will be used in screening tissue engineered medical products.

### Expanding Imaging Capabilities

The described three-tiered material library only has value if cell response across the library can be well characterized. A host of strategies exist for characterizing cell response; many fall beyond the scope of the Polymers Division and are pursued through external collaborators. On site, we have targeted visual imaging of cells through conventional microscopy, fluorescence microscopy, confocal microscopy, and optical coherence tomography (OCT). The OCT image below shows pores in red and tissue scaffolding in blue.



**Figure 2:** OCT image of a tissue engineering scaffold.

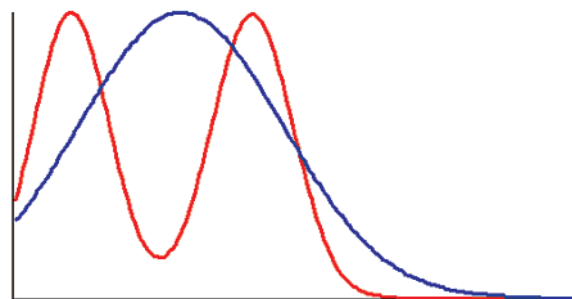
The very nature of the combinatorial methodology will require that image acquisition be well documented and unbiased in order to correlate cell response to material properties. We envision a streamlined process where cells are seeded onto a material, incubated, fixed, and stained following an established experimental protocol. An array of images would be collected and the entire surface mapped. Images would then be reduced to quantitative measures of cell response.

### Managing and Analyzing Data

The task of accurately overlaying data maps presents a significant challenge. For example, a thin film could be

prepared from a blend of two polymers. The film might consist of a composition gradient along one axis and might be annealed (processed) under a temperature gradient orthogonal to the composition gradient. Characterization of this film would begin by mapping processing conditions, i.e., composition and annealing temperature as a function of position. An array of AFM images may be taken to map the surface topography. An array of contact angles may be measured to map the surface energy. Finally, an array of images would be collected and analyzed to measure cell response. In order to identify correlations, each of these data maps must be in alignment.

Once data maps are aligned, a rigorous statistical analysis is necessary to quantify correlations and make meaningful hypotheses of causality. Material parameters can be analyzed following traditional engineering statistics. Data from living organisms requires an alternative strategy. Whether measuring general, morphological parameters such as cell area upon spreading or more specific parameters such as the regulation of gene expression, the cell response will fall within a distribution defined by the cell line. Unlike measured material parameters, variations from the mean may not be random, so reducing data to a mean and standard deviation can result in a loss of critical information.



**Figure 3:** An extreme example of two population distributions that are clearly different, yet they have the same average and standard deviation.

As such, images of cells are collected, analyzed, and reported in a manner that maintains the fullest description of a population distribution. Furthermore, when investigating the cell response to a variety of material scaffolds, evaluations are based on a statistical comparison between corresponding cell populations.

### For More Information on this Topic

N. Washburn, S. Kennedy, E. Amis

Niklason, L.E., Langer, R., "Prospects for Organ and Tissue Replacement," *JAMA*, February 7, 2001.

## NIST Combinatorial Methods Center

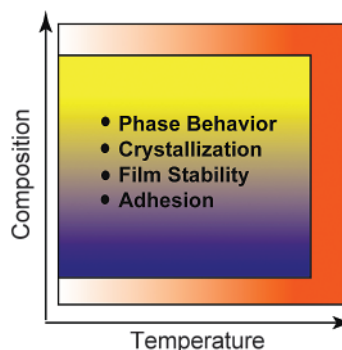
*The NIST Combinatorial Methods Center (NMC) was formally established in January 2002 to provide information and expertise on combinatorial methods to a wide range of industrial, academic and government institutions interested in acquiring combinatorial and high-throughput capabilities suited for materials research. The NCMC functions through two complimentary efforts. 1) A research program geared towards the development of techniques and instrumentation for the fabrication and analysis of novel combinatorial libraries. This research centers on novel gradient combi methods, where the NCMC has recognized expertise. 2) An outreach program designed to gauge industrial needs in combi research and effectively disseminate data, instrumentation design, best practices and protocols, and other information relevant to combi techniques.*

Combinatorial techniques offer a highly parallel, automated, and often miniaturized route for experimentation that allows hundreds or thousand of specimens to be fabricated and analyzed in a rapid and efficient fashion. Such techniques provide opportunities to significantly boost productivity, increase the scope of parameter-space exploration, and enhance the understanding of complex systems in a variety of scientific and technological disciplines. Indeed, in recent years the unmitigated success of combinatorial and high-throughput methods in the pharmaceutical industry and the genomics effort has spurred researchers in the materials science and chemical industries to reconsider their reliance on traditional “one-at-a-time” experimental approaches to product and knowledge discovery. However, several challenges impede the successful adaptation of combinatorial methods in these arenas. For example, pharmaceutical combi models, which emphasize product discovery, often do not provide insight into the structure/property/processing relationships that are central to materials research. In addition, techniques and instrumentation explicitly suited to the high-throughput fabrication and analysis of combinatorial libraries of interest to materials scientists need to be developed. Moreover, many institutions interested in acquiring combinatorial methods require information on how to incorporate such strategies into their research program.

In response to these technical and educational needs, the NIST Combinatorial Methods Center (NMC) was formally established in January 2002. A NIST-wide effort centered in the Polymers Division, the NCMC includes contributions from throughout MSEL and several other laboratories including Building and Fire Research, Physics, and Chemical Science and Technology Laboratories. The NCMC’s mission is twofold. As a research program focused upon the creation of novel specimen libraries and instrumentation, the NCMC advances the state-of-the-art in combinatorial methods geared towards materials research and discovery. A complimentary effort is an outreach program, which

serves to disseminate NCMC research products, instrument design, best protocols and practices, and other information relevant to the combi method. This organization also provides an effective means by which industrial needs are gauged.

NCMC combinatorial methods research is rooted in the so-called gradient approach. The core of gradient combi is the gradient specimen. These samples continuously vary in one property (e.g., film thickness) along a spatial coordinate over a prescribed range. By arranging two such gradients (e.g., thickness and temperature) in an orthogonal manner, a gradient library is created that exhibits every possible combination of properties within the scope of the constituent gradient specimens. Gradient libraries are particularly useful to materials scientists because they offer a convenient and thorough way in which to map parameter space. In addition, gradient libraries are especially amenable to examination via microscopy and microanalysis, which facilitates the illumination of structure–property relationships. Finally, as opposed to many robotics-oriented discrete approaches, gradient techniques can offer a cost-effective way of performing combinatorial studies, making them attractive to a wider range of institutions.



**Figure 1:** Scheme 1 — Gradient combinatorial library.

As they are the basic unit of gradient libraries, many NCMC research efforts concentrate upon the development of novel gradient specimens and processes, with polymer science being a focus in recent years. Methods for producing gradients in film thickness, composition and temperature formed the basis of previous NCMC studies.

This year, several new techniques were added to the NCMC repertoire. New instrumentation for generating gradients in ultraviolet-radiation (UV) exposure was central to this effort. Here, a UV slit-source is accelerated across a planar specimen. When this source is held in close proximity (< 5 mm) to the sample, UV-generated ozone can chemically modify self-assembled monolayer (SAM) treated sample surfaces resulting in a gradient in surface energy and/or chemical functionality. Depending upon the SAM employed, such surface energy gradients can span 70° in water contact angle. Larger source/sample distances are effective in producing gradients in light-induced crosslinking, polymerization, and degradation. Since the degree of UV exposure is controlled through stage motion, this instrument is particularly versatile. Gradient profile, depth and steepness are easily tuned for a wide range of applications. In another new technique, gradients in the height of topographic surface features are created. Here, topographic gratings are lithographically etched

into wedges of silsesquioxane “spin-on” oxides created via flow-coating. The resulting patterns, with heights ranging from (30 to 150) nm, provide a combi strategy for examining topography-mediated templating of film properties, making them useful for the development of thin-film optoelectronic devices and MEMS.

NCMC research also generates new techniques and instrumentation for the high-throughput measurement of materials properties. This year, efforts concentrated on combinatorial methods for evaluating mechanical properties and adhesion. Gradient film libraries mounted on deformable copper grids enable combinatorial examination of polymer failure mechanisms. In another technique, libraries prepared on rubbery polydimethylsiloxane supports allow high-throughput modulus measurements. Recently completed instrumentation facilitates sophisticated combinatorial measurements of adhesion via the Johnson–Kendall–Roberts (JKR) approach using micro-lens arrays. In addition, methods for performing combinatorial tests of interfacial fracture were developed in conjunction with a modeling effort that guides interpretation of experimental data.

Due to these and previous research efforts (some of which are detailed in this report), the NCMC has established a widely-recognized expertise in gradient combinatorial materials science. This impact is demonstrated by the success of the NCMC outreach program, described below.

### NCMC Outreach

The foundation of NCMC outreach is a membership program that invites industrial, academic, and government institutions to participate in a consortium designed to facilitate the advancement of combinatorial materials research. This program serves as a conduit through which NCMC research products are disseminated and industrial needs are gauged. Since the NCMC emphasizes relationships and collaboration that do not involve proprietary information, Center/member and member/member communication is maximized. However, collaborations that address specific industrial problems are established when necessary.

The NCMC has currently attracted 11 members (see table below), in part due to an extensive dissemination and recruiting effort that culminated in the inaugural NCMC conference held in San Diego, CA in January 2002.

Members are served through several routes. Foremost among these is a series of tri-annual members’ meetings

NCMC Members (as of July, 2002)	
Bayer Corp.	Air Force Research Laboratory
Rhodia Inc.	Honeywell International
Akzo Nobel Corp.	Gillette/Duracell R&D
Proctor & Gamble Co.	Rohm and Hass Co.
Exxon Mobil Research & Engineering	BASF
Air Products and Chemicals	

Figure 2: NCMC Members.

that showcase NCMC technical advances and protocols, distribute information on research conducted at NIST and elsewhere of relevance to combinatorial methods, and provide a forum in which current issues and needs in combinatorial and high-throughput research are discussed.

The first NCMC members meeting, held on April 26, 2002, was attended by over 20 representatives from 8 industrial institutions. Entitled, “Library Design and Calibration: *What you need to know and do before you look for hits*,” this meeting involved a variety of activities. Technical presentations detailed the design of combinatorial experiments using the gradient technique and methods for calibrating gradient libraries. The importance of these processes in combinatorial research was demonstrated through a case study that illustrated how calibration and design principles work in an actual research program. An NCMC staff-led discussion focused on combinatorial strategies for multicomponent formulations research and management of the massive amounts of data combinatorial studies necessarily produce. Laboratory demonstrations designed to provide practical first-hand knowledge about NCMC instrumentation and gradient techniques focused upon flow coating, composition and surface energy gradients, automated hot-stage optical microscopy, adhesion measurement instrumentation, infrared-imaging, and combinatorial mechanical testing. The second NCMC meeting, “Adhesion and Mechanical Properties,” is slated for October 2002.

This year has also seen numerous visits to NCMC facilities by member parties. For example, both Rhodia and the Air Force Research Laboratory sent staff to work alongside NCMC scientists on combinatorial projects. This type of interaction is especially useful to institutions that are new to combinatorial research and its effective implementation.

The new NCMC website (<http://www.nist.gov/combi>) provides information on the center and its activities, research publications from the NCMC and selected sources in the public domain, instrument schematics and specifications, and automation and analysis software. Additional resources, including browsable combinatorial data libraries, are also in development.

*“Combinatorial methods offer the possibility of accelerating industrial materials research. The NCMC is well suited to drive this new technology because of their excellent work in high-throughput application testing. . .and addressing industrial needs. Industry will benefit by getting started in combi earlier.”*

**Wolfgang Schrof**  
Polymer Physicist, BASF (NCMC Member)



### For More Information on this Topic

C. Davis, M. Fasolka, A. Karim, E. Amis (Polymers Division, NIST)

Visit the NCMC website at <http://www.nist.gov/combi>



## Advanced Manufacturing Methods

An increasingly competitive manufacturing environment drives the search for new materials and processing techniques to make them. In most cases, materials processing steps determine the microstructure and performance of the material while manufacturing costs determine price. Industry needs measurement methods, standards, and data that will help monitor, control, and improve processing methods. These tools are also needed to help understand materials processing and to develop new processing methods and materials with enhanced properties. This is as true for highly developed, well-established industries as it is for rapidly growing or emerging industries. It is also true for all types of materials, processes, and products. The industrial competitiveness of the United States depends on U.S. manufacturers' ability to use the measurement tools to develop and advance their manufacturing methods. In many cases, the needed tools are generic and their impact would be greatly enhanced if they became industry wide standards. Therefore, MSEL is working to develop measurement methods and standards to enable industry to achieve these goals. This work is often being conducted in close collaboration with industry through consortia and standards organizations. The close working relationship developed with industry through these organizations not only ensures the relevance of the research projects, but also promotes an efficient and timely transfer of research information to industry for implementation. Since different materials and industries frequently have similar measurements needs, and most industrial products have multiple materials components, this program covers the processing of ceramics, metals, and polymers.

Research in the Ceramics Division focuses on development of test methods for the assessment of contact damage and wear, development of test methods and predictive models for evaluation of mechanical properties at elevated temperatures, and development of models for prediction of coating properties and performance. One project focuses on low temperature co-fired ceramics (LTCC), a manufacturing method being developed largely for portable wireless modules because it promises to allow for a reduction in the size and cost of modules used in high-frequency applications while improving performance. Because dimensional tolerances are critical in this process, accurate measurements and predictive models of dimensional changes during sintering are necessary for the commercialization of LTCC modules. Measurement methods and predictive models for the overall shrinkage and the local variations in sintering near vias and interconnects are being developed.

Projects in the Metallurgy Division cover several processing and measurement methods. The performance of metallic components in products is strongly dependent on processing conditions that determine microstructural features, such as grain size and shape, texture, the distribution of crystalline phases, macro- and microsegregation, and defect structure and distribution. Expertise is applied from a wide range of disciplines, including thermodynamics, electrochemistry, fluid mechanics, diffusion, x-ray, and thermal analysis, to develop measurement methods and understand the influence of processing steps for industries as diverse as automotive, aerospace, coatings, and microelectronics. Rapidly growing and emerging industries such as biotechnology and nanotechnology are dependent upon the development of new advanced manufacturing methods that can produce metallic components with the desired characteristics and performance. Current projects focus on measurements and predictive models needed by industry to design improved processing methods, provide better process control, develop improved alloy and coating properties, and reduce costs. Important processing problems being addressed include melting and solidification of welds, solidification of single crystals, powder production and consolidation, and coating production by thermal spray and electrodeposition.

Polymeric materials have become ubiquitous in the modern economy because of their ease of processing. However, these materials can exhibit complex and sometimes catastrophic responses to the forces imposed during manufacturing, thereby limiting processing rates and the ability to predict ultimate properties. The focus of the Polymers Division is directed towards microscale processing, modeling of processing instabilities, and on-line process monitoring of polymeric materials. Our unique extrusion visualization facility combines in-line microscopy and light scattering for the study of polymer blends, extrusion instabilities, and the action of additives. Current applications focus on understanding and controlling the "sharkskin instability" in polymer extrusion and observation of the dielectric properties of polymer nanocomposites. Fluorescence techniques are developed to measure critical process parameters such as polymer temperature and orientation that were hitherto inaccessible. These measurements are carried out in close collaboration with interested industrial partners.

Contact: Kalman Migler

## Control of Extrusion Instabilities

*Polymeric materials have become ubiquitous in the modern economy because they are comparatively easy to process. However, polymeric materials exhibit complex and sometimes catastrophic response to the forces imposed on them during manufacturing. These instabilities prevent or retard processing. In this project we seek new measurement technologies to understand and control processing instabilities.*

### Kalman Migler

The manufacturability of important classes of polymers is limited by processing instabilities. Our goal is to fully understand the well-known instability (sharkskin) via development of new measurement technology that can unravel the relationship between polymer rheology, flow boundary conditions, and the resulting surface roughness. The output of the project will be to provide suppliers and users with guidelines for reducing this instability. This line-of-attack will then serve as a model for more complex processing operations in which flow instabilities hamper large-scale production.

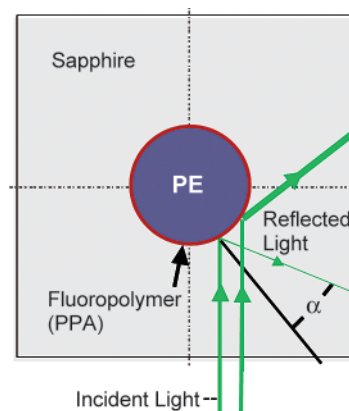
Our work published over the previous two years provided conclusive evidence regarding the nature of the flow conditions that exist during sharkskin melt fracture of polyethylene. We also provided the first direct evidence of how fluoropolymer additives modify the flow boundary condition so as to eliminate sharkskin.

However, the fluoropolymer additives are only effective when they efficiently migrate to the wall where they coat it, producing a thin fluoropolymer layer. There has been virtually no research to understand this complex phenomenon; in fact, reasonable theoretical arguments anticipate that the dispersed fluoropolymer droplets should migrate away from the wall. Understanding the mechanism of fluoropolymer deposition at the wall will optimize future additives and will provide insight into other manufacturing operations where these effects may occur.

Our approach is to conduct *in situ* measurements of the coating process by starting with pure polyethylene and monitoring the sharkskin. We then mix approximately 0.1% mass fraction fluoropolymer into the polyethylene and correlate the instantaneous thickness of fluoropolymer at the wall with the state of sharkskin and the decreasing pressure required to drive the polymer through the extrusion tube.

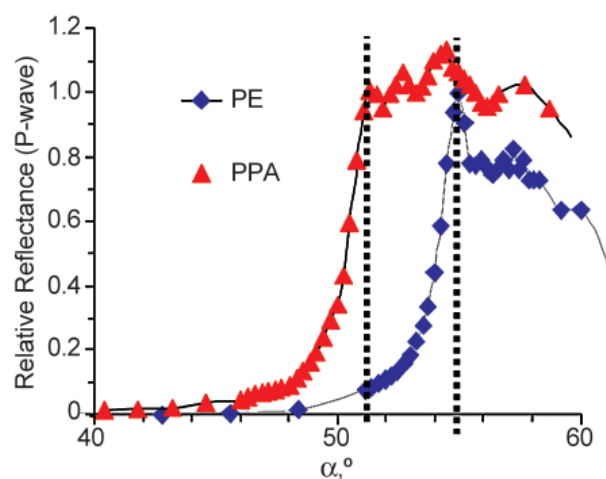
We have chosen an optical technique based on Total Internal Reflection (TIR), which is sensitive to the presence of a thin layer of fluoropolymer at the sapphire wall (see Figure 1). The principle is that a critical angle,  $\alpha$ , exists when light travels from a material with a high index of refraction to one with a low index of refraction (such as occurs in a swimming pool.)

We take advantage of the differing indices of refraction of the three materials: sapphire, polyethylene (PE) and fluoropolymer (polymer processing additive, PPA). When the polyethylene is in intimate contact with the wall (which causes sharkskin) the critical angle for TIR is  $53^\circ$ . When fluoropolymer displaces the polyethylene at the wall, the critical angle decreases.



**Figure 1:** Cross section of polymer extrusion tube also showing the relevant angles of the optical reflections.

Preliminary measurements indicate that a layer sensitivity of 25 nm may be achievable and that this technique may have application for a variety of extrusion instabilities such as the spurt phenomenon.



**Figure 2:** Reflectivity off the sapphire-polyethylene interface (diamonds) and off the sapphire-fluoropolymer interface (triangles).

### Contributors and Collaborators

K. Migler; Dow Chemical, 3M Chemical Company, Dupont-Dow Elastomers, McMaster University, University of Minnesota



## Process Monitoring of Polymer/Clay Nanocomposites

*Real-time, on-line measurements of resin materials properties are desirable not only because they preempt the need for post processing characterization but also because they can be used to monitor resin conditions, to detect problems with processing parameters, to control the process, and to predict performance of the final product. In this project, we are developing measurement techniques based on optical, dielectric, rheological, and ultrasonics techniques. NIST has filled an industry need by designing and constructing process sensors and by collaborating with industry partners in the application of new sensor technology to process monitoring.*

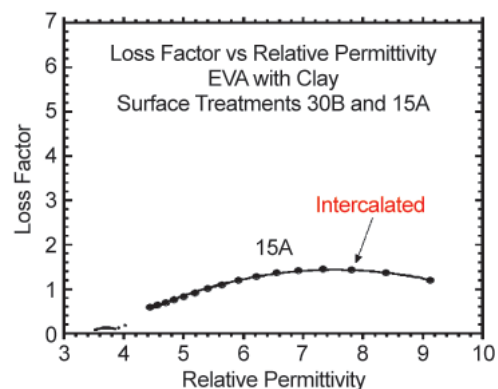
**Anthony J. Bur**

The state of the microstructure that forms during the compounding and mixing of clay and polymer is the primary factor determining composite performance. Current practice is to analyze the processed product off-line using transmission electron microscopy (TEM) and x-ray scattering to determine the extent of aggregate, intercalated, or exfoliated microstructure. In order to minimize the need for off-line measurements, we are developing on-line instrumentation that will yield real-time microstructure information using dielectric, rheology, and light transmission measurements. On-line data can provide a basis for developing R&D processing strategies that compounders can use to set process parameters that yield targeted product microstructure. Our approach to determining microstructure using on-line instrumentation is to correlate real-time observations with TEM, x-ray, and small angle neutron scattering (SANS) observations.

In the first phase of this project, real-time dielectric measurements were made using a ring-shaped ceramic dielectric cell that has interdigitated electrodes deposited on the inside surface of the ring. As resin flows through the ring, an electric fringing field intercepts the resin and the measured in-phase and out-of-phase currents are used to calculate the real and imaginary parts of the dielectric constant. Measurements carried out over a range of frequency from 500 Hz to 100 kHz yield dynamic information that characterize the electrical relaxation times of the composite.

Real-time dielectric measurements on polyethylene-ethyl vinyl acetate co-polymer (PE-EVA) mixed with organo modified clays reveal a correlation between microstructure and the dispersion in dielectric data as a function of frequency. In Figure 1, the dispersion is seen in the plot of the imaginary part of the dielectric constant versus the real part. In this plot, the DC conductivity has been subtracted out of the imaginary part in order to reveal the relaxation dynamics of the composite at higher

frequencies. Because these measurements are made in the melt at 150°C, ionic conductivity dominates the dispersion effects. This dispersion has its origins in the layered structure of the intercalated microstructure. The dielectric data in the figure are a direct result of the presence of microstructure in the form of silicate layers of smectite clay with organic polymer occupying the space between layers. From an electrical point of view, silicate layers interspersed with polymer resin behave as a series of capacitances and resistances giving rise to electrical relaxation dynamics having a broad distribution of relaxation times. It is our hypothesis that the shape and magnitude of this dispersion can be correlated with the microstructure that is revealed in TEM and x-ray observations.



**Figure 1:** The imaginary versus real part of the dielectric constant is shown for PE-EVA copolymer compounded with two clays, 15A and 30B at 150°C. X-ray measurements confirm that PE-EVA/15A clay is in the intercalated state and PE-EVA/30B clay is in the aggregate state. The broad dispersion seen in the 15A composite is due to intercalated microstructure.

These data are providing the platform for a collaboration with Chemical ElectroPhysics Corporation to develop a new dielectric slit die sensor with capability to measure rheological, optical transmission, and dielectric properties in real-time. The full package of data from this sensor will be the basis for designating the microstructure of the compounded composite.

Reference: A.J. Bur, S.C. Roth and M. McBrearty, *Rev. Sci. Instrum.*, **73**, p. 2097, (2002).

### Contributors and Collaborators

A.J. Bur, S.C. Roth, S.D. Hudson, C.R. Snyder, D.L. VanderHart (Polymers Division, NIST); C.J. Glinka, D. Ho (NIST Center for Neutron Research); J. Gilman (Fire Research Division, NIST); M. McBrearty (Chemical ElectroPhysics Corporation, Hockessin, DE)

## Liquid Crystalline Nanostructures: Phase Behavior and Processing

*In the search for new materials, relationships between molecular structure and material organization and properties must be established. By microscopic investigation of amphiphiles of novel molecular shape, we identify their phase behavior and explore how these materials can be aligned in the manufacture of useful devices.*

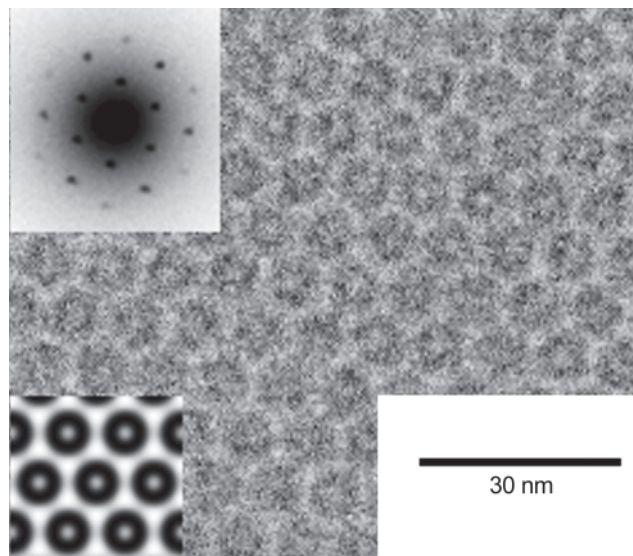
**Steven D. Hudson and Hu Duan**

Self-organized organic nanostructures with controlled optoelectronic properties that facilitate ultra-high density nanopatterning represent one of the challenges of molecular electronics. Similar materials that yield pores of precise size and chemical and ionic specificity represent another opportunity. To meet these challenges, we measure phase behavior of these materials and properties of their phase transitions. Transmission electron microscopy provides key information about the material organization. By Fourier analysis of high-resolution lattice images, the relative phase of diffracted beams is determined, thus providing complementary information for diffraction analyses.

This capability proved useful in the investigation of novel dendrons, having a dipeptide head unit and several aliphatic tail units. These molecules assemble into a hexagonal columnar phase at low temperature and, depending on molecular structure, either a cubic or a weakly birefringent phase at high temperature. Whereas some head units fail to form a special organization, the dipeptide unit segregates by itself in the center of the column, exhibiting a region of lower density (Figure 1). Similar triply segregated structure was observed in the cubic phase at high temperature. Segregation of the head unit can be very important and is responsible for high electronic carrier mobility in columns comprising molecules with donor and acceptor aromatic head groups.

Alignment of hexagonal columnar materials by appropriate surface treatment and/or processing procedure has been investigated. As mentioned above, some of the dipeptide dendrons exhibit a weakly birefringent phase at high temperature and a columnar hexagonal phase at lower temperature. At still higher temperature, the material forms an isotropic melt. Cooling slowly from the melt produces 100  $\mu\text{m}$ -sized grains of the high temperature phase. Upon cooling

further, an epitaxial relationship between this phase and the hexagonal columnar phase is observed.



**Figure 1:** High resolution TEM image of the hexagonal columnar phase of a dipeptide dendron. Inset upper left is the corresponding electron diffraction pattern, exhibiting (10), (11) and (20) reflections. Fourier analysis of the image also exhibited these reflections and determined their relative phase:  $- + +$ , whose combination results in the “hollow” cylinder appearance of the image. The resulting reconstructed image is inset bottom left.

The influence of shear flow on the order-disorder transition of a polymeric material that exhibits a hexagonal columnar phase was investigated. Whereas weak shear stress at temperatures slightly below the melting point align the microstructure, larger stresses cause melting. Upon cessation of shear, the hexagonal phase reforms by a row-nucleation mechanism that produces macroscopic alignment of the columns along the previous shear direction. Phase transition phenomena, therefore, have a significant influence over the alignment of the material.

### Contributors and Collaborators

S.D. Hudson, H. Duan (Polymers Division, NIST); V. Percec (University of Pennsylvania); K.D. Singer (Case Western Reserve University)

## Combinatorial Methods

The Combinatorial Methods Program develops novel high-throughput measurement techniques and combinatorial experimental strategies specifically geared towards materials research. These tools enable the industrial and research communities to rapidly acquire and analyze physical and chemical data, thereby accelerating the pace of materials discovery and knowledge generation. By providing measurement infrastructure, standards, and protocols, and expanding existing capabilities relevant to combinatorial approaches, the Combinatorial Methods Program lowers barriers to the widespread industrial implementation of this new R&D paradigm.

The Combinatorial Methods Program has adopted a two-pronged strategy for meeting these goals. The first of these is an active research and development program designed to better tailor combinatorial methods for the materials sciences and extend the state of the art in combinatorial techniques. Measurement tools and techniques are developed to prepare and characterize combinatorial materials libraries, often by utilizing miniaturization, parallel experimentation, and a high degree of automation. A key concern in this effort is the validation of these new approaches with respect to traditional “one at a time” experimental strategies. Accordingly, demonstrations of the applicability of combinatorial methods to materials research problems provide the scientific credibility needed to engender wider acceptance of these techniques in the industrial and academic sectors. In addition, the successful adoption of the combinatorial approach involves a highly developed “workflow” scheme. All aspects of combinatorial research, from sample “library” design and library preparation to high-throughput assay and analysis, must be integrated through an informatics framework which enables iterative refinement of measurements and experimental aims. Combinatorial Methods Program research projects give illustrations of how these processes are implemented effectively in a research setting.

NIST-wide research collaborations, facilitated by the Combinatorial Methods Program, have produced a wide range of new proficiencies in combinatorial techniques which are detailed in a brochure, “Combinatorial Methods at NIST” (NISTIR 6730), and online at

[www.nist.gov/combi](http://www.nist.gov/combi). Within MSEL, novel methods for combinatorial library preparation are designed to encompass variations of diverse physical and chemical properties, such as composition, film thickness, processing temperature, surface energy, chemical functionality, UV-exposure, and topographic patterning of organic and inorganic materials ranging from polymers to nanocomposites to ceramics. In addition, new instrumentation and techniques enable the high-throughput measurements of adhesion, mechanical properties, and failure mechanisms, among others. The combinatorial effort extends to multiphase, electronic, and magnetic materials, including biomaterials assays. On-line data analysis tools, process control methodology, and data archival methods are also being developed as part of the Program’s informatics effort.

The second aspect of the Combinatorial Methods Program is an outreach effort designed to facilitate technology transfer with institutions interested in acquiring combinatorial capabilities. The centerpiece of this effort is the NIST Combinatorial Methods Center (NCCM), an industry-university-government consortium organized by MSEL that became operational on January 23, 2002 via a kick-off meeting in San Diego. Although it is still in the growth stage, the impact of NCCM activities is readily apparent as 11 industrial partners and the Air Force Research Lab have already joined the NCCM membership program. The NCCM facilitates direct interaction between NIST staff and these industrial partners, and provides a conduit by which Combinatorial Methods Program research products, best practices and protocols, instrument schematics and specifications, and other combinatorial-related information can be effectively disseminated. This outreach is mediated in large part by a series of tri-annual workshops for NCCM members. The first NCCM meeting, “Library Design and Calibration,” was held on April 26, 2002 at NIST, and it provided information essential to starting a combinatorial research effort. The second meeting (October 2002) will concentrate on combinatorial approaches to adhesion and mechanical properties. Further information on NCCM can be found on the website at [www.nist.gov/combi](http://www.nist.gov/combi).

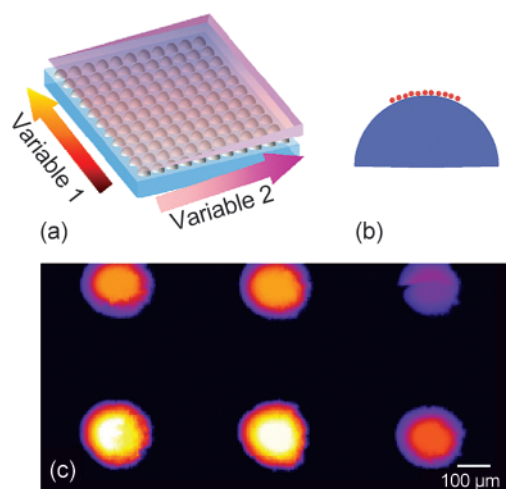
Contact: Alamgir Karim

## Combinatorial Adhesion and Failure

*Polymer interfaces play a critical role in numerous technologies including adhesives, paints and coatings, and biological systems. Previous research has shown that polymer interface formation and failure is dependent upon various material, processing, and environmental parameters. To explore this large parameter space efficiently, we have developed a combinatorial adhesion test based on the contact and separation of a microlens array. Combinatorial debonding measurement test method and concurrent simulations of dynamics of debonding at metal-semiconductor interface due to thermal expansion mismatch are developed.*

**Alfred J. Crosby and Alamgir Karim**

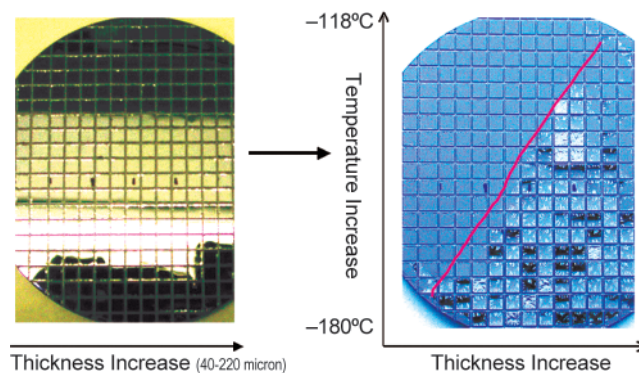
We have developed a Multilens Contact Adhesion Test (MCAT) to meet the demands of industry for a quantitative combinatorial technique to measure the adhesive strength of polymeric interfaces. Specifically, the MCAT involves a planar array of spherical caps (Figure 1(a)) contacting and separating from a complementary substrate. Using optical tracking of the contact area at each spherical cap and the measured relative displacement, we quantify the interfacial strength on an absolute scale. By fabricating the planar array, complementary substrate, or both using established gradient processing techniques, a combinatorial map of polymer adhesion can be produced. This combination of the MCAT with gradient library processing facilitates high-throughput screening of the effect of polymer adhesion phenomena. Initial demonstration measurements explored the effect of annealing temperature and coating thickness on the self-adhesion of thin polystyrene and



**Figure 1:** (a) Planar MCAT configuration; (b) Macrolens with surface microlenses; (c) Time evolution of multilens contact areas at fixed displacement. Color indicates time.

poly(dimethyl siloxane) films. The MCAT can also quantify weak surface forces that dictate interface formation. For these investigations, a modified geometry is used where the microlens array is cast on a large curvature surface, or macrolens (Figure 1(b)).

During the cooling of a laminated material (film/substrate) system with an initial interfacial crack at a stress-free edge, a further crack extension (debonding) along the interface occurs at a critical temperature due to the stress concentration near the crack tip. The Edge Delamination Test (EDT) is based on this debonding mechanism using the thermal stresses generated by the mismatch of the coefficients of thermal expansion during the cooling to cause separation of the film from the substrate. Subsequently, the film-substrate adhesion energy can be deduced from the failure map if the internal stress-temperature relation of the film is known. We use a test film that fails (debonds) due to the stress generated by an over-coating polymer layer having a thickness gradient. The bi-layer film is diced into a square grid pattern to form an array of individual edge delamination samples on the substrate (Figure 2). To initiate debonding, the specimen is quenched into a severe temperature gradient applied in the direction orthogonal to the thickness gradient. Simulations (not shown) predict interfacial debonding to occur in regions exceeding a critical stress that depends on the combination of local temperature and film thickness. The red-line failure map of Figure 2 as a function of temperature and film thickness is qualitatively in agreement with these simulations. Such a reliability map can be used to quantify the critical bond energy of the thin film in the sub-micron thickness range for semiconductor applications.



**Figure 2:** The experimental result of the combinatorial edge delamination test for PMMA adhesion to silicon substrate.

### Contributors and Collaborators

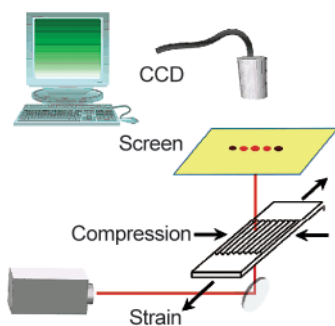
A.J. Crosby, R. Song, M. Chiang, A. Karim, E.J. Amis (Polymers Division, NIST)

## High-Throughput Mechanical Properties of Polymer Films

Thin films are increasingly being used in technological applications involving dielectric coatings, resist layers for lithography, electronic packaging, optical coatings, etc. The mechanical properties of these films is paramount for their effective utilization, but no high-throughput protocol to measure the mechanical properties of thin films has been available. We have developed a novel technique that rapidly measures the Young's modulus of thin film coatings from MPa to GPa. We also extend the copper grid test, a well-established method for studying crazing and fracture of glassy polymer films, to measurements in gradient thin film libraries.

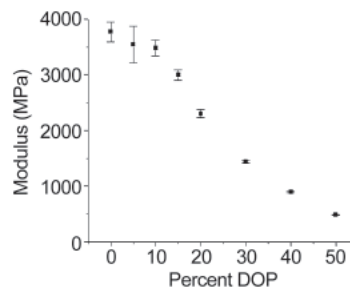
**Christopher M. Stafford and Alamgir Karim**

As technology continues to move towards smaller, thinner, lighter devices, polymeric thin films are increasingly being used as protective coatings, adhesives, and functional coatings in such devices. There is a growing need for test methods that can measure the mechanical properties (modulus, viscoelasticity, plastic deformation) of thin films since these material properties play a vital role in the ultimate performance of the end product. We present here a reliable, high-throughput technique by which the elastic modulus of a thin polymer film can be measured. This technique relies upon a highly periodic strain-induced buckling instability that arises from a mismatch of the moduli of a relatively stiff polymer coating on a soft silicone sheet. The modulus-dependent buckling wavelength, typically (1 to 10)  $\mu\text{m}$  for 100 nm thick glassy films, is rapidly measured by conventional light scattering. This technique is ideally suited for measurements of combinatorial libraries prepared by existing methodologies developed at NIST.



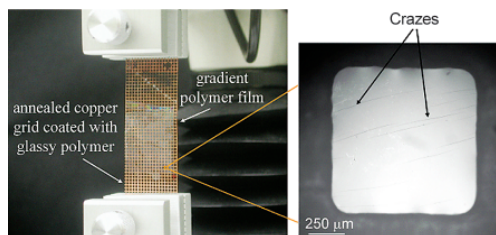
**Figure 1:** Setup of combi-thin film modulus apparatus.

As an example, Figure 2 shows the measured modulus of polystyrene films upon addition of dioctylphthalate (DOP). The modulus decreases in a sigmoidal fashion with increased loading of DOP. We are currently extending this technique to nanocomposite films, UV-curable coatings and adhesives, and multicomponent formulations.



**Figure 2:** Modulus of PS films as a function of loading (mass fraction) with a common plasticizer, dioctylphthalate.

The ductile copper grid to support and deform thin polymer films, developed more than 20 years ago for uniform films, is extended to study fracture properties of thin polymer films with gradient properties (i.e., molecular weight, tacticity, etc.). To validate and demonstrate this approach, the effects of film thickness,  $h$ , on craze structure was studied by transferring thickness gradients of isotactic polystyrene prepared by flow coating onto a copper grid and applying uniaxial strain (Figure 3). The crystallization morphology and kinetics of isotactic polystyrene (i-PS) were mapped previously using high-throughput techniques. Crazes, which lead to fracture in glassy polymers, can then be correlated to the morphology of crystalline i-PS on identically prepared gradient libraries to ultimately obtain structure– (mechanical) property relationship in a combinatorial manner.



**Figure 3:** A gradient thickness film of i-PS supported on a copper grid and mounted on a strain stage (left). An optical image of post-strain of one square grid showing craze structures (right).

“The authors have come up with a novel way to quickly measure the elastic modulus of thin film samples. I am convinced that this technique will quickly find its way to industrial application and help in the development of better materials.”

**K. Krishana**  
Sr. Scientist, Rhodia Inc.

### Contributors and Collaborators

C.M. Stafford, C. Harrison, K. Beers, A.J. Crosby, A. Karim, E.J. Amis (Polymers Division, NIST)

## Mapping the Effects of a Nucleating Agent on Polymer Crystallization

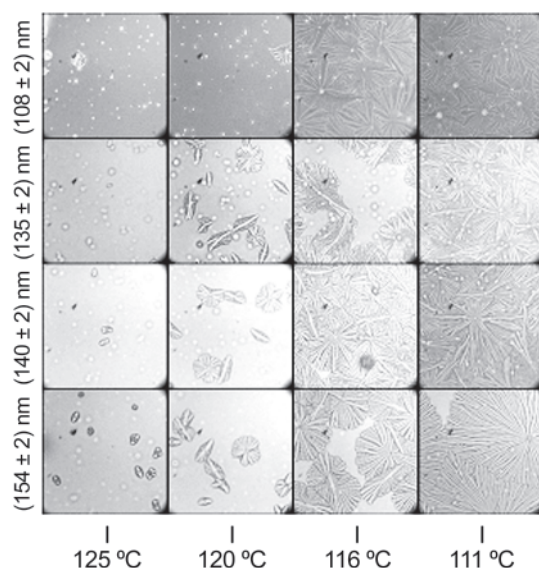
Crystallization rate is an important parameter in industrial processing of crystalline polymeric materials, affecting the cost-effectiveness of applications by influencing factors such as mold dwell times and processing temperatures. Nucleating agents can be used to control the rate of crystallization and affect the clarity, fracture toughness, and overall modulus in the host material. Using high-throughput methods, we investigate as a function of film thickness and undercooling temperature the effectiveness of 4-biphenyl carboxylic acid as a nucleating agent for polypropylene thin films.

**Marlon L. Walker and Alamgir Karim**

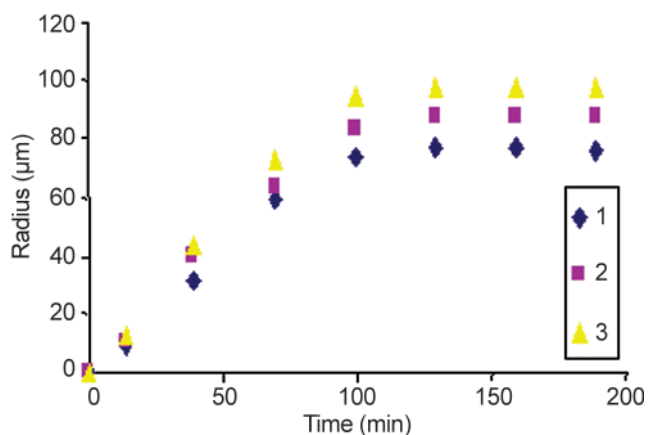
The advent of new catalytic techniques have resulted in the production of a wide variety of new polypropylenes with different molecular masses, branch content, and potentially novel chemistries. Use of these materials in various applications requires comprehensive evaluation of parameters such as crystallization rate, which directly affects the cost-effectiveness of the process. Nucleating agents can influence crystallization rate and alter the parameters in processing, allowing for better control of crystallization. A high-throughput method of evaluating the effects of nucleating agents on crystallization rate as a function of film thickness ( $h$ ) and temperature ( $T$ ) has been developed based on the gradient film technology developed in the Polymers Division at NIST.

Isotactic polypropylene films, neat and with 4-biphenyl carboxylic acid (BCA) as the nucleating agent, were made using the NIST flow coating technique. The film samples, having a gradient in  $h$  nominally between 50 nm and 150 nm, were annealed at 190 °C and then directly placed on a cooling stage possessing a temperature gradient between 100 °C and 140 °C, orthogonal to the thickness gradient. Optical images were taken before annealing and at regular intervals after placement on the gradient stage, allowing the evaluation of film behavior as a function of thickness and undercooling temperature with respect to time.

In Figure 1 is a subset of the optical data set taken using combinatorial methodologies for polypropylene with BCA. This montage of images represents 16 different ( $h, T$ ) combinations at virtually the same time. It can be seen readily that crystallite size and extent of crystallization increase with higher undercooling (lower temperatures). Figure 2 is a graph of the radial growth in time of the three crystallites present at the point in the optical subset located at a film thickness of 140 nm  $\pm$  2 nm and 125 °C. Crystallite growth can be followed as a function of time, yielding valuable information concerning the effectiveness of nucleating agents in crystallization.



**Figure 1:** Subset of high-throughput data set of optical images of polypropylene containing 4-biphenyl carboxylic acid undercooled at different temperatures for different thicknesses. Magnification is 500X.



**Figure 2:** Crystallite sizes as a function of time at 125 °C and an initial film thickness of approximately 140 nm.

These results help establish a high-throughput methodology for evaluating the effects of nucleating agents in polypropylene thin films. Ongoing projects in the Division indicate that this combinatorial method of nucleating agent evaluation is applicable to other polymer materials as well.

### Contributors and Collaborators

M.L. Walker, S.A. Buntin (Surface and Microanalysis Science Division, NIST); A. Karim, E.J. Amis (Polymers Division, NIST); A.P. Smith (Columbian Chemical Company, Marietta, GA)

## Interface of Materials with Biology

New materials and devices are radically changing the medical treatment of injury and disease, yet because of the rapid growth of this segment of the materials industry, an adequate measurement infrastructure does not yet exist. The program on the Interface of Materials with Biology develops measurement methods, standards, and fundamental scientific understanding at the interface between materials science and biological science. Within the health care industry, we focus on dental and medical sectors that apply synthetic materials for replacement, restoration, and regeneration of damaged or diseased tissue.

Five major activities constitute this program:

- The dental industry is primarily composed of small manufacturers with very little R&D capability. The dental materials projects, carried out in collaboration with the American Dental Association, located in the Polymers Division, fill that gap by developing improved materials and techniques, patenting and licensing these inventions, and, most importantly, providing technical assistance to the licensees for producing and improving their products. This has provided U.S. companies with products that successfully compete in a worldwide market. Our research focuses on improved understanding of the synergistic interaction of the phases of polymer-based composites and the mechanisms of adhesion to dentin and enamel. This approach will ultimately lead to materials with improved durability, toughness and adhesion to contiguous tooth structure.
- In this era of interdisciplinary approach to research, the Materials Reliability Division is providing an added dimension to studying diseases and cellular function. By taking a physical/mechanical approach to how cells function, respond, and remodel, we are able to provide insight into the progression of diseases using knowledge and skill sets typically absent in the biomedical community. We concentrate on mechanical property metrology for several biological systems, including natural as well as engineered tissue and spanning a considerable size range from individual neurons and muscle cells to complete pulmonary arteries. This necessitates the development of unique mechanical testing platforms ranging from electrical and mechanical probes of individual living cells to biaxial stressing systems. We interpret our measurements by focusing on the roles of structural elements such as cells, composition, and tissue anisotropy. This classical materials science approach to understanding properties is proving invaluable to the biomedical community.
- The tissue engineering industry shows the potential for explosive growth in the coming years as biomedical research is moving from academic science to industrial application at an increasing rate. Work in the Polymers

Division seeks to bridge the gap between knowledge generation by cell biologists and product development in industry. In collaboration with the Chemical Science and Technology Laboratory, we are developing measurement methodologies and reference materials to use in assessing interactions in complex systems of living cells with synthetic materials. The expected outcomes of this work include methods to use reference substrates that induce specific cellular responses and engineered DNA vectors that act as fluorescent reporters of cellular responses.

- Regenerating form and function to bone defects in an elderly, osteoporotic population of Americans is a daunting challenge. To meet this challenge, the Polymers Division is collaborating with the American Dental Association to develop metrology methods to characterize the biocompatibility of synthetic bone grafts. Quantitative methods being developed include assays for adhesion, viability, proliferation, and differentiation of bone cells, as well as optical coherence tomography and confocal microscopy for measuring tissue ingrowth. The combinatorial approach is used to rapidly identify compositions and surface features that provide desirable properties such as biocompatibility and mechanical durability.
- The NIST Center for Neutron Research and the NIST Biotechnology Division are engaged in the study of biomimetic films that serve as models of cell membranes and which are of fundamental importance in understanding such key biological processes as phospholipid self-assembly, molecular recognition, and cell-protein interactions. Recent improvements in neutron reflectometry at the NCNR, coupled with advances in biomimetic film fabrication at metallic interfaces pioneered in the Biotechnology Division, afford enhanced sensitivity for probing membranes and membrane-protein complexes. New phase sensitive measurement techniques and model-independent data analysis methods have demonstrated the feasibility of obtaining reliable depth profiles of membrane structures in contact with biologically relevant aqueous environments, achieving subnanometer spatial resolutions.

Fundamental to much of the work in this program is the recognition that surfaces and interfaces play a critical role in biological systems and, in particular, in the interactions of synthetic or designed materials with biological systems and function. By providing the unique expertise in the NIST Materials Science and Engineering Laboratory to characterization of surfaces and interactions at interfaces in biomaterials, we will accelerate the introduction of improved materials and help provide the means to assure quality control that is critical to this industry.

Contact: Eric J. Amis

## Structure–Property Relationships in Dental Polymers

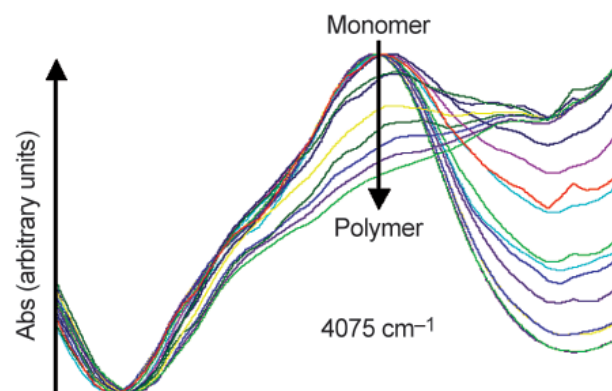
*Polymer based dental materials are increasingly being used in dentistry and allied biomedical fields. As part of a joint research effort supported by the National Institute of Dental and Craniofacial Research and also involving collaboration with the American Dental Association Health Foundation Paffenbarger Research Center, NIST is providing the dental industry and the dental profession with a comprehensive knowledge base regarding polymeric dental materials that will help elucidate the in vitro and in vivo performance of these materials.*

### Joseph M. Antonucci

This project is directed toward building fundamental understanding of how monomer structure, comonomer compositions, and initiator systems can influence the photopolymerization process and matrix formation of polymeric dental materials, e.g., composites. With composites, the influence of both the filler and interfacial phases also must be considered as critical factors affecting matrix formation and ultimate composite properties. Usually, dental matrix polymers are described simply as highly cross-linked networks with little or no chemical structural characterization done beyond a measurement of final vinyl conversion. Although the results of physical and mechanical property testing also have been widely reported for dental polymers, these data are more useful when correlated with the effects of monomer structural and resin compositional variations on the development of cross-linked polymers. A similar but more difficult challenge exists with regard to finding generalizable structure–property correlations in composites.

In addition, this project is intended to define the currently unknown co-reactivity of structurally different co-monomers than those that are typically used in the formation of dental polymers. For lack of this type of information, the reactivity and cross-linking potential of dental methacrylate monomers are generally assumed to be equal. The use of selected model monomers is designed to demonstrate the influence of specific structural features on monomer reactivity and polymer properties. Such information should have a significant impact on the processing and development of improved materials. An examination of the polymerization of non-methacrylate vinyl monomers, such as vinyl esters and vinyl ethers, with conventional dental monomers such as Bis-GMA offers a means to modify network formation and ultimately dental polymers/composites. For example, it was shown that modification of a typical Bis-GMA dental resin composite with neo-decyl vinyl ester improved flexural strength when compared to that of the unmodified composite.

Recently, we employed near infrared (NIR) spectroscopy in the analysis of dental polymers and demonstrated its ability to monitor both vinyl conversion and water absorption. Also with NIR spectroscopy, it is relatively easy to determine how the filler phase of composites can influence both vinyl conversion and water uptake of clinically relevant size composite specimens. In contrast to conventional gravimetric water sorption studies, NIR spectroscopy allows the differentiation between free water and water that is hydrogen-bonded either with one or with two hydrogen bonds, thereby elucidating the type of hydrophilicity of the polymer network. NIR spectroscopy also can be used, more effectively than mid-IR spectroscopy, to monitor the conversion of oxirane (epoxy) monomers during and after their photo-cationic polymerization (Figure 1) as well as the synthesis of hydroxylated methacrylates from epoxy monomers such as glycidyl methacrylate.



**Figure 1:** Siloxane-epoxide/TEGDMA comonomer mixtures.

Currently, we are investigating several high-molecular mass-alternative resins to Bis-GMA, as well as new types of high-molecular mass-diluent monomers, for their efficacy in reducing residual vinyl unsaturation, polymerization shrinkage, stress and water uptake. Alternative initiator systems are also under investigation in an effort to enhance photopolymerization efficiency and improve the quality of polymer matrix formation. The results of these studies should extend well beyond the dental materials venue to include a significant number of other applications that rely on the rapid formation of cross-linked polymeric networks as a means of achieving materials with optimal properties.

### Contributors and Collaborators

J.M. Antonucci, M.D. Weir, D.W. Liu, N.D. Richards (Polymers Division, NIST); S. Dickens (American Dental Association Health Foundation Paffenbarger Research Center); J.W. Stansbury (University of Colorado, Boulder)



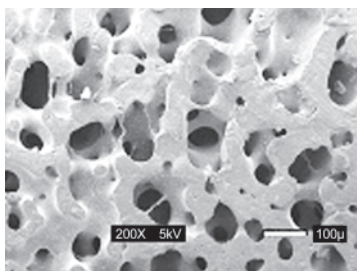
## Characterization and Modeling of Tissue Engineering Scaffolds

*Polymeric scaffolds form the basis for a wide range of potential therapies being developed by the tissue engineering industry. In the Polymers Division, we are developing a measurement infrastructure to meet the needs of this growing field by providing reference materials and test methods for measuring structure, mechanical properties, rates of cell infiltration and adhesion, and immune responses.*

### Newell Washburn and Francis Wang

The tissue engineering industry is faced with a broad range of complex measurement issues. The devices these companies are producing have strict requirements on mechanical performance, ability to guide tissue development, and the inflammatory responses provoked by the implants. We are developing a measurement infrastructure to meet these needs. Of particular importance is the development of meaningful *in vitro* tests for assessing these parameters. Such tests would greatly reduce research and development costs where screening products in animal tests represents a significant expenditure.

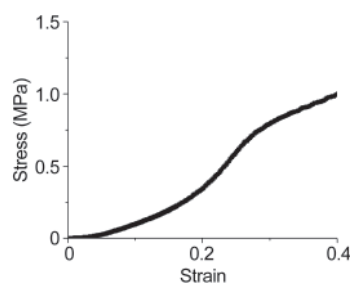
Porous polymeric scaffolds are the basis for many of the therapies currently under development. A representative scaffold, produced in our labs, is shown in Figure 1. The device is made of a biocompatible polyester and has a continuous network of pores with characteristic diameter on the order of 100  $\mu\text{m}$ .



**Figure 1:** Porous polymer scaffold for tissue engineering applications.

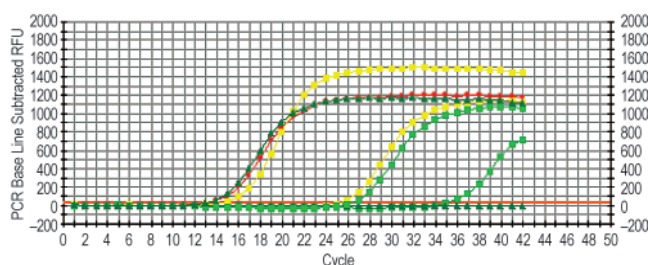
This porous network is designed to allow cells to infiltrate and permeate the scaffold to initiate tissue development. The rate at which this process occurs is a crucial factor in determining the performance of the device. We are developing transmigration assays to measure this using a collagen gel as a model extracellular matrix. Scaffolds are embedded in a gel and removed after several days. The rate of cell migration from the gel to the scaffold is assessed using fluorescence microscopy and correlated with structural features of the scaffold surface.

The mechanical performance of the scaffold is also greatly influenced by the microstructure. The bulk modulus may be reduced by two orders of magnitude over that of the solid polymer, which may limit their use in load-bearing applications. A sample stress-strain curve is shown in Figure 2 and the nonlinear response is attributed to failures occurring in different structural elements. The elements leading to such failures need to be controlled during device processing, and we are developing sensitive mechanical tests to be complemented by three-dimensional structural characterization in order to prepare guidelines for quality control.



**Figure 2:** Stress-strain curve for tissue engineering scaffold.

Once implanted, these devices can elicit serious inflammatory responses from the patient. The main cells responsible for these responses are the macrophage, which coat the device and attempt to consume it. Macrophage response is mediated through soluble signaling molecules called cytokines, and we are adapting real-time polymerase chain reaction (RT-PCR) techniques to help predict cellular response (Figure 3).



**Figure 3:** Sample RT-PCR experiment showing a trial using 4.4  $\mu\text{m}$  and 1.4  $\mu\text{m}$  poly(methyl methacrylate) particles and 264.7 macrophages.

### Contributors and Collaborators

N. Washburn, F. Wang, L. Bailey, C. Simon, C. Khatri (Polymers Division, NIST); T. Quinn, D. McColskey (Materials Reliability Division, NIST); W. Guthrie (Statistical Engineering Division, NIST); *Industrial and academic collaborators:* NIAMS, NIDCR, FDA, ATS, Rutgers

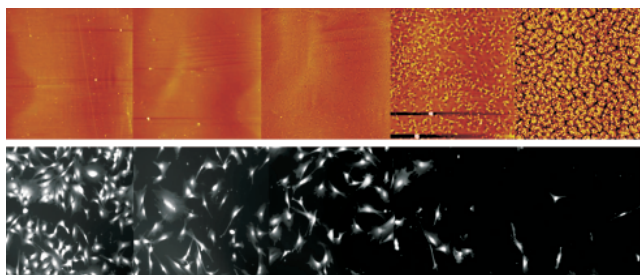
## Metrology for Tissue Engineering

The tissue engineering industry is developing new materials and devices that promise to radically change the medical treatment of injury and disease. In order to do so, an adequate measurement infrastructure is necessary to bridge the gap between cell biologists, materials scientists, product engineers, and regulatory agencies. To meet this need, we are developing a library of reference materials, high-throughput techniques for screening material libraries, and an informatics approach for data analysis and interpretation.

### Scott Kennedy and Newell Washburn

The Polymers Division seeks to extend high throughput materials characterization into the realm of biomaterials and tissue engineering. Considering the vast parameter space facing the tissue engineering industry, extending NIST expertise into this arena follows naturally. The effort has evolved into developing three interwoven toolsets: material library preparation, high-throughput screening, and statistical treatment of population distributions.

The library of materials available for investigating cell-biomaterial interactions continues to expand. At present, the library encompasses the following material parameter space: surface energy, crystallinity, roughness, topological patterns, compliance, degradability, and a limited range of chemical patterns. Gradient sample preparation facilitates exploring these discrete parameters; Figure 1 illustrates the power of the gradient methodology applied to crystallinity.



**Figure 1:** AFM images taken across a PLA film annealed under a temperature gradient (top), and fluorescence microscopy images of cells fixed and stained 72 hours after uniform seeding (bottom).

This work has attracted interest from potential customers as the expanding library of gradient materials may help to identify and develop benchmark SRMs. Toward this end, strategies are being fleshed out for preparing orthogonal gradients and decorating surfaces with functional groups. An automated peptide synthesizer is also being integrated into this effort.

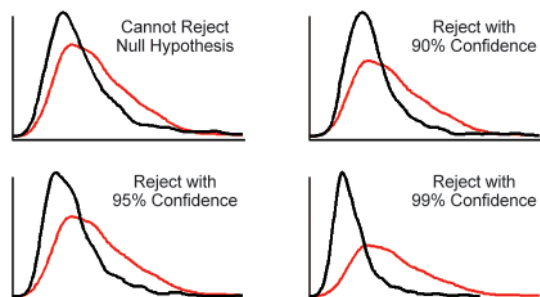
Initial progress in library preparation exposed image acquisition and analysis as bottlenecks in the high-throughput approach. The following highlights

underscore the framework established for streamlining the process of screening cell-material interactions.

- A fully automated, multi-channel image acquisition system is operational and capable of z-stack compiling for auto-focusing or extended depth of field imaging.
- A versatile image analysis software package with integrated macros reduces image files to data files.
- A versatile graphing and analytical software package with integrated macros performs rigorous statistical analysis and facilitates data visualization.

At present, image files are reduced to data files that document general cellular information such as area, perimeter, roundness, and asymmetry. As more sophisticated cell-staining protocols are added to the existing arsenal, data files will include more specific information describing cell populations.

The power of the streamlined process manifests itself in that information from thousands of *adherent* cells can be documented in a reasonable amount of time. Thus, screening cell-biomaterial interactions can now be based on a rigorous statistical comparison of large, unbiased populations. The significance of this effort was evident at a recent Gordon Conference where this work generated interest amongst industrial and academic representatives alike. Figure 2 illustrates a working standard by which cell populations could be qualitatively and quantitatively compared.



**Figure 2:** Population distributions from a PCL control (red) and structurally similar sugar containing polyesters (black). All distributions were smoothed using a kernel density estimator and represent a sampling of approximately 1000 cells. Quantitative comparisons result from a two sample Kolmogorov–Smirnov test against the null hypothesis that both samples come from the same distribution.

### Contributors and Collaborators

S. Kennedy, N. Washburn, L. Bailey, A. Sehgal, C. Simon (Polymers Division, NIST); A. Plant, J. Elliott (Biotechnology Division, NIST); W. Guthrie (Statistical Engineering Division, NIST); *Industrial and academic collaborators:* NICHHD, NIDCR, FDA, ATS, ILS, Rutgers University, Brooklyn Polytech

## Materials for Micro- and Optoelectronics

U.S. microelectronics and related industries are in fierce international competition to design and produce smaller, lighter, faster, more functional, and more reliable electronics products more quickly and economically than ever before. At the same time, there has been a revolution in recent years in new materials used in all aspects of microelectronics fabrication.

Since 1994, the NIST Materials Science and Engineering Laboratory (MSEL) has worked closely with the U.S. semiconductor, component, packaging, and assembly industries. These efforts led to the development of an interdivisional MSEL program committed to addressing industry's most pressing materials measurement and standards issues central to the development and utilization of advanced materials and material processes. The vision that accompanies this program — to be a key resource within the Federal Government for materials metrology development for commercial microelectronics manufacturing — is targeted through the following objectives:

- Develop and deliver standard measurements and data;
- Develop and apply *in situ* measurements on materials and material assemblies having micrometer- and submicrometer-scale dimensions;
- Quantify and document the divergence of material properties from their bulk values as dimensions are reduced and interfaces contribute strongly to properties;
- Develop models of small, complex structures to substitute for, or provide guidance for, experimental measurement techniques; and
- Develop fundamental understanding of materials needed in future micro- and opto-electronics and magnetic data storage.

With these objectives in mind, the program presently consists of projects led by the Metallurgy, Polymers, Materials Reliability, and Ceramics Divisions that examine and inform industry on key materials-related issues. These projects are conducted in concert with partners from industrial consortia, individual companies, academia, and other government agencies. The program is strongly coupled with other microelectronics programs within government and industry, including the National Semiconductor Metrology Program (NSMP) at NIST.

Materials metrology needs are also identified through industry groups and roadmaps including the International Technology Roadmap for Semiconductors (ITRS), International SEMATECH, the IPC-Embedded Passive Devices Taskgroup, the IPC Lead-free Solder Roadmap, the National Electronics Manufacturing Initiative (NEMI) Roadmap, the Optoelectronics Industry Development Association (OIDA) roadmaps, and the National [Magnetic Data] Storage Industry Consortium (NSIC).

Although there is increasing integration within various branches of microelectronics and optoelectronics, the field can be considered to consist of three main areas. The first, microelectronics, includes needs ranging from integrated circuit fabrication to component packaging to final assembly. MSEL programs address materials metrology needs in each of these areas, including, for example, lithographic polymers and electrodeposition of interconnects, electrical, mechanical, and physical property measurement of dielectrics (interlevel, packaging, and wireless applications), and packaging and assembly processes (lead-free solders, solder interconnect design, thermal stress analysis, and co-fired ceramics).

The second major area is optoelectronics, which includes work that often crosses over into electronic and wireless applications. Projects currently address residual stress measurement in optoelectronic films, and wide bandgap semiconductors. Cross-laboratory collaborations with EEEL figure prominently in this work.

The third area is magnetic data storage, where the market potential is already large and growing and the technical challenges extreme. NSIC plans to demonstrate a recording density of 40 times today's level by 2006. To reach these goals, new materials are needed that have smaller grain structures, can be produced as thin films, and can be deposited uniformly and economically. New lubricants are needed to prevent wear as the spacing between the disk and head becomes smaller than the mean free path of air molecules. MSEL is working with the magnetic recording industry to develop measurement tools, modeling software, and magnetic standards to help achieve these goals. MSEL works in close collaboration with the Electronics and Electrical Engineering Laboratory, the Physics Laboratory, the Information Technology Laboratory, and the Manufacturing Engineering Laboratory as partners in this effort.

Contact: Eric K. Lin

## Characterization of Porous Low-k Dielectric Constant Thin Films

*NIST is working to provide the semiconductor industry with unique on-wafer measurements of the physical and structural properties of porous thin films important to their use as low-k dielectric materials. The methodology utilizing several complementary experimental techniques to measure the average pore and matrix morphology has been expanded to include pore size distributions. New methods have been developed to measure closed pore content and matrix morphology in films having complex structures with any morphological type.*

**Barry J. Bauer and Wen-li Wu**

The next generation of integrated circuits will require feature sizes that demand new low-k interlayer dielectric materials. To address problems with power consumption, signal propagation delays, and crosstalk between interconnects, dielectric constants will have to reach unprecedented values. One avenue to low-k dielectric materials is the introduction of nanometer scale pores into a solid film to lower its effective dielectric constant. While these modifications change the dielectric constant favorably, other important parameters such as physical strength and barrier properties will also change, often in an unfavorable way. Characterization of the pore structure is crucial to rapid development of new dielectric materials, and new measurement methods are necessary.

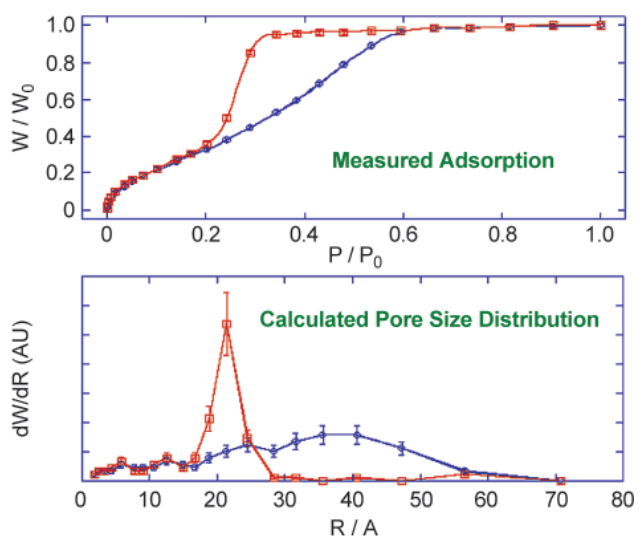
The small sample volume of 1  $\mu\text{m}$  films and the need to characterize the films on silicon wafers narrows the number of available measurement methods. We have been providing standard characterization using a combination of small angle neutron scattering (SANS), high-resolution x-ray reflectivity (HRXR), and ion scattering techniques. These measurements are performed directly on films supported on silicon substrates so that processing effects can be investigated. New methods are required, however, to provide more detailed information necessary to complete the product development.

During the past year, we have continued our efforts on characterization of current industrially-relevant materials through International SEMATECH, and by new collaborations with Dow Chemical and IBM. More significantly, we have perfected new techniques for more thorough and accurate film characterization.

International SEMATECH, a consortium of microelectronics companies, provided more than 20 separate samples for characterization by NIST. The structural information provided by NIST is placed into a master database that includes data from a variety of sources, detailing both the structural and material properties needed to evaluate candidate materials. Member companies make extensive use of the data to

guide the development of low-k dielectric materials for integration into future devices.

Finally, we have evaluated and perfected new measurement methods to more thoroughly and accurately characterize pore and matrix morphology. Capillary porosimetry has been applied to HRXR measurements to determine pore size distributions, rather than simple averages. By the use of a carrier gas and control of vapor pressure through thermal methods, the accuracy and speed of the measurements have greatly improved. Based on these findings, an automated measurement system has been designed and is under construction with the ultimate goal of providing a measurement technique that can be transferred to the materials suppliers and chip manufacturers.



**Figure 1:** Representative mass gain and pore size distribution calculated from HRXR porosimetry measurements (AU = arbitrary units).

New techniques have been developed that measure SANS from films that have been infused by mixtures of normal toluene and toluene in which hydrogens have been replaced by deuterium. The match point measures where the neutron contrast matches that of the wall material. By filling the open pores with contrast match fluids, SANS reveals the closed pore content and size. The relative open and closed pore content is becoming increasingly important to low-k applications.

### Contributors and Collaborators

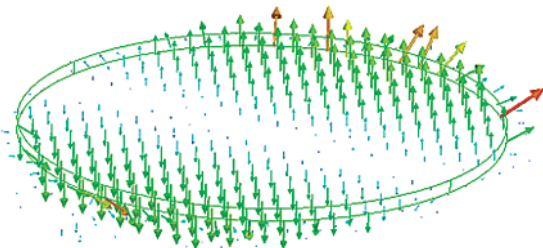
B.J. Bauer, H.J. Lee, R.C. Hedden, C.L. Soles, H. Wang, D. Liu, W.L. Wu (Polymers Division, NIST); C. Glinka (NIST Center for Neutron Research); J. Wetzel, J. Lee (International SEMATECH); B. Landes (Dow Chemical); M. Baklanov (IMEC); D. Gidley (University of Michigan); W. Chen, E. Moyer (Dow Corning); S. Yang (Lucent)

## Dielectric Metrology for Polymer Composite Films in the Microwave Range

*Novel dielectric hybrid materials based on organic resins and ferroelectric ceramics with high dielectric constants have been identified by the industry as key dielectrics for advancing miniaturization and functional performance of microwave electronics. The objective of this project is the development of broadband dielectric metrology for such materials and fundamental understanding of the high frequency relaxation mechanism in relation to structural and molecular attributes.*

**Jan Obrzut**

We have developed an accurate broadband measurement technique that enables dielectric measurements at microwave frequencies of up to several GHz. The broadband test methods currently in use by the industry are based upon a lumped element approximation and are limited to frequencies below a few hundred megahertz. Our new technique is based on the observation and theoretical analysis of fundamental mode propagation in thin film dielectrics terminating a coaxial air-filled transmission line. The 3D vector plot of the electric field of the first fundamental mode, simulated inside a high-k specimen, is shown in Figure 1.



**Figure 1:** The vector plot of the electric field,  $E$ , of the first fundamental mode inside the film specimen ( $\epsilon^* = 34.6 - j1.6$ ) terminating an AP-7 coaxial line. The arrows indicate the direction and strength of the electric field  $E$ .

In contrast to the assumption of the lumped element model, the field in the specimen section is not uniform. At a resonant frequency of about 8.2 GHz, the magnitude of the electric field,  $E$ , shows two maxima localized near the edge of the specimen, while the minimum magnitude of field  $E$  extends along the specimen diameter. The corresponding plot of the magnetic field,  $H$ , is parallel to the propagation direction. Both  $E$  and  $H$  fields appear to decay rapidly at the boundary between the high-k dielectric and air. The results of numerical simulations confirm our earlier experimental analysis that, at microwave frequencies, the film specimen becomes a transmission line with propagation direction along the film diameter rather than its thickness.

The new broadband methodology enables measurements at frequencies of 100 MHz to 10 GHz with the precision required by new electronic technologies. In partnership with the Institute for Interconnecting and Packaging Electronic Circuits, IPC, we initiated a standard test method development and chair the IPC-D37-d test method subcommittee for Embedded Passive Devices. We guided the design of the test protocol and made arrangements with co-sponsoring member companies for round robin evaluation.

Our capability to measure the dielectric relaxation times in the sub-nanosecond regime and the relaxation strength for wide range of dielectric permittivity values is used to quantify dispersion, alignment, and structure in hybrid materials. Using the broadband study, we demonstrated that the composites of organic polymer resins filled with ferroelectric ceramics exhibit a dominant intrinsic high-frequency relaxation behavior. Such dielectric properties were beneficial in eliminating the electromagnetic noise in processors and logic devices. We have confirmed that the fastest dielectric relaxation process is controlled by the dipolar dynamics of the polymer matrix while the dielectric loss arises from the difference in coupling between the relaxed and unrelaxed dipoles. Our new numerical models can quantitatively correlate the dependence of the real and imaginary parts of the complex permittivity on the volume fraction of the ceramic filler.

We have developed constrained regularization algorithms to obtain a continuous distribution function of relaxation times. The method is able to resolve multiple relaxation processes without any *a priori* assumptions about their character. It may be generalized to different types of fundamental relaxation processes and not restricted to a superposition of Debye-like functions. This approach will help judge the identity between microscopic and macroscopic relaxation behavior of polymer composite systems. It also allows us to link broadband dielectric spectroscopy with other techniques such as time domain spectroscopy, photon correlation spectroscopy and NMR.

### Contributors and Collaborators

O. Anopchenko, N. Noda and J. Obrzut (Polymers Division); B. Rust (Mathematical and Computational Sciences Division); R. Croswell (Motorola); R. Charbonneau (Storage Tech.); D. McGregor (DuPont); T. Hubbing (University of Missouri); R. Greenlee (Merix); J. Murry (Litton); Tom Newton (IPC); R. Foly (DOD); J. Peiffer (3M); L. Patch (NCMS); D. Senk (Shipley); R. Sheffield (Nortel)

## Polymer Photoresists for Next-Generation Lithography

*Photolithography, the process used to fabricate integrated circuits, is the key enabler and driver for the microelectronics industry. As lithographic feature sizes decrease to the sub-100 nm length scale, significant challenges arise because both the image resolution and the thickness of the imaging layer approach the macromolecular dimensions characteristic of the polymers used in the photoresist film. Unique high-spatial resolution measurements are developed to reveal limits on materials and processes that challenge the development of photoresists for next-generation sub-100 nm lithography.*

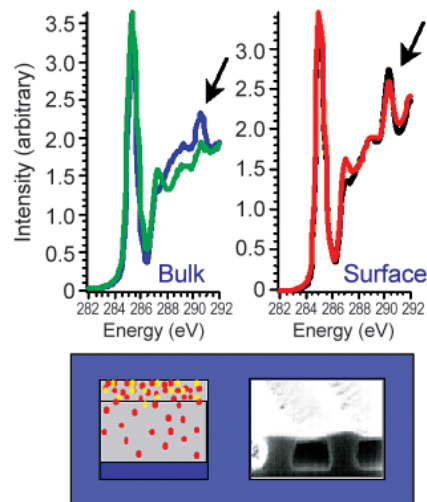
**Eric K. Lin**

Photolithography is the driving technology used by the microelectronics industry to fabricate integrated circuits with ever decreasing sizes. In this process, a designed pattern is transferred to the silicon substrate by altering the solubility of areas of a polymeric photoresist thin film through an acid catalyzed deprotection reaction after exposure to radiation through a mask. To fabricate smaller features, next-generation photolithography will be processed with wavelengths of light requiring photoresist films less than 100 nm thick and dimensional control to within 2 nm. Material and transport issues arise when fabricating structures over these length scales. To date, the materials and processes needed to fabricate sub-100 nm features have not been selected.

To advance this key fabrication technology, we work closely with industrial collaborators to develop and apply high-spatial resolution and chemically specific measurements to understand changes in material properties, interfacial behavior, and process kinetics at nanometer scales and to provide high-quality data needed in advanced modeling programs.

Over the past year, we have applied and enhanced unique measurement methods and computer simulation tools to provide new insight and detail into the complex physico-chemical processes used in advanced chemically-amplified photoresists. These methods include x-ray and neutron reflectivity (XR, NR), small angle neutron and x-ray scattering (SANS, SAXS), incoherent elastic neutron scattering (IENS), near-edge x-ray absorption fine structure (NEXAFS), combinatorial methods, x-ray standing waves with fluorescence (XSW), nuclear magnetic resonance (NMR), molecular dynamics (MD) simulations, and atomic force microscopy (AFM). In particular, XR and NR studies with specially designed model materials were used to profile the reaction front with nanometer resolution (see Highlights), NEXAFS measurements have been extended to depth profile the chemical composition of the top 5 nm of a polymer film surface, SAXS measurements have been performed in transmission on patterned structures to complement

earlier SANS studies, and AFM techniques have been adapted to begin study of the mechanical properties of interfacial polymer layers and structures.



**Figure 1:** NEXAFS carbon-edge spectra from the bulk and surface of a model photoresist before (blue/black) and after exposure and bake (green/red). A delay time of 5 min was imposed after exposure and before a bake. The reaction is incomplete only at the surface (peak signature at arrows) corresponding to surface base (yellow) contamination as illustrated.

Our experimental and theoretical methods have been used to understand important technical problems in the development of next-generation materials. These topics include: the spatial evolution of the reaction-diffusion process as a function of temperature and time; the domain size and distribution of photoacid generator molecules within a model photoresist polymer matrix; the microscopic dynamics of photoresist polymers in thin films; the segregation and distribution of small molecule contaminants, solvents, and moisture in ultrathin polymer layers; investigation of the anti-reflective coating-photoresist interface for material sources of compromised line-profile control; development contributions to the measured line-edge roughness; and the structural characterization of critical dimensions and line-edge roughness in lithographically-fabricated patterned structures.

### Contributors and Collaborators

E.K. Lin, C.L. Soles, J.L. Lenhart, R.L. Jones, V.M. Prabhu, F.W. Starr, J.F. Douglas, P.M. McGuigan, D.L. VanderHart, W.L. Wu (Polymers Division); D.A. Fischer, S. Sambasivan, J. Woicik (Ceramics Division); S.K. Satija, C.J. Glinka (NCNR); D.L. Goldfarb, M. Angelopoulos (IBM T.J. Watson Research Center); B.M. Trinqué, S.D. Burns, C.G. Willson (University of Texas); R. Puligadda, Y. Wang, D. Guerrero (Brewer Science)

## Materials Property Measurements

This program responds both to MSEL customer requests and to the DOC 2005 Strategic Goal of “providing the information and framework to enable the economy to operate efficiently and equitably.” For example, manufacturers and their suppliers need to agree on how material properties should be measured. Equally important, engineering design depends on accurate property data for the materials that are used.

The MSEL Materials Property Measurement Program works toward solutions to measurement problems, on scales ranging from the macro to the nano, in four of the Laboratory’s Divisions (Ceramics, Materials Reliability, Metallurgy, and Polymers). The scope of its activities goes from the development and innovative use of state-of-the-art measurement systems, to leadership in the development of standardized test procedures and traceability protocols, to the development and certification of Standard Reference Materials (SRMs). A wide range of materials is being studied, including polymers, ceramics, metals, and thin films (whose physical and mechanical properties differ widely from the handbook values for their bulk properties).

Projects are directed to innovative new measurement techniques. These include:

- Measurement of the elastic, electric, magnetic, and thermal properties of thin films and nanostructures (Materials Reliability Division);
- Alternative strength test methods for ceramics, including cylindrical flexure strength and diametral compression (Ceramics Division); and
- Coupling micromechanical test methods with failure behavior of full-scale polymer composites through the use of microstructure-based object-oriented finite element analysis (Polymer Division in collaboration with the Automotive Composites Consortium).

The MSEL Materials Property Measurement Program is also contributing to the development of test

method standards through committee leadership roles in standards development organizations such as ASTM and ISO. In many cases, industry also depends on measurements that can be traced to NIST Standard Reference Materials (SRMs). This program generates the following SRMs for several quite different types of measurements.

- Charpy impact machine verification (Materials Reliability Division);
- Hardness standardization of metallic materials (Metallurgy Division);
- Hardness standardization and fracture toughness of ceramic materials (Ceramics Division); and
- Supporting the Materials Property Measurements Program is a modeling and simulation effort to connect microstructure with properties. The Object-Oriented Finite-Element (OOF) software developed at NIST is being used widely in diverse communities for material microstructural design and property analysis at the microstructural level.

In addition to the activities above, the Materials Reliability, Metallurgy, Ceramics, and Polymers Divisions provide assistance to various government agencies on homeland security and infrastructural issues. Projects include assessing the performance of structural steels as part of the NIST World Trade Center Investigation, advising the Bureau of Reclamation (BOR) on metallurgical issues involving a refurbishment of Folsom Dam, advising the Department of the Interior on the structural integrity of the U.S.S. Arizona Memorial, advising the U.S. Customs Service on materials specifications for ceramics, and advising the Architect of the Capitol on repair procedures for cracks in the outer skin of the Capitol Dome.

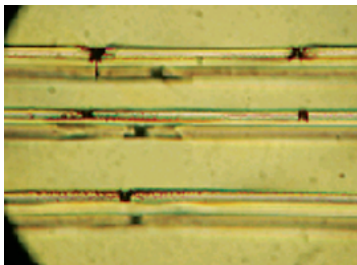
Contact: Gale Holmes

## Characterization and Modeling of Failure in Fiber Composites

Failure prediction is critical to the use of fiber-reinforced composites in many applications. Multi-fiber composites are being used to conduct fundamental studies into the nucleation of failure in fibrous composites. During this research period, we have prepared our first sets of model 3-D E-glass fiber arrays. Research on these arrays showed that matrix cracks induce more damage to the surrounding matrix resin. Below  $50\ \mu\text{m}$ , fiber-fiber interactions, as quantified by the interfacial shear strength, were found to depend on the inter-fiber spacing.

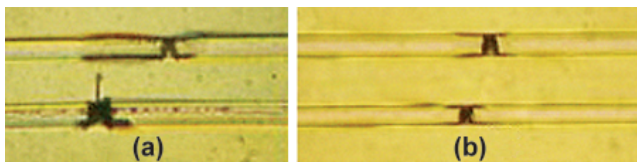
**Gale A. Holmes and Charles C. Han**

During this research year, the first sets of 3-D E-glass fiber arrays were prepared and analyzed (see Figure 1) using sized and un-sized fibers prepared by our industrial collaborators. 3-D arrays are necessary to provide failure behavior information about fully constrained fibers.



**Figure 1:** 3-D Multi-fiber array of sized fibers. The three out of focus fibers are on a plane approximately  $70\ \mu\text{m}$  below the in-focus fibers.

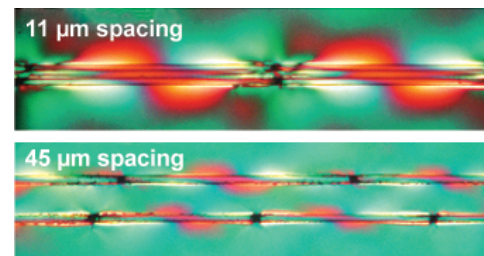
Analytical results indicate that matrix cracks induce more damage to the surrounding matrix resin (see Figure 2), with the intensity of the damage being dependent on the inter-fiber spacing. Initial finite element results (not shown) suggest that the most intense interaction between the shear bands (see 2001 MSEL Annual Report) emanating from the matrix crack shown in Figure 2 and adjacent fibers occurs at a distance of approximately  $15\ \mu\text{m}$ .



**Figure 2:** Pair of sized (a) and un-sized (b) fibers spaced  $\approx 2$  fiber diameters apart. These representative images indicate that matrix cracks induce more damage to the surrounding matrix resin of adjacent fibers.

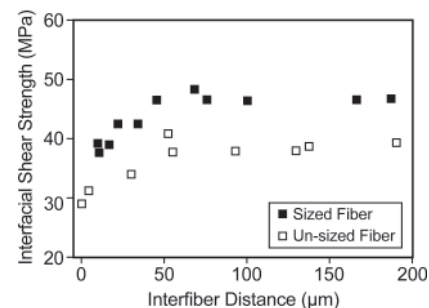
Damage in these specimens will also be monitored by optical coherence tomography (OCT). Images of the multi-fiber specimens can be found in the “Multi-modal Imaging Using Optical Coherence Tomography” project summary.

At a fiber spacing of  $11\ \mu\text{m}$ , the breaks in adjacent fibers are not random. Random fiber breaks between fibers occurs when the inter-fiber distance is at least  $45\ \mu\text{m}$  (see Figure 3).



**Figure 3:** Effect of inter-fiber spacing on randomness of fiber breaks. Note intensity of birefringence pattern between fibers.

The interfacial shear strength exhibited by the individual fibers (sized and un-sized) in an array was found to depend, up to  $\approx 50\ \mu\text{m}$ , on the inter-fiber spacing. The interfacial shear strength above this value was constant (see Figure 4).



**Figure 4:** Interfacial shear strength vs. inter-fiber distance.

Two journal papers are being prepared detailing the results of this research and several supporting publications have been prepared and submitted. Results related to the multi-fiber arrays have also been presented at several conferences (e.g., SAMPE 2002 and ANTEC 2002).

### Contributors and Collaborators

G.A. Holmes, C.K. Moon, W.G. McDonough, C.C. Han, M. Cicerone, M.Y.M. Chiang, J.P. Dunkers (Polymers Division, NIST); E. Pohl (OSi Specialties — Crompton Corporation); Owens Corning



## Materials Structure Characterization

Materials science and engineering is the area of science concerned with understanding relationships between the composition, structure, and properties of materials and the application of this knowledge to the design and fabrication of products with a desired set of properties. Thus, measurement methods for the characterization of materials structure are a cornerstone of this field. MSEL supports a wide array of techniques and instrumentation for materials measurements. Facilities include optical and electron microscopy, optical and electron scattering and diffraction, and major x-ray facilities at the National Synchrotron Light Source (NSLS) at Brookhaven Laboratory, and at the Advanced Photon Source (APS) at Argonne National Laboratory.

Synchrotron radiation sources provide intense beams of x-rays enabling leading-edge research in a broad range of scientific disciplines. Materials characterization using x-rays from synchrotron sources forms a major part of the Materials Structure Characterization Program. This includes the development and operation of experimental stations at the NSLS and at the APS. At the NSLS, NIST operates a soft x-ray station in partnership with Dow and Brookhaven National Laboratory. At the APS, NIST is a partner with the University of Illinois at Urbana/Champaign, Oak Ridge National Laboratory, and UOP, in a collaboration called UNICAT. At both facilities, NIST scientists, and researchers from industry, universities, and government laboratories, perform state-of-the-art measurements on a wide range of advanced materials. Studies currently underway include: ceramic coatings; defect structures arising during deformation of metals, ceramics, and polymers; defect structures in semiconductors and single-crystal proteins; and atomic-scale and molecular-scale structures at surfaces and interfaces in polymeric, catalytic, and metal/semiconductor systems.

Ceramic powders are precursors for over 80% of ceramic manufacturing. As a result, a major focus in the Ceramics Division is the accurate and reliable measurement of the physical and chemical properties of ceramic powders, including sub-micrometer and nanometer sized powders. These measurements are critical to ensuring processes and products of high quality, minimal defects, and consequent economic benefits. Another area of concern to ceramic manufacturing is powder dispersion in a fluid vehicle for shape forming and other uses. The chemical and physical characteristics of powders dispersed in liquids are evaluated to understand the influence of surface charge, dissolution, precipitation, adsorption, and other physicochemical processes on the dispersion behavior. In addition to these activities, standard reference

materials for use as primary calibration standards and national/international standards for particle size and size distribution, pore volume, and particle dispersion measurements are being developed in collaboration with industrial partners, measurement laboratories, and academic institutions in the U.S., Europe, and Asia.

The NIST effort in materials characterization has a strong emphasis on electron microscopy, which is capable of revealing microstructures within modern nanoscale materials and atomic-resolution imaging and compositional mapping of complex crystal phases with novel electronic properties. The MSEL microscopy facility consists of two high-resolution transmission electron microscopes (TEM) and a high-resolution, field-emission scanning electron microscope (FE-SEM) capable of resolving features down to 1.5 nm. Novel experimental techniques using these instruments have been developed to study multilayer and nanometer-scale materials.

Through this MSEL Program, measurement methods, data, and standard reference materials (SRMs) needed by the U.S. polymers industry, research laboratories, and other federal agencies are provided to characterize the rheological and mechanical properties of polymers and to improve polymer processibility. In response to critical industry needs for *in-situ* measurement methodologies, a substantial effort is underway to develop optical, dielectric, and ultrasonic probes for characterizing polymer processing. Improved methods for determining molecular mass distribution of polymers are developed because of the dramatic effect it has on processibility and properties. Mechanical properties and performance are significantly affected by the solid-state structure formed during processing. Importantly, unlike many other common engineering materials, polymers exhibit mechanical properties with time dependent viscoelastic behaviors. As a result, techniques are being developed that measure the solid-state structure and rheological behavior of polymeric materials. Recent program activities exploit advances in mass spectrometry using matrix assisted laser desorption ionization (MALDI) to develop a primary tool for the determination of the molecular masses of synthetic polymers, with particular emphasis on commercially important polyolefins. The polymer industry and standards organizations assist in the identification of current needs for SRMs, and based on these needs, research on characterization methods and measurements is conducted leading to the certification of SRMs.

Contact: Chad R. Snyder

# Polymer Standards

*Reference Materials, RM, and Standard Reference Materials, SRM, are produced to address needs of the producers, processors, and users of synthetic polymers for calibration of instruments, assessment of laboratory proficiency, test method development, and materials improvement. Research supports development of standard test methods for characterizing the molecular structure and use properties of polymers that are needed to optimize synthesis of polymers and improve their performance.*

### Bruno Fanconi and Charles Guttman

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NIST supplies the only polyethylene molecular mass standards for calibration of size exclusion chromatographs, the principal instrument used by industry to characterize the molecular mass distribution of polymers. This year, we will certify a replacement for SRM 1483, a polyethylene mass standard whose supply will soon be exhausted. Research is conducted in mass spectrometry of synthetic polymers to provide industry with better methods to measure molecular mass distribution. Previous work on polystyrene resulted in the first polymer molecular mass standard produced with the complete mass spectrum, measured by mass spectrometry, as ancillary data. Based on the success of that work, a collaborative effort was initiated among standards laboratories in Europe, the U.S. and Japan to establish a standard protocol for measurement of the mass distribution of polystyrene by mass spectrometry. The draft standard method is under final review by the participating organizations. Arrangements have been made to submit the method to standards developing organizations for acceptance as a standard method.

Three SRMs were produced in the past year that assist polymer producers and processors in making reliable measurements of the rheological properties of polymers. Two of the SRMs are melt flow rate standards that are employed to calibrate instruments used to assess the processibility of polymer resins. The NIST melt flow rate standards are referenced

in the ASTM standard test method that is widely used to characterize the processibility of polymers. The third SRM, a poly(dimethylsiloxane) fluid, is intended primarily for use in calibration and performance evaluation of instruments used to determine the viscosity and first normal stress difference in steady shear, or to determine the dynamic mechanical storage and loss moduli and shift factors through time-temperature superposition. This SRM also serves the needs of instrument manufacturers and testing laboratories as a secondary standard for calibrating viscometers.

In recognition of the increasing role of synthetic polymers in medical applications, we supply reference materials for test method development, benchmarking properties, and materials improvement. In response to recommendations of a NIST/Industry workshop on reference materials and data needs for medical use of polymers, an activity was initiated to measure material properties of acrylic polymers used in intraocular lenses for generation of reference database and reference materials. In collaboration with vendors of intraocular lens (IOL) materials, testing laboratories, the National Institutes of Health, and LSU Medical school, data acquisition has commenced on a series of IOL polymers for the purpose of building a reference material database and supply of reference IOL biomaterials to aid research and development of improved materials.

Members of an ASTM subcommittee developing an improved test method for determination of degree of crosslinking resulting from irradiation of ultra-high molecular weight polyethylene, UHMWPE, sought our assistance in providing NIST RM 8456, a medical grade UHMWPE, in a form suitable for the method. Sufficient quantity has been manufactured for issuance as a reference material for comparisons among different test methods.

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### Contributors and Collaborators

W. Blair, B. Fanconi, K. Flynn, C. Guttman, C. Schultheisz, J. Tesk (Polymers Division, NIST); S. Leigh (Statistical Engineering Division, NIST)

## Polyolefin Mass Spectrometry

The mass distribution of a polymer is critical to how they are processed and their resultant properties. Mass spectrometry, MS, is exploited to characterize molecular architecture of saturated hydrocarbon polymers that is difficult, or impossible, to measure by other methods. The work focused on polyolefins, the dominant type of commercial polymer, that exhibit a plethora of molecular architectures owing to advances in synthesis.

### William E. Wallace

Polyethylene and polypropylene dominate the synthetic polymer commercial market. Their dominance has been spurred on by new developments in metallocene catalysts that provide an unprecedented level of synthetic control. A polymer's molecular mass and molecular-mass distribution are critical in determining its performance properties. Mass spectrometry is currently the most promising method for obtaining accurate molecular mass and absolute molecular mass distributions.

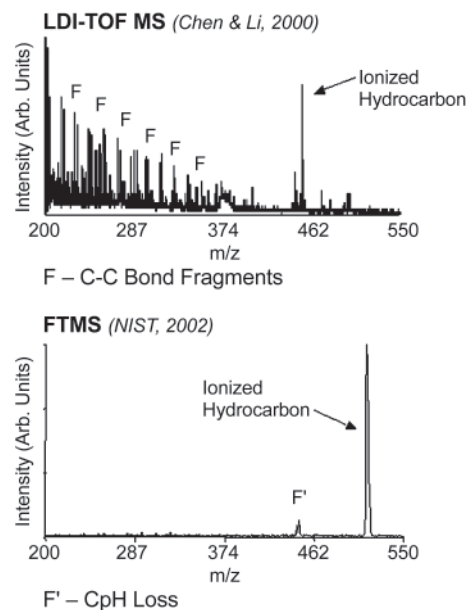
Molecular mass determination by mass spectrometry requires the formation of intact macromolecular ions in the gas phase. This is typically accomplished by the gas-phase association of metal cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cu}^+$ ,  $\text{Ag}^+$ ) with polar or polarizable functional groups on the polymer. Polymers that lack such functional groups (like polyethylene and polypropylene) have not been amenable to mass spectrometric characterization and cannot be analyzed for molecular mass distribution using existing techniques of metal cationization.

In the previous year a new method was introduced for the mass spectrometry of saturated polyolefins whereby an organic cation is covalently bonded to the vinyl end-group of the polymer to produce the necessary ionization for the creation of intact gas-phase macromolecules by matrix-assisted laser desorption ionization (MALDI). This year the "covalent cationization" methodology was further optimized to produce mass spectra for higher molecular mass materials than had been achieved previously by our group and more than six times greater than found in the literature. (See Technical Highlight in this report for more details).

The Polymers Division has also researched the use of organometallic cationization as a way to create intact gas-phase macromolecular ions of fully saturated materials. Our goal in the past year was to develop the methodology for ionization of saturated hydrocarbon inside the mass spectrometer with minimal fragmentation. We selected the  $\eta_5$ -cyclopentadienyl cobalt ion ( $\text{CpCo}^+$ ) because, unlike the reactive bare transition metal ions, it has been shown to react with short-chain linear alkanes ( $2 < n < 6$ ) exclusively by dehydrogenation with no evidence of C-C bond cleavage.

To test the feasibility of the  $\text{CpCo}^+$  ion as a charging agent, we conducted reactivity studies with three medium chain length n-alkanes using Fourier-transform ion cyclotron resonance mass spectrometry. We report that the  $\text{CpCo}^+$  ion reacts predominantly by double dehydrogenation of all three alkanes with no C-C bond cleavage observed.

The figure below compares mass spectra for ionization of n-octacosane (C-28) by the existing bare transition metal cation method (laser desorption time-of-flight mass spectrometry, LDI-TOF MS) and our method using the organometallic chemistry method (Fourier transform mass spectrometry, FTMS). The reaction of C-28 with  $\text{Co}^+$  produces the charged hydrocarbon (adduct) as well as extensive fragmentation. In contrast, the  $\text{CpCo}^+$  ion reaction with C-28 yields the charged hydrocarbon with minimal fragmentation.



**Figure 1:** Mass spectra ionization using bare transition metal cation method vs. organometallic chemistry method.

Our goal for FY03 is to extend the organometallic cationization measurements to low-mass polyolefins.

### Contributors and Collaborators

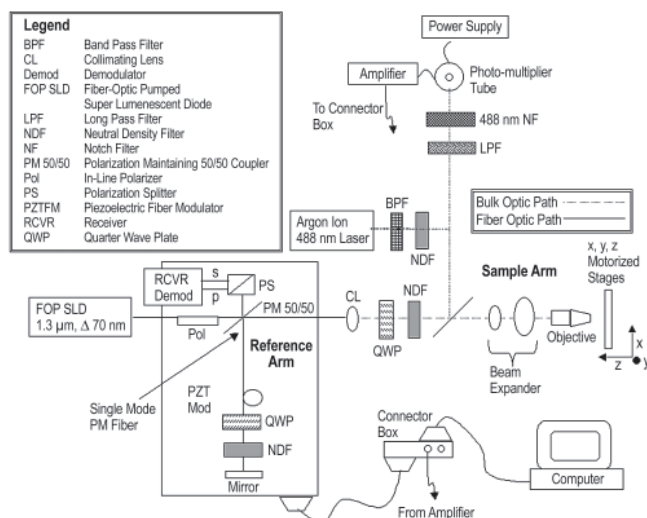
B.J. Bauer, W.R. Blair, H.C.M. Byrd, B.M. Fanconi, C.M. Guttman, S. Lin-Gibson, D.L. Vanderhart, W.E. Wallace, A. Weaver, S.J. Wetzel (Polymers Division); A.J. Kearsley (Mathematical and Computational Sciences Division); D.A. Fischer (Ceramics Division); L. Li (University of Alberta); D.R. Ridge (University of Delaware); J.E. Girard (American University)

## Multi-Modal Imaging Using Optical Coherence Tomography

The impact of multi-modal imaging is shown most clearly in medical imaging. By combining magnetic resonance imaging and positron emission tomography, the physician diagnoses more effectively than using either technique alone. This same approach is taken in our program on multi-modal imaging of materials. The goal of this work is to gain new insight into material systems by simultaneously imaging structure, function, and dynamics. Multi-modal imaging is anticipated to have the earliest and most direct impact on Division efforts in tissue engineering and composite mechanics.

### Joy Dunkers and Marcus Cicerone

The multi-modal imaging effort is built around a technique called optical coherence tomography (OCT). In short, OCT is a non-invasive, non-contact, highly-sensitive structural technique for three-dimensional imaging of highly scattering materials using interferometry. Our first generation OCT performed structural imaging only with an axial (z) resolution of 20  $\mu\text{m}$ . This past year has been spent implementing the second generation OCT (Figure 1) which not only possesses two types of functional imaging but also boasts vast improvements in imaging speed, resolution, and instrument stability. We have increased the data acquisition speed by 50X and the modulator accuracy by 6X by implementing a piezoelectric based fiber modulator.



**Figure 1:** Second generation optical coherence tomography (OCT).

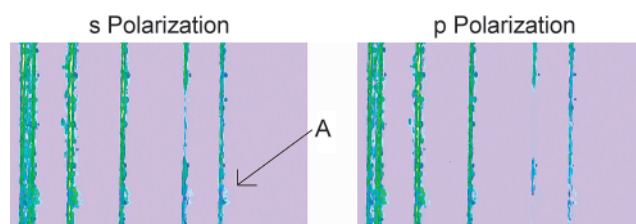
Three hybrid techniques were developed: confocal OCT (C-OCT), confocal fluorescence and C-OCT (C-FL/C-OCT), and polarization sensitive OCT (PS-OCT). C-OCT takes advantage of the exceptional

sensitivity inherent in an optical coherence measurement and uses a confocal optical configuration to significantly improve the axial resolution over standard OCT. We obtain lateral and axial resolutions of 0.5  $\mu\text{m}$  and 1.0  $\mu\text{m}$ .

Confocal fluorescence microscopy has proven to be a powerful technique for understanding structure–function relationships, especially in the biological fields. The C-FL consists of an air-cooled argon ion laser, optical filters for excitation and emission wavelength selection, and a photo-multiplier tube detector (Figure 1). In our instrument, fluorescence is collected from a spot within the sample that coincides with the near infrared focal spot. The two types of information are obtained simultaneously. If the sample contains fluorescent markers that signify particular function, this technique yields functional information that is in registration with the structural information from C-OCT.

PS-OCT allows us to obtain a quantitative, spatially resolved map of birefringence. Because local structural strain or macromolecular orientation can lead to optical birefringence, we can quantify these properties. Circularly polarized light is used in the sample arm to make the results independent of sample orientation. Detection of birefringence is accomplished by monitoring the vertical (s) and horizontal (p) components of the light returning from the sample.

PS-OCT images (230  $\mu\text{m}$  wide and 500  $\mu\text{m}$  high) from a glass fiber and epoxy dogbone (Figure 2) show intact fibers. Birefringence, and therefore residual stress, would manifest itself as an extinction of either polarization. These images show that virtually no residual stress exists with this large fiber spacing, as expected.



**Figure 2:** PS-OCT images from a glass fiber and epoxy dogbone at 230  $\mu\text{m}$  wide and 500  $\mu\text{m}$  high show intact fibers (arrow A).

### Contributors and Collaborators

G.A. Holmes, W.G. McDonough, N.R. Washburn (Polymers Division, NIST); J. Bush, S. Bell (Optiphase Inc., Van Nuys, CA)

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## Quantifying Dispersion and Properties of Carbon Nanotube Composites

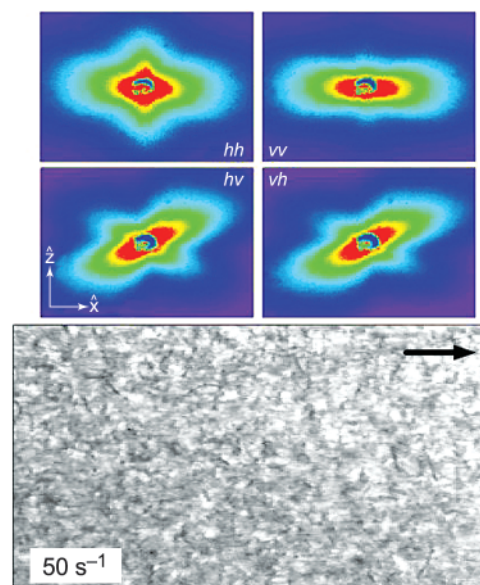
*Inorganic fillers are frequently used to enhance polymer properties. New attributes may be achieved with exotic nanoparticles, provided that the underlying science is well developed. Both multi- and single-wall carbon nanotubes offer the promise of novel polymer nanocomposites, with potential applications in conducting plastics, reinforced plastics, flame retarding plastics, and novel optical materials. Issues of critical importance are dispersion and alignment, and how these influence bulk physical properties.*

**Erik K. Hobbie, Jack F. Douglas, and Charles C. Han**

Nanocomposite materials engineered from polymers and carbon nanotubes offer the promise of polymer composites with greatly enhanced electrical, thermal, optical, and structural properties. For example, measurements performed at NIST have recently demonstrated significantly-enhanced flame retardation in polypropylene and multi-walled carbon nanotube composites at loadings of only 1% nanotubes by mass. As inorganic filler in a polymer matrix, the anisotropy of carbon nanotubes makes them structurally unique in that the tube diameter can be the same order of magnitude as the radius of gyration of the polymer, yet the aspect ratio of the tubes can be exceptionally large and the tubes themselves can exhibit extreme mechanical strength. In addition to the resolution of fundamental issues concerning the fractionation, functionalization, and dispersion of multi- and single-walled carbon nanotubes in a wide array of organic solvents and polymer matrices, efficient bulk processing of nanotube-polymer composites will depend on both a detailed understanding of the response of polymer-nanotube melts to simple steady shear flow and a convenient but quantitative measure of tube dispersion.

Investigations involving multi-walled carbon nanotubes (MWNT's) have focused on developing an optical metrology for *in situ* observations of MWNT's dispersed in polymer melts under simple shear flow. These measurements employ polarized light scattering and optical microscopy to quantify the structural anisotropy of sheared nanotube melts, as shown in Figure 1. The requirement is that the melt be sufficiently dilute or the sample sufficiently thin for optical measurements to be used. We have mapped out the orientation of the tubes as a function of Deborah number in the suspending medium and observed orientation of the tubes along both the flow direction and the vorticity direction. We anticipate that these measurements will have applications in the injection molding of conducting plastic parts, for example.

Small-angle neutron scattering is also being used to quantify dispersion in composites of polymers and single-walled carbon nanotubes (SWNT's). This work is being done in collaboration with the University of Pennsylvania. Composite samples prepared at varying degrees of dispersion have been investigated using small-angle neutron scattering (SANS), and the shape of the scattering curve as a function of scattered wave vector has been used to extract a quantitative measure of the SWNT dispersion and diameter. Transmission electron microscopy (TEM) has been used to confirm the extent of dispersion. In the near future, we will measure the dielectric spectrum of these polymer nano-composites and evaluate in-line dielectric spectroscopy as a tool for quantifying nanotube dispersion *in situ* during processing.



**Figure 1:** Optical data for a PB/MWNT dispersion ( $3.5 \times 10^{-3}$  mass fraction MWNT,  $T = 40^\circ\text{C}$ ) at a shear rate of  $50.0 \text{ s}^{-1}$ . Orientation of the tubes along the vorticity direction is evident in the micrograph, in the anisotropy of the hh and vv patterns, and, to a lesser extent, in the orientation of the intensity lobes in the hv and vh patterns. The flow direction is horizontal and the vorticity direction is vertical. The micrograph is  $200 \mu\text{m}$  wide.

### Contributors and Collaborators

H. Wang, J. Obrzut, D.L. VanderHart, S.D. Hudson, H. Kim, S. Lin-Gibson (Polymers Division, NIST); T. Kashiwagi (Fire Research Division, NIST); E.A. Grulke (University of Kentucky); K.I. Winey (University of Pennsylvania); K. McElrath, D. Colbert (CNI)

## Characterization and Modeling of the Interfaces and Interphases of Polyolefin Blends

*Process modeling may facilitate design of optimal conditions for processing polymer blends, provided that the complex structure and behavior of these materials are treated adequately. Techniques and methodologies are developed to define and characterize rheological, morphological, and interfacial properties of multiphase polymer blends as a function of processing parameters, such as composition, shear stress, and crystalline structure. Constitutive relationships are formulated for process modeling needs.*

**Charles C. Han, Howard Wang,  
and Frederick R. Phelan, Jr.**

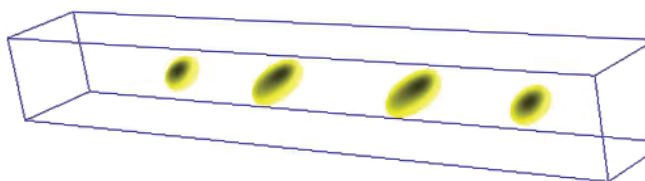
During the past year, extensive experimental work has been carried out to understand the effect of blending and thermal history on structure development in polyethylene-hexene/polyethylene-butene (PEH/PEB) blends employing both real and reciprocal space techniques. This work represents the first comprehensive investigation of polymer blends that exhibit both liquid phase separation and crystallization.

Using phase-contrast optical microscopy, both crystal super-structure growth and phase-separation kinetics were measured in blends of various compositions at various temperatures. Measurements of crystal-growth kinetics show that blends and pure PEH exhibit similar growth regimes. Phase-separation in the blends is very slow, and nonlinear hydrodynamic effects dominate the domain coarsening. Atomic force microscopy studies show that the surface crystal morphology can be fibrous, spherulitic, or dendritic depending on both composition and quench depth. Transmission electron microscopy reveals bulk semi-crystalline morphology in more detail. For example, blending with PEB swells the inter-lamellae spacing, implying the inclusion of non-crystallizable chains within the lamellar stacks. In another example, when a critical blend is allowed to phase separate for an extended period before further lowering the temperature for crystallization, distinct lamellar crystals form within the co-existing PEH-rich and PEB-rich domains, leading to a morphology characterized by hierarchical length scales.

Simultaneous small and wide-angle x-ray scattering measurements on crystal growth have been carried out at the National Synchrotron Light Source (NSLS) at Brookhaven National Labs (BNL). Isothermal crystallization of blends, which follow either a 1-step quench from a homogeneous melt or a 2-step quench to an intermediate temperature for phase separation followed by a quench to a lower temperature, has been studied extensively.

The effect of simple shear flow on crystallites in suspension in polyolefin blends has been investigated using light scattering and microscopy. To account for both the structural anisotropy and the flow-induced orientation, polarized light scattering is employed, with the polarizer and analyzer set at horizontal (H) and vertical (V) orientations (parallel or perpendicular to the flow direction, respectively). It is found that crystallites orient along the vorticity direction at low shear rate, whereas at high shear rate, crystal super-structures melt, and the morphology becomes a mixture of large crystallites oriented along the vorticity direction and thin lamellae sheets aligned with the flow direction. After cessation of shear, the crystals aggregate to form necklace structures and hundred-micron sized balls.

Simulations of isolated droplets at super-critical capillary numbers in steady, homogeneous shear flow have also been carried out using a Lattice Boltzmann scheme. The goal is to understand drop breakup mechanisms and develop models for this that can be applied to complex flows, such as injection molding. It has been observed that a super-critical droplet first deforms into an elongated liquid thread with “dumbbell” type ends. Sub-critical “child” drops pinch off the ends of the thread in a continual process until the depleted original is itself below critical. Results for  $Ca_0 = 0.45$  (where  $Ca_c = 0.4$ ) are shown in Figure 1, where the final configuration of the new droplet family is observed. There are four drops, all stable, below the critical Capillary number. There is evidence of a distribution in sizes. The initial child drops that are formed are larger than subsequent ones.



**Figure 1:** The final state for case 1. There are four drops all below critical. The initial “child” drops that are formed are larger than the subsequent ones.

### Contributors and Collaborators

K. Shimizu, G.Z.G. Wang, G. Matsuba, F. Landis, H. Kim, E.K. Hobbie (Polymers Division, NIST); N. Martys (BFRL, NIST); B.S. Hsiao (SUNY); D. Lohse (Exxon)

## Polymers Division FY02 Annual Report Publication List

### Characterization and Measurement — Method Development

#### Computational Methods

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## Polymers Division

### Chief

**Eric J. Amis**

Phone: 301-975-6762

E-mail: eric.amis@nist.gov

### Deputy Chief

**Chad R. Snyder**

Phone: 301-975-4526

E-mail: chad.snyder@nist.gov

### NIST Fellows

**Charles C. Han**

Phone: 301-975-6772

E-mail: charles.han@nist.gov

### Group Leaders

#### Characterization and Measurement — Method Development

**Wen-li Wu**

Phone: 301-975-6839

E-mail: wen-li.wu@nist.gov

#### Standards and Data

**Bruno M. Fanconi**

Phone: 301-975-6769

E-mail: bruno.fanconi@nist.gov

#### Internal Capabilities

**Chad R. Snyder**

#### Electronics Materials

**Eric K. Lin**

Phone: 301-975-6743

E-mail: eric.lin@nist.gov

#### Biomaterials

**Eric J. Amis, Acting**

#### Multiphase Materials

**Charles Han**

#### Processing Characterization

**Kalman Migler**

Phone: 301-975-4876

E-mail: kalman.migler@nist.gov

#### Multivariant Measurement Method

**Alamgir Karim**

Phone: 301-975-6588

E-mail: alamgir.karim@nist.gov

## Research Staff

**Amis, Eric J.**

**eric.amis@nist.gov**  
Neutron, x-ray and light scattering  
Polyelectrolytes  
Viscoelastic behavior of polymers  
Dendrimers and dendritic polymers  
Functional biomaterials

**Anopchenko, Oleksiy S.**

**oleksiy.anopchenko@nist.gov**  
Dielectric relaxation spectroscopy  
X-ray scattering  
Microwave spectroscopy techniques

**Antonucci, Joseph M.**

**joseph.antonucci@nist.gov**  
Synthetic and polymer chemistry  
Dental composites, cements and adhesion  
Initiator systems  
Interfacial coupling agents  
Remineralizing polymer systems

**Ashley, Karen+**

**karenmashley@hotmail.com**  
Polymer thin films  
Dewetting  
Combinatorial measurements

**Balizer, Edward+**

Neutron, x-ray scattering  
Polymer electrostriction

**Barnes, John D. +**

**john.barnes@nist.gov**  
Gas and vapor transport in polymers  
X-ray scattering  
Computer applications in polymer measurements

**Bauer, Barry J.**

**barry.bauer@nist.gov**  
Polymer synthesis thermal characterization  
Neutron, x-ray and light scattering  
Dendrimers, metallic ions nanocluster  
Porous low-k thin film characterization

**Beers, Kathryn**

**kathryn.beers@nist.gov**  
Crystallization in thin films  
Optical light scattering  
Controlled/living polymerizations

**Bencherif, Sidi**

**sidi.bencherif@nist.gov**  
Mass spectrometry  
Chemical modification

**Blair, William R.**

**william.blair@nist.gov**  
Polymer analysis by size exclusion  
Chromatography  
Mass spectrometry of polymers

**Bowen, Rafael L.\***

**rafael.bowen@nist.gov**  
Adhesion  
Dental composites  
Novel monomer synthesis

**Bur, Anthony J.**

**anthony.bur@nist.gov**  
Dielectric properties of polymers  
Fluorescence and optical monitoring of  
polymer processing  
Piezoelectric, pyroelectric polymers  
Viscoelastic properties of polymers

**Carey, Clifton M.\***

**clifton.carey@nist.gov**  
Dental plaque  
Microanalytical analysis techniques  
Phosphate chemistry  
Ion-selective electrodes

**Chang, Shu Sing+**

Thermal properties of polymeric and  
composite materials  
Composite process monitoring  
Electronic packaging materials  
Polymer phase transitions  
Precision electrical and temperature  
measurements

**Chen, Erqiang+**

**erqiang\_chen@hotmail.com**  
Polymer morphology  
Phase behavior of block copolymers  
Polymer blends

**Chen, Wei+**

**wchen2.email.com@dcrn.e-mail.com**  
X-ray and neutron scattering  
Low dielectric constant material characterization

**Cherng, Maria\***

**maria.cherng@nist.gov**  
Calcium phosphate biomaterials

**Chiang, Chwan K.**

**c.chiang@nist.gov**  
Electroluminescent polymers  
Residual stress  
Impedance spectroscopy

- Chiang, Martin Y.**  
**martin.chiang@nist.gov**  
 Computational mechanics (finite element analysis)  
 Strength of materials, fracture mechanics  
 Engineering mechanics of polymer-based materials  
 Bi-material interface
- Chow, Laurence C.\***  
**laurence.chow@nist.gov**  
 Calcium phosphate compounds and biomaterials  
 Dental and biomedical cements  
 Solution chemistry  
 Topical dental fluorides
- Cicerone, Marcus T.**  
**marcus.cicerone@nist.gov**  
 Protein stabilization  
 Glass transition theory  
 Optical coherence tomography  
 Confocal microscopy
- Crosby, Alfred**  
**alfred.crosby@nist.gov**  
 Polymer adhesion  
 Polymer fracture  
 Viscoelasticity  
 Elastomers  
 Block copolymers
- Dähnhardt, Jan-Erik +**  
 Self-curing dental repair resin
- Davis, G. Thomas +**  
**george.davis@nist.gov**  
 Electronic packaging  
 Polymer crystallization  
 X-ray diffraction of polymers  
 Polarization distribution  
 Piezoelectricity in polymers
- Davis, Cher**  
**cher.davis@nist.gov**  
 NIST Combinatorial Methods Center  
 Polymer nanocomposites  
 Polymers synthesis  
 Combinatorial methods and measurements
- DeReggi, Aime S**  
**aime.dereggi@nist.gov**  
 Polarization-depth profiles in polymers  
 Space charge in dielectrics  
 Ferroelectric polymers  
 Polymeric piezo- & pyroelectric devices
- Dickens, Sabine\***  
**sabine.dickens@nist.gov**  
 Dental composites  
 Dental adhesives  
 Transmission electron microscopy
- Di Marzio, Edmund A. +**  
**edmund.dimarzio@nist.gov**  
 Statistical mechanics of polymers  
 Phase transitions  
 Glasses  
 Polymers at interfaces
- Douglas, Jack F.**  
**jack.douglas@nist.gov**  
 Theory on polymer solutions, blends, and filled polymers  
 Transport properties of polymer solutions and suspensions  
 Polymers at interfaces  
 Scaling and renormalization group calculation  
 Conductivity/viscosity of nanoparticle filled systems  
 Crystallization of polymers
- Duan, Hu +**  
**hu.duan@nist.gov**  
 Electron microscopy  
 Self-assembly and liquid crystals
- Dunkers, Joy P.**  
**joy.dunkers@nist.gov**  
 Optical coherence tomography  
 Image analysis  
 Fiber optic spectroscopy  
 Infrared microspectroscopy of polymers
- Eanes, Edward D. +**  
**edward.eanes@nist.gov**  
 Structure of bones and teeth  
 Calcium phosphate compounds as dental materials  
 Effects of solution and biological molecules on precipitation of calcium phosphates  
 Liposome studies
- Eichmiller, Frederick C.\***  
**frederick.eichmiller@nist.gov**  
 Clinical dentistry  
 Composites  
 Dentin adhesives
- Eidelman, Naomi N.\***  
**naomi.eidelman@nist.gov**  
 Prevention of calcification in the cardiovascular system  
 Effect of phosphonates, cholesterol and phospholipids on calcium phosphate formation  
 Characterization of calcified deposits by FTIR microscopy
- Esker, Alan R. +**  
**alan.esker@nist.gov**  
 Membrane mediated polymer interdiffusion  
 Phase separation kinetics of polymer blends

**Fanconi, Bruno M.**

**bruno.fanconi@nist.gov**  
Infrared & Raman spectroscopy of polymers  
Structure of polymers  
Polymer fracture  
Process monitoring of polymer composites

**Fasolka, Michael J.**

**mfasolka@nist.gov**  
Combinatorial methods and measurements  
Nanopatterned substrates  
Nanohybrid structures  
Surface energy patterning and control  
Surfaces and interfaces

**Flaim, Glenn M.\***

**glenn.flaim@nist.gov**  
Fabricating dental composites

**Floyd, Cynthia J. E. +**

**cynthia.floyd@nist.gov**  
Dental composites

**Flynn, Kathleen M.**

**kathleen.flynn@nist.gov**  
Permeability measurements and database  
Flow visualization experiments  
Web page development

**Fowler, Bruce O. +**

**bruce.fowler@nist.gov**  
Infrared and Raman spectroscopy  
Structure of calcium phosphates, bones,  
and teeth  
Composites

**Frukhtbeyn, Stanislav +**

**stan.frukhtbeyn@nist.gov**  
Calcium phosphate compounds and biomaterials  
Topical dental fluorides

**Galvin, Agnes Ly.\***

**agnes.galvin@nist.gov**  
Clinical dental assistant  
Adhesion measurements

**George, Laurie A.\***

**laurie.george@nist.gov**  
Glass-ceramics

**Giuseppetti, Anthony A.\***

**anthony.giuseppetti@nist.gov**  
Casting of dental alloys  
Mercury-free amalgam alternative

**Goldschmidt, Robert +**

**robert.goldschmidt@nist.gov**  
Mass spectrometry of polymers  
Chemical analysis

**Guttman, Charles M.**

**charles.guttman@nist.gov**  
Solution properties of polymers  
Size exclusion chromatography  
Mass spectrometry of polymers

**Han, Charles C.**

**charles.han@nist.gov**  
Phase behavior of polymer blends  
Phase separation kinetics of polymer blends  
Polymer characterization and diffusion  
Shear mixing/demixing and morphology  
control of polymer blends  
Static, time resolved, and quasi-elastic  
scattering of light and neutron

**Harrison, Christopher**

**christopher.harrison@nist.gov**  
Combinatorial methods  
Mechanical properties  
Polymer thin film properties  
Modulus measurements

**Hedden, Ronald**

**ronald.hedden@nist.gov**  
Siloxane polymers: synthesis and properties  
Nanoporous thin films  
Gel permeation chromatography

**Hobbie, Erik K.**

**erik.hobbie@nist.gov**  
Light scattering and optical microscopy  
Dynamics of complex fluids  
Shear-induced structures in polymer blends  
and solutions

**Holmes, Gale A.**

**gale.homes@nist.gov**  
Composite interface science  
Chemical structure-mechanical property  
relationships for polymers  
Polymer chemistry  
Mass spectroscopy

**Hudson, Steven D.**

**steven.hudson@nist.gov**  
Electron microscopy  
Polymeric surfactant and interfacial dynamics  
Self-assembly and liquid crystals  
Nanocomposites  
Biomaterials

**Hu, Tengjiao**

**tengjiao.hu@nist.gov**  
Dynamic light scattering  
Small-angle x-ray scattering  
Atomic force microscopy

- Hussain, Latiff\***  
**latiff.hussain@nist.gov**  
 Monomer polymer synthesis, characterization, testing  
 Dental composites, adhesives
- Jeon, Hyun Sik+**  
**hyunsik.jeon@nist.gov**  
 Shear light scattering and optical microscopy  
 Structure and morphology of two-phase elastomer blends under shear
- Jianmei, He+**  
**jianmei.he@nist.gov**  
 Computational mechanics (finite element modeling)  
 Adhesive joints  
 Structural optimization
- Jones, Ronald+**  
**ronald.jones@nist.gov**  
 Neutron and x-ray scattering  
 Neutron reflectivity  
 Polymer surfaces and thin films  
 Polymer phase transitions and computer simulation
- Kano, Kenji**  
**kkano@nist.gov**  
 Dielectric relaxation of polymers  
 Nonlinear dielectric and conductive spectroscopy
- Karim, Alamgir**  
**alamgir.karim@nist.gov**  
 Polymer fillers and nanocomposites  
 Patterning of thin-polymer blend films on inhomogenous surfaces  
 Neutron and x-ray reflection, scattering, AFM and optical microscopy  
 Thin-film phase behavior of polymer blends  
 Combinatorial thin-film polymer coatings
- Kharchenko, Semen**  
**semen.kharchenko@nist.gov**  
 Stress optical properties  
 Birefringence  
 Viscoelastic Properties
- Kelly, J. Robert+**  
**robert.kelly@nist.gov**  
 Calcium phosphate cements  
 Dental ceramics  
 Failure analysis; dental prostheses  
 Finite element analysis  
 Weibull analysis
- Kennedy, Scott B. +**  
**scott.kennedy@nist.gov**  
 Tissue engineering  
 Biomaterials  
 Block copolymers  
 Combinatorial surface patterns
- Kennedy, Sharon L.**  
**sharon.kennedy@nist.gov**  
 Lithographically patterned surfaces  
 Biomaterials  
 Combinatorial patterned arrays  
 Combinatorial polymer blends  
 Combinatorial phase behavior of polymer blends
- Khatri, Chetan A. +**  
**chetan.khatri@nist.gov**  
 Monomer/polymer synthesis and characterization
- Khoury, Freddy A.**  
**freddy.khoury@nist.gov**  
 Crystallization, structure and morphology of polymers  
 Analytical electron microscopy of polymers  
 Wide-angle and small-angle x-ray diffraction  
 Structure and mechanical property relationships
- Kumar, Sanat+**  
**kumar@plmsc.psu.edu**  
 Polymer coatings and thin films  
 Simulations  
 Physical properties of polymers  
 Phase separation  
 Multiphase polymer systems
- Lee, Hae-Jeong+**  
**hae-jeong.lee@nist.gov**  
 X-ray reflectivity  
 Small-angle neutron scattering  
 Synthesis and characterization of low dielectric constant thin films
- Lenhart, Joseph L.**  
**joseph.lenhart@nist.gov**  
 Sensors  
 Interphase structure  
 Polymer films and interfaces  
 Near-edge x-ray absorption fine structure  
 X-ray and neutron reflectivity
- Li, Bizhong+**  
 Polymer processing  
 Polymer blends  
 Polymer-clay processing
- Liao, Nam S.\***  
**nam.liao@nist.gov**  
 Synthesis and testing of dental adhesives  
 Internal stress of composition due to polymerization

**Lin, Eric K.**

**eric.lin@nist.gov**  
Polymer thin films and interfaces  
Polymeric photoresists for lithography  
Small angle neutron scattering  
Statistical mechanics  
X-ray and neutron reflectivity

**Liu, D.-W.**

**da-wei.liu@nist.gov**  
Polymer synthesis  
Thermal gravimetric analysis  
Differential scanning calorimetry  
Gel permeation chromatography  
Infrared spectroscopy  
Nuclear magnetic resonance  
Scanning electron microscopy  
Atomic force microscopy

**Mager, Carie +**

**carie.mager@nist.gov**  
Toughening bioceramics  
Fracture mechanics

**Markovic, Milenko\***

**milenko.markovic@nist.gov**  
Calcium phosphate chemistry  
Biomineralization (normal and pathological)  
Crystal growth and dissolution kinetics  
Heterogeneous equilibria

**Mathew, Mathai\***

**mathai.mathew@nist.gov**  
Crystallography  
Calcium phosphate compounds

**Maurey, John M. +**

**john.maurey@nist.gov**  
Ultracentrifugation  
Rayleigh light scattering  
Osmometry  
Densimetry  
Refractometry  
Intrinsic viscosity

**McDonough, Walter G.**

**walter.mcdonough@nist.gov**  
Processing and cure monitoring polymer composites  
Failure and fracture of polymers  
Polymer composite interfaces

**McKenna, Gregory B. +**

**greg.mckenna@coe.ttu.edu**  
Failure, yield and fracture of polymers  
Nonlinear viscoelasticity  
Molecular rheology  
Physics of polymer glasses  
Rubber thermodynamics and mechanics  
Mechanics of composites

**McGuiggan, Patricia**

**patricia.mcguiggan@nist.gov**  
Atomic force microscopy  
Viscoelastic properties

**Migler, Kalman**

**kalman.migler@nist.gov**  
Effects of shear and pressure on phase behavior  
Fluorescence and optical monitoring of polymer processing  
Liquid crystals  
Shear-induced two phase structures  
Polymer slippage

**Mopsik, Frederick I. +**

**frederick.mopsik@nist.gov**  
Dielectric measurements and behavior  
Automated measurement design  
Computerized data analysis and programming  
Electrical properties of polymers

**Mueller, Herbert J. \***

**herb.mueller@nist.gov**  
Dental biomaterials  
Interfacial interactions via electrochemical and infrared spectroscopy  
Chevron notch fracture toughness  
Mechanical properties via nondestructive methods

**Nakatani, Alan I. +**

**alan.nakatani@nist.gov**  
Polymer blends and solution properties under shear  
Small-angle neutron scattering  
Phase behavior of polymer blends  
Filled polymers  
Rheo-optical behavior of polymers

**Noda, Natsuko +**

**natsuko.noda@nist.gov**  
Impedance spectroscopy  
Dielectric characterization of composites  
Photolithography  
Nanocomposites

**Obrzut, Jan**

**jan.obrzut@nist.gov**  
Dielectric relaxation spectroscopy  
Electronic properties of polymers and composites  
Electronic packaging  
Microwave and optical waveguides  
Photoelectron spectroscopy (x-ray and UV)  
Reliability, stress testing

**Parry, Edward E. \***

**edward.parry@nist.gov**  
Dental appliance and crown and bridges fabrication  
Machine shop applications



- Pathak, Jai A. +**  
**jai.pathak@nist.gov**  
 Polymer rheology  
 Polymer dynamics  
 Glass transition  
 Polymer blends
- Pfeiffer, Carmen+**  
**carmen.pfeiffer@nist.gov**  
 Dental resins  
 Monomer synthesis
- Phelan, Jr., Frederick R.**  
**frederick.phelan@nist.gov**  
 Resin transfer molding: modeling and processing studies  
 Viscoelastic flow modeling  
 Flow in porous media  
 Lattice Boltzmann methods
- Pochan, Darrin+**  
**pochan@udel.edu**  
 SEM & TEM of polymeric materials  
 Wide-angle and small-angle x-ray scattering  
 Block copolymer phase behavior
- Popielarz, Roman+**  
**roman.popielarz@nist.gov**  
 Polymer synthesis and characterization  
 Photo-polymerization
- Prabhu, Vivek M.**  
**vmprabhu@nist.gov**  
 Small-angle neutron scattering  
 Polyelectrolytes  
 Light scattering  
 Polymer thin films
- Roth, Steven C.**  
**steven.roth@nist.gov**  
 Piezoelectric polymer transducers-fabrication and applications  
 Vacuum deposition of metals  
 Calibration of polymer transducers  
 Microcomputer interfacing  
 Fluorescence measurements
- Schmidt, Gudrun+**  
**gudrun.schmidt@nist.gov**  
 Polymer blends  
 Liquid crystalline polymers  
 Polymer-clay interaction  
 Light and neutron scattering
- Schultheisz, Carl R. +**  
**schultheisz@ntsb.gov**  
 Failure of composites  
 Experimental mechanics  
 Torsional dilatometry  
 Physics of polymer glasses  
 Polymer rheology
- Schumacher, Gary E.\***  
**gary.schumacher@nist.gov**  
 Clinical dentistry  
 Composites  
 Dentin adhesives
- Sehgal, Amit+**  
**amit@nist.gov**  
 Biomaterials, cell-surface biophysics  
 Polymer thin films  
 Polyelectrolytes and conducting polymers  
 Structure and dynamics of polymer solutions  
 Light scattering and fluorescence  
 photobleaching recovery
- Sieck, Barbara A.\***  
**barbara.sieck@nist.gov**  
 Calcium phosphate compounds  
 Chemical analysis  
 Remineralization
- Simon, Carl G., Jr.**  
**carl.simon@nist.gov**  
 Biocompatibility  
 Cytotoxicity  
 Signaling in human platelets  
 Bone marrow cell lineage/trafficking
- Skrtic, Drago\***  
**drago.skrtic@nist.gov**  
 Calcium phosphates as dental materials  
 Liposome studies
- Smith, Archie+**  
**archie.smith@nist.gov**  
 Combinatorial (high-throughput) experimental design and development  
 Polymer crystallization behavior  
 Thin-film block copolymer behavior  
 Nanofilled polymer behavior  
 Electron, atomic force, x-ray and light microscopies
- Snyder, Chad R.**  
**chad.snyder@nist.gov**  
 Polymer crystallization  
 WAXD and SAXS of polymeric materials  
 Thermal expansion measurements  
 Thermal analysis of polymers  
 Dielectric measurements and behavior  
 Nanocomposite properties
- Soles, Christopher**  
**csoles@nist.gov**  
 Polymer dynamics  
 Inelastic neutron scattering  
 Low-k dielectric thin films  
 X-ray and neutron reflectivity techniques  
 Polymer thin films and lithography  
 Ion beam scattering techniques

**Son, Younggon +**

**Younggon.son@nist.gov**  
Polymer processing  
Polymer phase behavior  
Interfacial phenomena

**Song, Rui +**

**rsong@nist.gov**  
Combinatorial methods and measurements  
Polymer debonding  
Polymer adhesion and failure  
Polymeric peel tests

**Stafford, Christopher +**

**chris.stafford@nist.gov**  
Polymer adhesion  
Surfaces and interfaces  
Polymer thin films

**Stansbury, Jeffrey W.**

**jeffrey.stansbury@nist.gov**  
Synthetic chemistry  
Polymers and polymer composites  
Polymerization of expanding monomers  
Fluorinated polymers  
Polymerization kinetics

**Starr, Francis**

**francis.starr@nist.gov**  
Dynamics of filled polymers  
Slow dynamics in soft condensed matter  
Molecular dynamics simulations and parallel computing

**Takagi, Shozo\***

**shozo.takagi@nist.gov**  
Crystallography  
X-ray diffraction  
Calcium phosphate biomaterials  
Topical fluoridation  
De- and remineralization

**Tesk, John A.**

**john.tesk@nist.gov**  
Biomaterials: industrial relations  
Bond strength characterization  
Casting of alloys  
Strength of dental systems  
Thermal expansion and properties of dental materials  
Finite element studies  
Porcelain-metal systems  
Weibull analysis  
Wear testing, orthopaedic materials  
Reference biomaterials

**Tung, Ming S.\***

**ming.tung@nist.gov**  
Chemistry of calcium phosphate compounds  
Remineralization studies  
Standard reference materials

**VanderHart, David L.**

**david.vanderhart@nist.gov**  
Measurement of orientation in polymer fibers and films  
Solid-state NMR of polymers  
Measurement of polymer morphology at the 2–50 nm scale  
Pulsed field gradient NMR

**Van Zanten, John H. +**

**jhvanzan@unity.ncsu.edu**  
Complex fluids  
Polymer interfaces  
Scattering of light, neutrons & x rays  
Biophysics  
Interfacial phenomena  
Scanning-probe microscopy

**Vogel, Gerald L.\***

**gerald.vogel@nist.gov**  
Dental plaque chemistry, chemistry of calcium phosphates  
Microanalytical techniques

**Wallace, William E.**

**william.wallace@nist.gov**  
Surface and interface behavior  
Electron spectroscopy  
Mass spectrometry

**Wang, Chia-Ying**

**cywang@nist.gov**  
Small-angle x-ray scattering  
Polymer diffusion  
Microphase transitions of block copolymers  
Fluorescence spectroscopy of polymers

**Wang, Francis W.**

**francis.wang@nist.gov**  
Photophysics and photochemistry of polymers  
Fluorescence spectroscopy  
Cure monitoring of polymerization  
Tissue engineering

**Wang, Howard +**

**hao.wang@nist.gov**  
Multiple phase transitions in polymer  
Wetting, segregation and transport in polymer  
Structure and dynamics in polymer gels

**Washburn, Newell**

**newell.washburn@nist.gov**  
Tissue engineering  
Polymer blends  
Biomaterial interfaces  
Viscoelastic properties of polymers

**Weaver, Alia +**

**alia.weaver@nist.gov**  
Mass spectrometry of polymers

**Weir, Michael**

**michael.weir@nist.gov**  
Biomaterials  
Tissue engineering  
Biodegradable hydrogels  
Combinatorial analysis  
UV and fluorescence spectroscopy of polymers

**Wetzel, Stephanie**

**stephanie.wetzel@nist.gov**  
Mass spectrometry of polymers  
Data analysis  
Chemometrics

**Wu, Wen-li**

**wen-li.wu@nist.gov**  
Neutron and x-ray scattering and reflectivity  
Electron microscopy  
Mechanical behavior of polymers and composites  
Polymer surfaces and interfaces

**Yurekli, Koray +**

**kyurekli@jetson.uh.edu**  
Polymer nanocomposite  
Phase separation  
Thin films and interfaces  
Neutron and light scattering

**Xie, Baosheng+**

Testing micro tensile and micro-shear  
bond strength

**Xu, Hockin\***

**hockin.xu@nist.gov**  
Silver alloy alternative to amalgam  
Wear and fatigue  
Fiber and whisker reinforcement

**Zhang, Yubao+**

**yubao.zhang@nist.gov**  
Dynamic light scattering  
Polyelectrolytes  
Small-angle neutron scattering

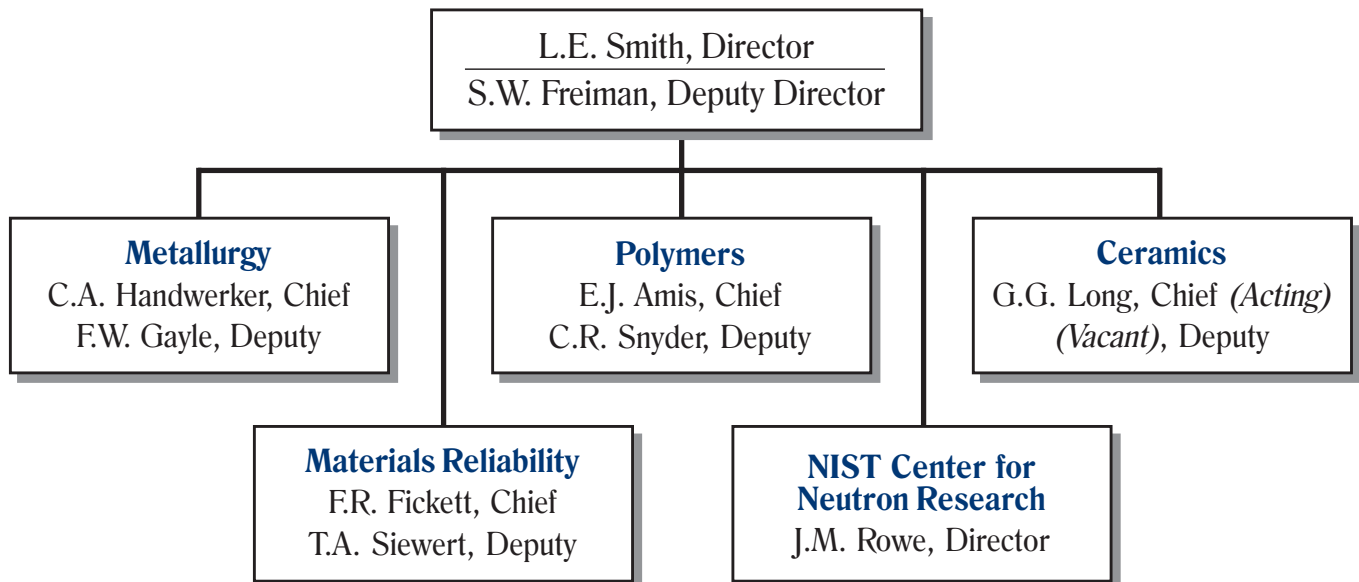
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\* Research Associate  
+ Guest Scientist

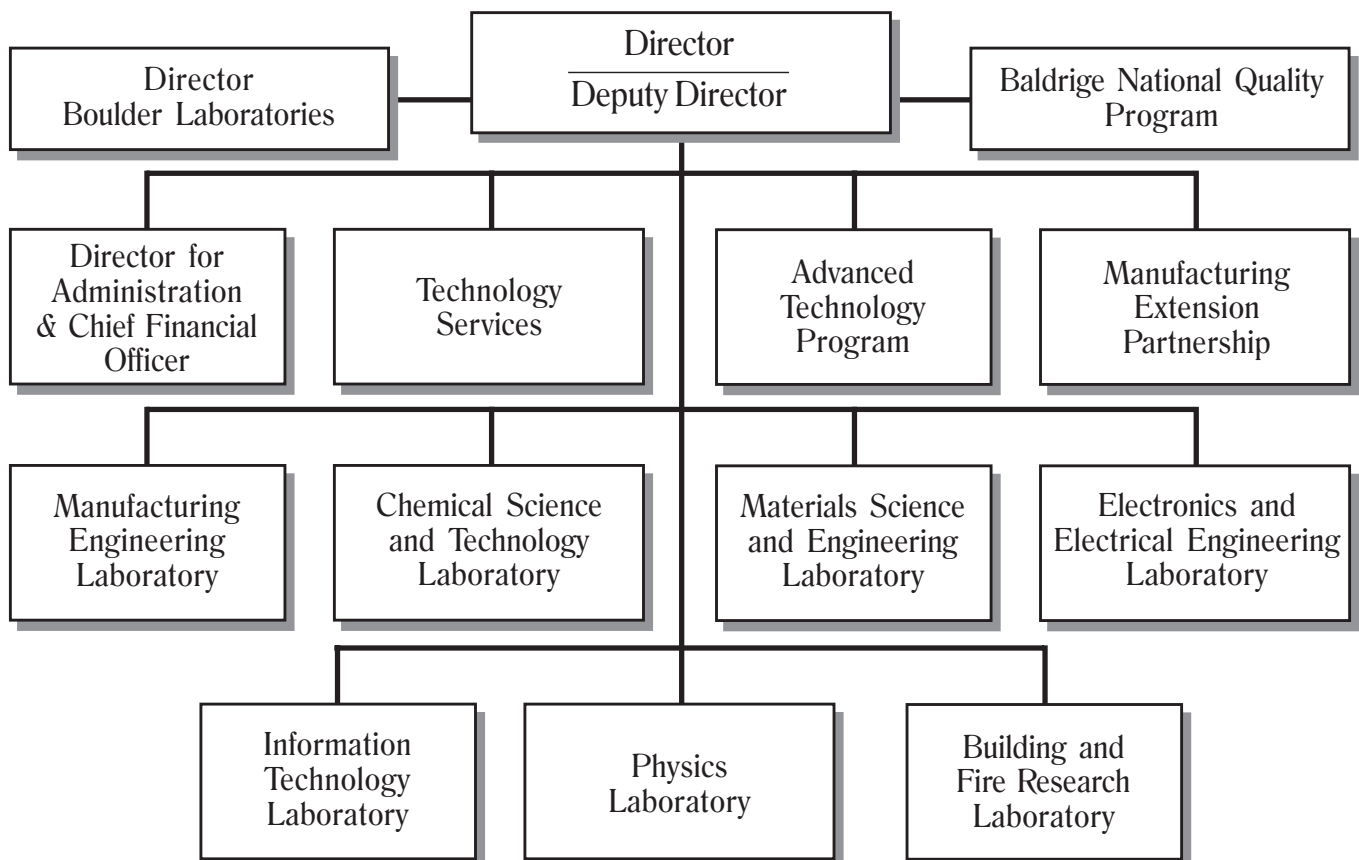


## Organizational Charts

### Materials Science and Engineering Laboratory



### National Institute of Standards and Technology



## Polymers Division (854.00)

Eric Amis, *Division Chief*  
 Chad Snyder, *Deputy Chief*  
 Dawn Bradley, *Division Secretary*  
 Karen Hollingsworth, *Secretary*

**Characterization & Measurement (854.01)**  
 Chad Snyder, *Group Leader*  
 Bronny Webb, *Secretary*

**Method Development**  
 Wen-li Wu

**Standards & Data**  
 Bruno Fanconi

**Internal Capabilities**  
 Chad Snyder

J. Dunkers      J. Lenhart  
 R. Hedden      S. Lin-Gibson  
 R. Jones        V. Prabhu  
 F. Landis        F. Starr

M. Byrd        W. Wallace  
 W. Blair        J. Maurey  
 K. Flynn        A. Weaver  
 C. Guttman      S. Wetzel  
 J. Tesk          J. Girard

M. Chiang        F. Khoury  
 M. Cicerone      D. Liu  
 A. DeReggi      W. McDonough  
 J. Douglas       D. Vanderhart  
 S. Hudson        H. Duan

**Electronics Materials (854.02)**  
 Wen-li Wu, *Group Leader*  
 Bronny Webb, *Secretary*

**Biomaterials (854.03)**  
 Eric Amis, *Acting Group Leader*  
 Barbara Faverty, *Secretary*

**Multiphase Materials (854.04)**  
 Charles Han, *NIST Fellow*  
 Barbara Faverty, *Secretary*

B. Bauer        O. Anopchenko  
 C. Chiang        H. Lee  
 E. Lin            N. Noda  
 J. Obrzut        W. Sakai  
 C. Soles

J. Antonucci      M. Weir  
 S.B. Kennedy      C. Khatri  
 C. Simon          N. Richards  
 F. Wang            L. Bailey  
 N. Washburn

E. Hobbie        G. Matsuba  
 G. Holmes        C. Moon  
 F. Phelan        G. Schmidt  
 C. Schultheisz    K. Shimizu  
 E. Feresenbet    H. Wang  
 J. He              Z. Wang  
 H. Kim

**Processing Characterization (854.05)**  
 Kalman Migler, *Group Leader*  
 Trish Snoots, *Secretary*

**Multivariant Measurement Methods (854.06)**  
 Alamgir Karim, *Group Leader*  
 Trish Snoots, *Secretary*

A. Bur            S. Kharchenko  
 P. McGuiggan    J. Pathak  
 S. Roth          Y. Son

K. Beers        A. Sehgal  
 A. Crosby      C. Harrison  
 C. Davis        A. Smith  
 M. Fasolka     R. Song  
 S.L. Kennedy   C. Stafford  
 K. Ashley      K. Yurekli

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