# Polymers Division
# FY 2004 Programs and Accomplishments

# MSEL

## Materials Science and Engineering Laboratory

## On the Cover:

From the front cover and continuing on to the back, the images shown are, respectively:

Fig. 1 – Optical coherence microscope/confocal fluorescence microscope image of a polymer tissue engineering scaffold;

Fig. 2 – False color micrograph of a nanoporous insulation film using the strain induced elastomer buckling instability for mechanical measurements (SIEBIMM) method;

Fig. 3 – Profilometry image of a fluidics device master prepared by patterning an optical resin; and

Fig. 4 – Image displaying the Fourier transform of the average line cross section in a photoresist after etching as measured by critical dimension small angle x-ray scattering (CD-SAXS).

More information about each of these topics can be found within this report.

MATERIALS SCIENCE AND ENGINEERING LABORATORY

FY 2004 PROGRAMS AND ACCOMPLISHMENTS

# Polymers Division

Eric J. Amis, Chief

Chad R. Snyder, Deputy

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# Executive Summary

The NIST homepage summarizes the key vision for the National Institute of Standards and Technology *. . .working with industry to foster innovation, trade, security and jobs*. This vision guides the choices of research in the Polymers Division. In this annual report, we have tried to give you an update on our current projects and a glimpse of some of the scientific highlights of 2004.

Our researchers supporting the electronics materials industry continue to have strong interactions with industry, research organizations, and scientific peers. International SEMATECH remains a strong supporter of our work, pushing forward with next generation low-k dielectric materials. Building on some previous work with IBM, we have now partnered with SEMATECH to extend our investigations of the fundamentals of the lithographic process. This year, we completed our work on dielectric metrology for embedded passive devices and initiated two new projects: one in organic electronics and the other in nanoimprint lithography. Both technologies are expected to play prominent roles in the future generations of semiconductor electronics, and there are tremendous scientific and technical challenges to address before that promise is realized.

Following completion of our work on polyolefin mass spectrometry, we returned to a focus on quantitative mass spectrometry of polymers. Our ultimate goal is a standard method for quantitation of the absolute molecular mass distribution of polymers, which would enable researchers to produce their own reference standards. This year an interlaboratory comparison has given us insight into ways to quantify the accuracy and repeatability of matrix-assisted laser desorption-ionization mass spectrometry (MALDI-MS) in the identification of multiple end groups that result from polymer synthesis. Our processing characterization work continues to break new ground in rheology with the recent observation of suppression of die swell for extruded polymers blended with a small quantity of multiwall carbon nanotubes.

Our biomaterials-related work continues to attract attention on several fronts, from our collaboration with the American Dental Association Foundation on dental restorative materials to our 3-dimensional structural/functional imaging techniques that allow for *in-situ* imaging of cell growth in tissue engineering scaffolds. To further our understanding of the interface of materials with cell biology, we are extending our imaging capabilities beyond structure and function to chemistry, through development of broadband coherent anti-Stokes Raman scattering (CARS) microscopy. CARS microscopy holds the potential to enable further understanding in regenerative medicine by deciphering metabolic state and cell type *in-vitro*. Other exciting advances have been made in methodology for evaluation of the biocompatibility of materials using Quantitative Reverse Transcriptase Polymerase Chain Reaction (QRT-PCR).

Our combinatorial and high-throughput researchers continue to be recognized as pioneers and valuable partners in accelerated materials research, and our NIST Combinatorial Methods Center (NCMC) continues to attract new industrial members. The latest in the string of innovative approaches has demonstrated the adaptation of microfluidic (µF) technology to fabricate polymer molecule libraries that are compatible with other high-throughput measurement methods. In addition to this advance in µF technology, we now have a µF method of measuring interfacial tension in complex fluids. Our work on adhesion has progressed with high-throughput methods to enable rapid quantification of performance through visualization of debonding mechanisms across libraries of adhesive conditions.

This year we responded to some specific requests from other government agencies including a collaboration with NIST's Office of Law Enforcement Standards on long-term stability and durability of polymeric materials for ballistic resistant armor (*e.g.*, "bulletproof vests"). Based on our expertise in composite fibers, we are developing a minimally invasive technique to test polymeric fibers from ballistic armor currently in service. We hope to establish the critical links between chemical structure, mechanical properties, ballistic resistance, and long-term stability.

As usual, only a portion of our work is included in this report, so please visit **www.nist.gov/polymers** for more details. On our site, you can also download copies of any of our publications.

As always, I welcome your comments.

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

# Coherent Anti-Stokes Raman Scattering (CARS) for *In-Situ* Chemical Imaging of Tissue Engineering Constructs

*Design issues relating to bioactive devices for regenerative medicine reflect the spatial and chemical complexity of biological and materials issues and their interactions. Tools developed for the purpose of aiding understanding of these systems must have sufficient discriminatory power to sort out this complexity. We have introduced a relatively simple broadband spectroscopic microscopy based on CARS that can be used to rapidly acquire volumetric, chemically-specific images with submicrometer resolution.*

## Marcus T. Cicerone

Biological research in general could be significantly aided by a high-resolution, chemically sensitive volumetric imaging method that allows rapid, non-invasive study of processes on the tissue, cellular and sub-cellular levels. The need for such a method is particularly acute in the field of tissue engineering, where cycles of cell-seeding and analysis can take months. Standard analysis methods are labor intensive and destructive, so multiple endpoint studies must be performed and temporal correlation assumed. Non-invasive micro-spectroscopic imaging could alleviate many problems associated with the evaluation of tissue scaffolds both by allowing continuity of analysis on a single scaffold construct, and by maintaining spatio-temporal information.

Our vision is the creation of a non-invasive microscopic imaging technique that rapidly discriminates between an arbitrary number of chemically distinct structures or species in a spatially resolved way within a biological system. We envision that this would be done without staining or otherwise intrusively manipulating the system. We expect that such a microscopy tool would have a significant impact on the way *in-vitro* tissue-engineering studies are carried out.

While our vision may sound fanciful, the basis for such powerful and generally applicable chemical discrimination was established many decades ago via vibrational spectroscopy. Our contribution has been to marry broadband vibrational spectroscopy, with its inherent chemical resolving power, to a nonlinear, multiphoton microscopy (CARS microscopy), which has already been demonstrated to have significant utility for non-invasively imaging biological systems, even in the absence of significant chemical resolving power.

Microscopic coherent anti-Stokes Raman scattering (μCARS) can answer important imaging needs of the biological research community, including relative non-invasiveness, rapidity, and chemical specificity. CARS provides chemical specificity through its intrinsic sensitivity to molecular vibrational transitions. CARS is sensitive to the third order polarizability, $\chi^{(3)}$, which has nonresonant and resonant components, the latter being related to the Raman scattering cross section. Therefore, μCARS uses Raman (vibrational) susceptibility as a contrast mechanism, but it is approximately $10^3$ more efficient than spontaneous Raman scattering.
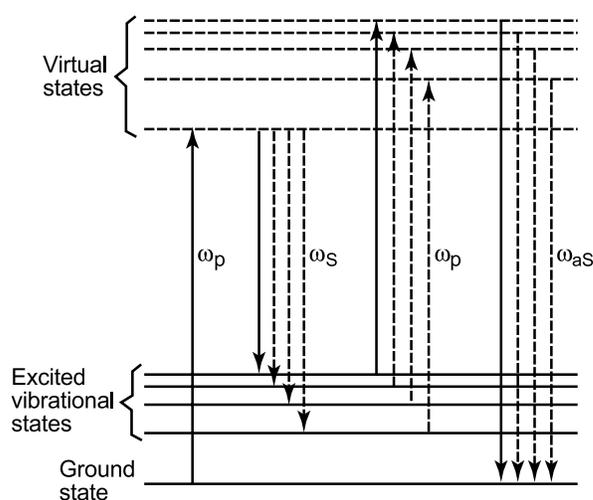


**Figure 1:** *Energy level diagram for single frequency CARS process (solid vertical arrows) and broadband CARS (solid and dashed vertical arrows).*

The solid vertical lines of Figure 1 represent transitions made by molecules in the "classic" CARS scheme. Molecules in a sample of interest are promoted to a specific energy $E = \hbar (w_p - w_S)$, where $\omega_p$ and $\omega_S$ are the frequencies of the near infrared pump and Stokes light pulses, respectively, and $\hbar$ is $h/2\pi$ where $h$ is Planck's constant. If that energy corresponds to a particular excited vibrational state in the molecule, that state is populated. A subsequent probe photon (also $\omega_p$) promotes the vibrationally excited molecule to another (higher) virtual state, from which it relaxes and emits an anti-Stokes photon at a specific frequency, $\omega_{aS}$. The flux of anti-Stokes photons detected is proportional to the number of molecules initially prepared in the targeted vibrationally excited state. To date, this "classic" μCARS scheme has been used to acquire only single-frequency or narrowband (200 cm$^{-1}$) vibrational information, and thus, chemical specificity is limited to only one or two species simultaneously.

We have developed, and demonstrated for the first time, a CARS microscope that yields vibrational spectra over a 2500 cm$^{-1}$ range. This method can give chemically specific information for multiple species simultaneously. Furthermore, information about subtle changes in such things as metabolic state or phenotype of cells, which are of interest when considering cell-scaffold interactions, can be extracted from these broadband vibrational spectra.

Figure 1 illustrates that the key to increased bandwidth of vibrational sensitivity in CARS is an increased bandwidth of the Stokes light. As our Stokes light source, we have used continuum light generated from ultrafast light pulses passed through a tapered optical fiber. Our apparatus uses the 785 nm output of a Ti:Sapphire oscillator (200 mW, 76 MHz, 150 fs pulses) fed into a tapered nonlinear fiber, 9 mm long with a 2 μm diameter waist to create a continuum that spans the wavelength range (500 nm to 1100 nm). A spectrally narrow portion of the same oscillator output is used for the pump and probe light.

At a total optical power of 21 mW and 0.8 NA focus, the photon flux density on the sample is sufficiently low that we do not damage even rapidly dividing live cells. At this low light level, we are able to acquire reasonably good broadband spectra in about 20 ms. Image scanning is performed by moving a sample through the focus of an objective using a motorized microscope stage. We employ an intensified CCD camera to detect the anti-Stokes light after it has been spectrally dispersed by passing through a spectrograph.

Figure 2a is a first demonstration of this method; it is an image of a tertiary polymer containing equal parts of polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(ethylene terephthalate) (PET); the polymer blend was annealed at 250 °C for 120 s, then melt-pressed at this temperature. Spatially-resolved spectra were obtained by broadband μCARS, and pseudo-colors were assigned to each pixel based on the primary polymer component — red, green, and yellow for PMMA, PS, and PET respectively. The reference spectra used for identification are plotted in Figure 2b, with an arbitrary vertical shift applied for clarity.

The primary polymer component within an image pixel (*i.e.*, the pixel "identity") was determined as follows. First, the CARS spectra from the image and the reference spectra were systematically normalized by the nonresonant background. Next, a dot product was calculated between the spectrum belonging to the pixel in question and the sections of each reference spectrum enclosed by the hatched boxes in Figure 2b. The dot product yielding the greatest value of the three determined the assigned polymer identity for that pixel. The reference spectra sections were amplitude-scaled such that a dot product of each with itself gave the same value. Using

this procedure, we could assign a polymer identity to each pixel with a standard uncertainty of 0.01.
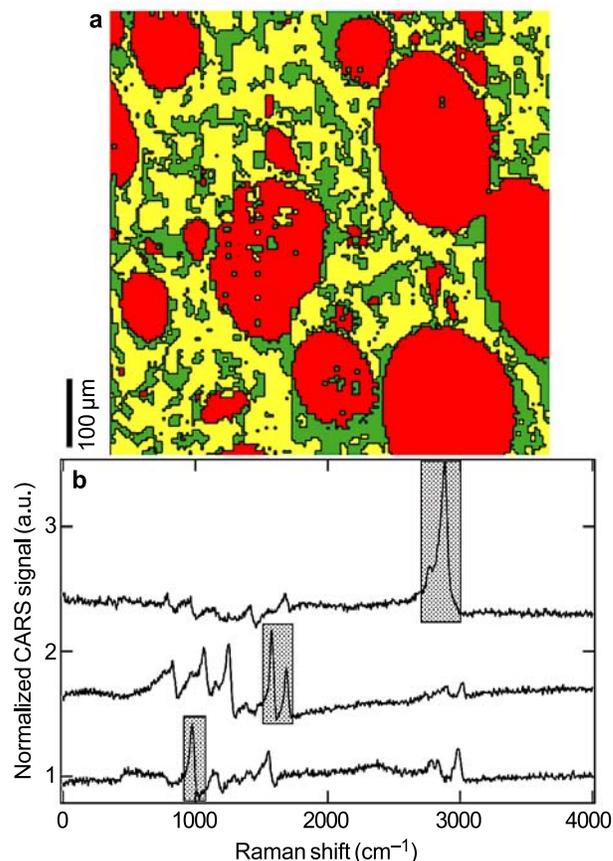


*Figure 2:* Panel a) — Pseudo-color image, generated with broadband CARS microscopy, of phase-separated polymer blend including equal parts of PMMA, PS, and PET. The colors red, green and yellow correspond to PMMA, PS, and PET respectively. Panel b) — Reference spectra used for computing dot products with the spectra from each pixel in panel a. The hatched boxes indicate spectral regions that were used for computing dot products (see text for discussion).

An account of this work has been accepted for publication in *Optics Letters*. We will also report on the new method at the 2004 "Vibrational Spectroscopy" and "Biomedical Imaging" Gordon Research Conferences (2004), and the August 2004 American Chemical Society National Meeting.

## For More Information on this Topic

T.W. Kee (Polymers Division, NIST)

# Use of Reverse Transcriptase Polymerase Chain Reaction (RT-PCR) to Measure Cellular Responses

*The goal of this work was to develop a set of genetic markers of cellular responses to provide improved measurement of biomaterial performance. This set of markers gives information on important phenomena such as cell proliferation, matrix production, and inflammation. We have developed genetic tests based on Quantitative Reverse Transcriptase Polymerase Chain Reaction (QRT-PCR) for assessing these complex cellular responses.*

## LeeAnn Bailey and Matthew L. Becker

The interface between the biomaterial and the cell is a critical point of interaction for tissue-engineered products. The nature of both the physical and chemical interactions can cause cells to transmit a variety of critical biological signals. In response to external stimuli, cells initiate a genetic response to determine which regulatory pathway the cell will traverse (Figure 1). These pathways include chronic and acute inflammation, differentiation, proliferation, and extracellular matrix production, which ultimately affects the well-being of the cell and determines the success of the tissue-engineered scaffold. We have developed a set of genetic tests based on Quantitative Reverse Transcriptase Polymerase Chain Reaction (QRT-PCR) for assessing complex cellular responses.
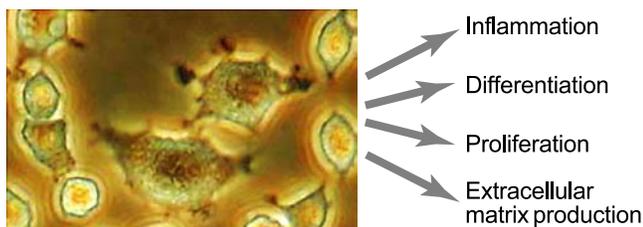


**Figure 1:** *Scaffold interactions can lead to cellular inflammation, differentiation, proliferation, and extracellular matrix production.*

In a typical experiment, mRNA is extracted from a cell population following a defined incubation period with the substrate. Using a reverse transcriptase (RT) enzyme, mRNA is converted to the cDNA template necessary for amplification. Then the cDNA, gene specific primers, a DNA polymerase, and a fluorescent moiety are utilized to amplify and label the amplicon generated. The gene product accumulation is then measured during the exponential phase of the amplification reaction (Figure 2). The copy number is obtained by extrapolating to a standard gene curve of known concentration and copy number to yield quantitative data. The assay also includes the analysis of mRNA that does not change in relative abundance (18S), which serves as an internal control.
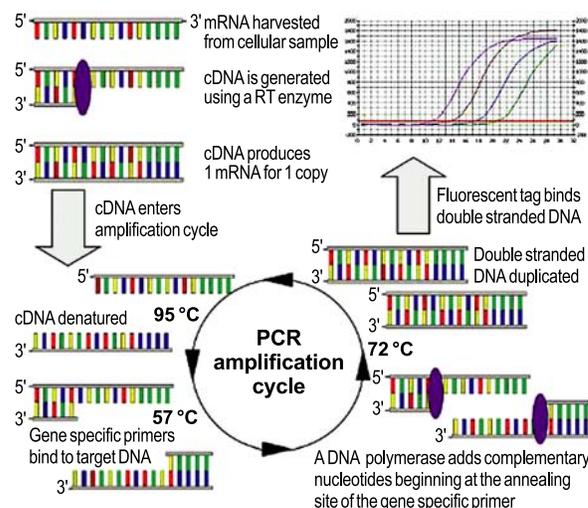


**Figure 2:** *RT-PCR is based on the detection of a fluorescent species that binds to double-stranded DNA produced proportionally during PCR amplification cycles.*

The Biomaterials Group in the Polymers Division has successfully created a model system to evaluate the biocompatibility of materials *in-vitro* using QRT-PCR. The method has been adapted to measure both DNA and RNA sequence levels present in cellular populations and determined to be substrate independent. Current technique sensitivities can detect one gene copy from a single cell and provides accurate, reproducible measurements regarding the genetic profile of the cell at a given time point. Table 1 includes a brief list of the numerous biological processes and specific gene markers being utilized in ongoing research.

Table 1: **A brief list of the gene specific markers utilized in the Biomaterials Group's current research efforts and their corresponding biological processes**

| Process | Gene Marker |
| --- | --- |
| Inflammation | IL-1β, TNF-α |
| Matrix Production | Fibronectin, Collagen I & II, Actin |
| Differentiation | Aggrecan, Osteopontin, Osteocalcin |

Recently completed QRT-PCR studies have documented quantitatively the inflammatory response of murine macrophages that have phagocytosed poly(methyl methacrylate) (PMMA) microspheres and/or been exposed to lipopolysaccharide (LPS). The studies have yielded great insight regarding the initiation and propagation of tumor necrosis factor-$\alpha$ (TNF-$\alpha$) and interleukin-1$\beta$ (IL-1$\beta$) cytokine profiles. The cell populations treated with LPS or PMMA microspheres singly resulted in an elevation of cytokine levels compared to the untreated control. RAW 264.7 cells incubated with LPS and PMMA particles demonstrated a synergistic effect by producing a marked increase in the level of cytokine expression, over control levels.
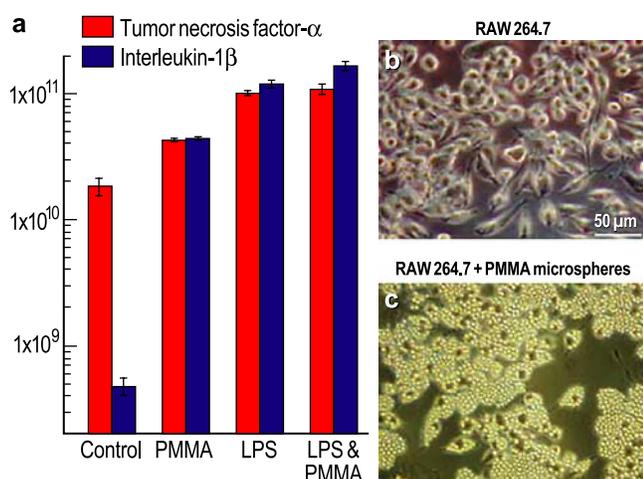


Figure 3: *Gene copy number of IL-1$\beta$ and TNF-$\alpha$ after 8 h of incubation with poly(methyl methacrylate) microspheres (PMMA), lipopolysaccharide (LPS), both PMMA and LPS, and an untreated control,* **a**. *The photos on the right depict untreated RAW 264.7 murine macrophages,* **b**, *and macrophages phagocytosing PMMA microspheres,* **c**.

There are numerous other applications that QRT-PCR is currently being applied to both inside and outside the Polymers Division. Application of nanotechnology in healthcare is generating significant enthusiasm, but little is known about the consequences of nanoparticles and functionalized nanostructures on biological systems. One question of critical importance concerns the inflammatory effects of nanometer-scale materials. The inflammatory response to peptide functionalized shell cross-linked (SCK) nanoparticle was found to be dependent, with respect to functionality and concentration. These studies have laid the foundation for the additional measurements of other nanoparticle systems, which can be coupled to a myriad of biologically relevant peptides or pharmacological agents.

Additionally, QRT-PCR technology has been utilized to investigate the genetic expression profiles of several biological model systems such as:

1) Fibronectin, collagen, and actin regulation in tissue-engineered scaffolds, thin films, and polymer blends.

2) Inflammatory responses to dental adhesives and bonding resins.

3) Inflammatory responses to metal alloy implant materials, both in particulate and solid form.
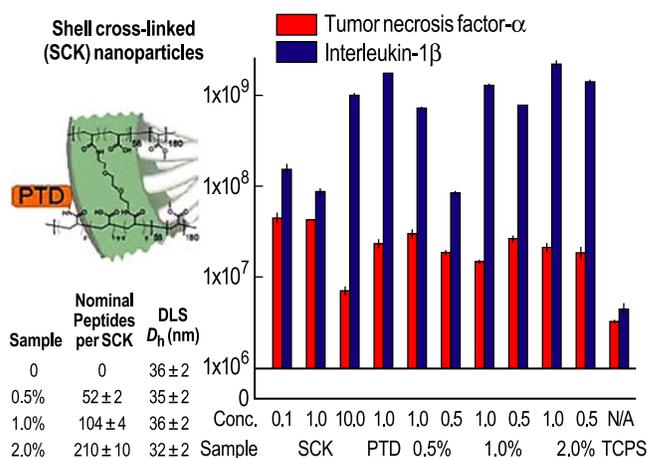


Figure 4: *Shell cross-linked (SCK) nanoparticles functionalized with different amounts of the protein transduction domain (PTD) of HIV-1 Tat causes statistically significant increases in IL-1$\beta$ production after 24 h of incubation that is functionalization and concentration dependent.*

In summary, QRT-PCR is a high-throughput, versatile measurement tool that can quantify an extensive range of genetic measurements in tissue-engineered products.

## For More Information on this Topic

L. Bailey, N. Washburn, C.G. Simon, E. Chan, and F.W. Wang, "The Quantification of Inflammatory Cellular Responses Using Real-Time Polymerase Chain Reaction (RT-PCR)," *Journal of Biomedical Materials Research* **69A(2)**, 305–313 (2004).

M.L. Becker, L.O. Bailey, and K.L. Wooley, "Peptide Derivatized Shell Crosslinked (SCK) Nanoparticles. 2) Biocompatibility Evaluation," *Bioconjugate Chemistry,* in press.

## Collaborators

N.R. Washburn, J.C. Cooper (Polymers Division, NIST); K.L. Wooley (Washington University); J. Kohn (Rutgers)

# Profiling the Photoresist-Liquid Interface: Fundamentals for Immersion Lithography and Polymer Dissolution

*Recent advancements in the semiconductor industry have resulted in new problems involving the photoresist-liquid interface. For immersion lithography, the water profile within a resist film impacts pattern quality from changes in photoacid generator diffusion or optical transparency. For the development step, where a latent image is realized into the final structure, an improved understanding of photoresist swelling and dissolution mechanisms is needed to address stringent line-edge roughness requirements. Data from neutron reflectivity measurements provide critical insight needed to understand and optimize next-generation photoresists and process strategies.*

**Bryan D. Vogt and Vivek M. Prabhu**

## Introduction

Polymer thin film photoresists comprise the materials foundation for the production of semiconductor devices with nanoscale dimensions. The extension of optical methods has been problematic due to challenges arising from the implementation of shorter exposure wavelengths. The past focus of the semiconductor industry has been the development of sufficiently transparent photoresist materials for future exposure sources. However, future progress requires depth profile information at the photoresist–liquid interface, due to the emergence of immersion lithography and the increased influence of the photoresist development process on lithographic performance.

Using neutron reflectivity (NR), NIST successfully quantified the profile of water and aqueous base counterions in model photoresist films. NR provides structural information regarding the composition profile normal to the thin-film surface with isotopic selectivity between protons and deuterium. Selective deuteration of components in the system allows for the quantification of water or counterion distribution within photoresist films despite the negligible differences in physical density. This data provide critical insight needed to refine models for immersion lithography and polymer dissolution.

## Immersion Lithography: Water Profile

Recently, immersion lithography has emerged as the key strategy to extend existing optical tools. A liquid, such as water, is placed between the lens and photoresist thin film to enhance resolution.

The industry anticipates using immersion lithography for production in 2007 at the 65 nm node. The role of liquids in contact with photoresist films is important; not only for component leaching and contamination, but also due to the detrimental influence of trace levels of water on the reaction and diffusion of photoacid generators. Additionally, a non-uniform water profile within thin films leads to incorrect assumptions regarding the transmission and reflection at the photoresist–anti-reflective coating interface.
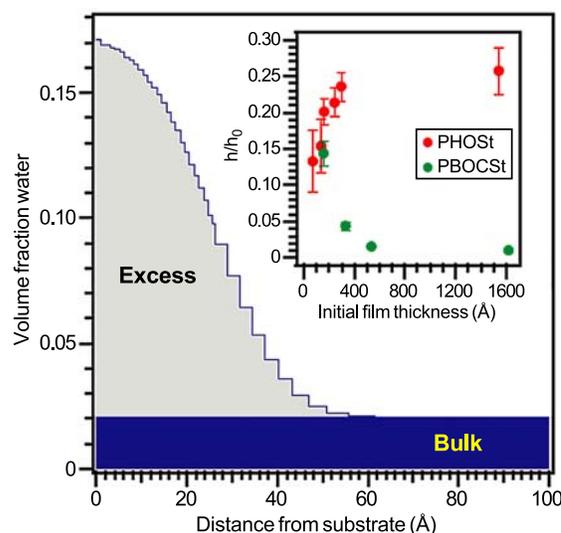


**Figure 1:** *Volume fraction of water distributed near the PBOCSt/HMDS treated substrate during immersion, as determined by neutron reflectivity. The excess of water at the substrate reaches a maximum concentration of 17 % by volume. Inset: Dependence of initial film thickness on the total film swelling for two model photoresists in thin and ultrathin films.*

Figure 1 shows the measured volume fraction profile of water versus the distance from a trimethylsilane-primed silicon oxide interface. Far from the substrate, the 248 nm photoresist, poly(4-*tert*-butoxycarbonlyoxystyrene) (PBOCSt), shows bulk water absorption near 2.5 %. However, significant deviations occur near the interface. An excess of water, up to 17 %, extends 40 Å from the substrate. This enriched interfacial water was previously unknown and unaccounted for.

In contrast, a depletion of water was observed for poly(4-hydroxystyrene) (PHOSt), the developer soluble resist, even though the bulk of the film absorbs 25 %. This depletion indicates the interface cannot accommodate excess water. It appears that the relative hydrophobicity between polymer and substrate controls the amount of interfacial water.

The total film swelling is also observed to be a function of the initial thickness and interfacial water. For thinner resist films the interfacial water dominates the swelling as shown in the inset to Figure 1 for PBOCSt and PHOSt. For these different resists, the swelling becomes similar for ultrathin films with thickness less than 200 Å. The data are consistent with an interfacial water thickness and content for each film thickness. The interfacial concentration is strongly dependent upon the surface chemistry, but relatively independent of the photoresist material or film thickness.

## Dissolution Effects: Aqueous Base Profile

The development step of a latent image in an aqueous base contributes significantly to undesirable line-edge roughness (LER). There is a strong need for improved dissolution models incorporating photoresist-developer interactions. A key component is the depth profile of the aqueous base counterion through a photoresist film because it controls the dissolution mechanisms that lead to unacceptable LER. We provided the first direct measurement of the aqueous base distribution (tetramethylammonium hydroxide) (TMAH) within the film. These measurements quantify the extent of developer penetration and the influence of ionization on the response of the photoresist to the developer solution.

We used a zero-average contrast (ZAC) experiment where the neutron scattering length density of a thin film of poly(norbornene hexafluoroisopropanol) (PNBHFA), a model 157 nm photoresist, is matched to the developer solution with a $D_2O/H_2O$ mixture. As shown in the schematic of Figure 2, the contrast matched film and solvent (equal color) eliminates neutron contrast at this interface. However, when base ($d_{12}$–TMAH) enters the film, the reflectivity contrast is enhanced. These changes allow quantification of both film swelling and the base profile through the film.
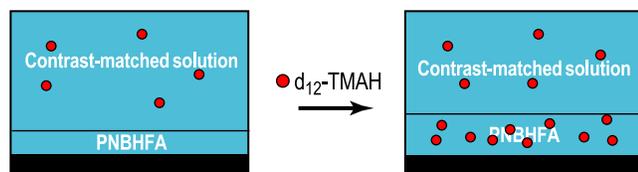


*Figure 2: Schematic of the zero-average neutron reflectivity experiment. The contrast between the film and solvent are equal, only the enrichment of deuterated aqueous base within the film provided the reflectivity enhancement.*

The volume fraction of $d_{12}$–TMA$^+$ is plotted versus distance from the substrate in Figure 3 for four different equilibrating concentrations of base. The change in the counterion profile illustrates the advancement of the swollen solid front. A key finding was that the film expansion proceeds via base transport throughout the entire film rather than gradually through the film. In addition, a depletion of base was observed at the substrate. The film-solution interfacial width increases with higher base concentration. These measurements show that ionization-induced swelling occurs at the dissolution front. At even higher base concentrations, the photoresist film dissolves quickly. Understanding the transition from swelling to rapid dissolution with base concentration will provide guidance into developer-induced roughness.
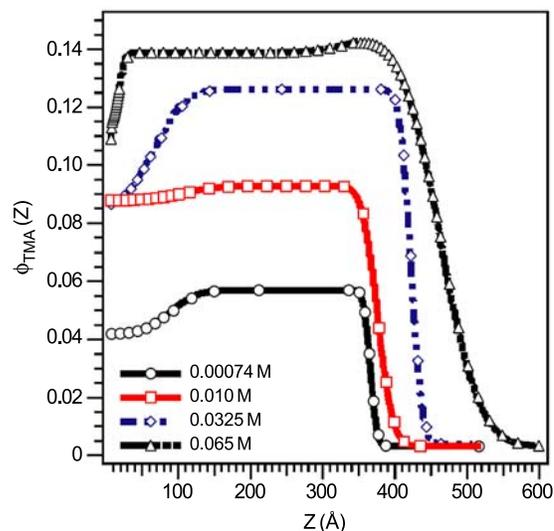


*Figure 3: Volume fraction profiles of $d_{12}$-TMA$^+$ within the PNBHFA film. The aqueous base profile illustrates the enhanced swelling and content within the thin film with higher equilibrating base concentration.*

These base profilometry experiments were followed by a deswelling step by rinsing with pure water. The rinse kinetically traps base within the film where it could contaminate other processes during device fabrication.

NR measurements provide new information about the liquid–photoresist interface needed to improve current models of dissolution. In future work, we will examine the effects of liquid–photoresist interactions on surface roughness with atomic force microscopy measurements of surface features.

## For More Information on this Topic

C. Soles, M. Wang, C. Wang, R. Jones, W. Wu, E. Lin (Polymers Division, NIST); S. Satija (NCNR, NIST); D. Goldfarb, M. Angelopoulos (IBM T.J. Watson Research Center); H. Ito (IBM Almaden Research Center).

B.D. Vogt, *et al.*, "Water immersion of model photoresists: Interfacial influences on water concentration and surface morphology," *J. Microlithography, Microfabrication, and Microsystems*, in press.

# Dielectric Metrology and Test Methods Supporting Embedded Passive Device Technology

*Embedded passive devices require high dielectric constant hybrid materials consisting of filled polymers to advance miniaturization and functional performance of high-speed electronics. New metrology methods were developed to address the needs of the electronics industry. Two test methods, a* Test Method for Dielectric Permittivity and Loss Tangent of Embedded Passive Materials from 100 MHz to 12 GHz *and a* Test Method for Dielectric Withstanding Voltage *were completed and have received wide acceptance by industry as new test methods to accelerate the development of embedded passive device technology.*

**Jan Obrzut**

## Introduction

Continuous reductions in the electrical charge required to drive logic gates and storage cells have resulted in tremendous progress in miniaturization and density of integrated circuits. However, enhanced functional performance increasingly depends on passive components such as capacitors, resistors, and inductors, where the dielectric permittivity and impedance characteristics of the material control spatial dimensions, time scale, speed, shapes and amplitude of electronic signals. Passive devices have not shrunk in size as rapidly as active devices and occupy an increasingly larger area and mass fraction of electronic subassemblies.
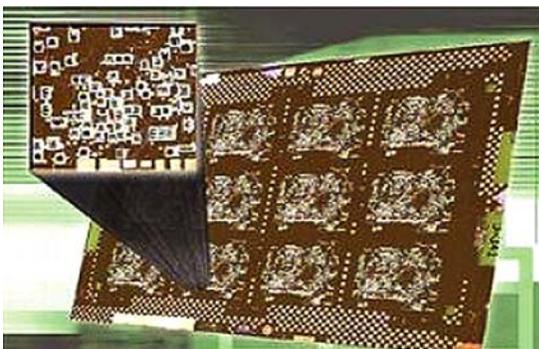


Buried resistor inner layer for Delphi engine control module board.

Significant advantages arise if passive devices are integrated directly into the circuit board as embedded passive devices rather than discretely attached with automated assembly. These include much thinner and sleeker electronics such as cell phones, decreased

manufacturing costs, better electrical performance, and enhanced design flexibility. Companies including Gould, Shipley, Ohmega, MacDermid, DuPont, Motorola, Oak-Mitsui, 3M, and Sanmia have devoted millions of dollars to advance this technology in an effort that represents a huge transition for the electronics industry.

High dielectric constant hybrid materials consisting of filled polymers are essential for advancing miniaturization and functional performance. There are significant challenges in developing new thin-film materials that require enhanced electrical performance characteristics, such as impedance and high dielectric constant (high-k), in order to operate at higher microwave frequencies and at increased voltage strengths. Consequently, new metrology and test methods are needed to address the specific behavior of thin film specimens and to better understand the relation between functional performance and the structural attributes of the materials.

The materials and testing requirements for Embedded Passives Technology are outlined in the National Electronics Manufacturing Initiative (NEMI) 2004 Roadmap. A need for new standard test methods for embedded materials was identified by the Association Connecting Electronic Industries (IPC), Roadmap 2005 Outlook Update, IPC Embedded Passive Device Standard Committee D-39. In partnership with industry, NIST chaired a test methods task group to communicate and collaborate with industrial partners. This year, two new test methods were accepted and will be used extensively by industry to accelerate implementation of this new technology.

## Dielectric Permittivity and Loss Tangent

The development of new thin-film materials that exhibit enhanced electrical performance characteristics, such as impedance and high dielectric constant (high-k), requires a broadband measurement technique for measuring permittivity at microwave frequencies (100 MHz to 12 GHz). Instead of expensive, single-test microwave strip test structures, NIST forwarded a general measurement strategy of incorporating a thin passive film material into a device that is comprised of a capacitive or resistive termination in a transmission line. The technique is based on the observation and theoretical analysis of the fundamental mode propagating at high frequencies in thin film dielectrics that terminate a coaxial air-filled transmission line. The development of the method involved nearly 50 active industrial partners and was reviewed by more than 300 other parties.
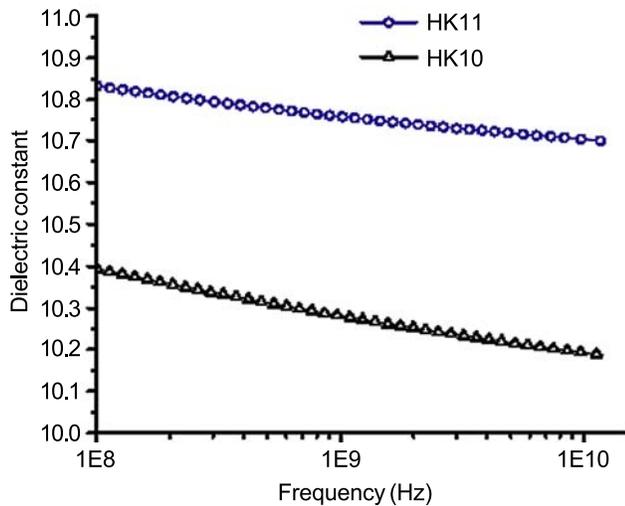
***Figure 1:*** *Dielectric constant of high-k polyimide-based composite films determined according to the Standard Test Method. (HK10 is a 25 µm thick composite; HK11 is a 14 µm thick composite).*

An example measurement of the dielectric constant for a high-k material obtained from DuPont is shown in Figure 1. We guided the design of the test protocol and made arrangements with co-sponsoring member companies for round robin evaluation of the measurement method. The work resulted in a test document "Test Method for Dielectric Permittivity and Loss Tangent of Embedded Passive Materials from 100 MHz to 12 GHz," which has received wide industrial acceptance and recommendation as a new standard test method.

This new capability to measure the dielectric properties at high frequencies for a wide range of dielectric permittivity values is also used to quantify dispersion, alignment, and structure in hybrid materials. For example, we demonstrated that composites of organic polymer resins filled with ferroelectric ceramics exhibit a dominant intrinsic high-frequency relaxation behavior. Such dielectric properties are beneficial in enhancing performance of processors and logic devices.

## Dielectric Withstanding Voltage

The dielectric breakdown of thin film materials is also a significant issue in embedded passive devices. Due to a thin film configuration, nonlinear effects may be activated at moderate bias levels and contribute to the dielectric breakdown. A non-linear dielectric measurement methodology was developed and applied for testing passive materials at high electric fields and voltages.

NIST-developed experimental set-up and testing procedures demonstrated the unambiguous determination of the dielectric withstanding voltage of embedded passive materials. In contrast to conventional procedures, the specimen voltage and current are determined as complex quantities from the corresponding time-resolved voltage waves. The new

testing procedure represents an extension compatible with the existing standard test method, but is better suited for capacitive and resistive thin film materials.

The specimen impedance and the loss tangent of the material can be determined by performing complex algebra calculations. It was found that thin-film materials for embedded passives do not exhibit a flat impedance characteristic, as is the case for conventional dielectrics, but the impedance sharply decreases with increasing voltage. The voltage withstanding condition may be attributed to a voltage range where the impedance characteristic remains insignificantly affected by the applied voltage. An equivalent impedance comparison indicates that high-k organic composites can withstand only a small fraction of the conventional dielectric withstanding voltage.

The NIST-developed procedure of recording and analyzing waveforms also allows the evaluation of specific characteristics of materials that cannot be readily evaluated with conventional techniques. This measurement procedure is especially suitable for detecting and analyzing non-linear dielectric effects that can result from polarization reversal and rectifying barriers. Such effects may appear at relatively low voltages in nano-sized interfaces, composites, and sub-micron thin dielectric films that are of interest to emerging technologies.

## For More Information on This Topic

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# High-Throughput Measurement of Interfacial Tension

*High-throughput (HT) tools to measure properties of complex fluids will greatly facilitate formulations science. Industrial members of the NIST Combinatorial Methods Center viewed a new HT method to measure interfacial tension as a primary need for product development. We have addressed this challenge with a novel microfluidic, high-throughput strategy to materials research and development.*

**Steven D. Hudson, João T. Cabral, and Kathryn L. Beers**

By developing microfluidic (µF) instrumentation to measure the behavior of polymers in complex fluids, we aim to demonstrate exciting new approaches to formulation science. With fast, flexible methods of designing and assembling milli-scale models of emulsion or colloid processing tools, high-throughput screening and optimization of new materials and discovery of new applications can be achieved across multiple stages of process development. Chemical suppliers and their customers will be able to obtain more and higher quality data relevant to the polymer additive properties critical to their business.

Most current µF technology is directed toward life science applications with devices designed primarily for low viscosity, aqueous solutions. We have developed a soft lithographic technique, which imparts solvent resistance to our devices and facilitates the integration of both aqueous and organic media. Multiple compositions can be evaluated by varying the input of either phase. Combinatorial µF systems can then be developed to measure viscosity, interfacial tension, and stability of emulsions in an automated and high-throughput manner. Our systems allow multiple feedstocks to be mixed in a range of compositions and have their above-mentioned properties measured over a range of temperatures. We envision a combinatorial factory in which materials synthesis, characterization, and processing are integrated.

As a first step towards this goal, and in consultation with industrial sponsors from ICI National Starch and Procter and Gamble, we are developing an instrument to measure interfacial tension of water/oil systems that is accurate within a few percent over a wide range of interfacial tension (from 0.1 to 50 mN/m). Moreover, microfluidic technology is well-suited to kinetic analysis, since the properties of the fluid can be analyzed at different points along the channel. In this way, dynamic interfacial properties associated with interface age, as well as quasi-equilibrium properties, are accessible.

We have implemented the HT instrument using a microfluidic device connected to fluid pumps and mounted on a microscope equipped with a fast camera. Experiment and data handling is computer controlled, featuring a real-time image analysis program. The device is fabricated using a novel rapid prototyping (RP) technique reported earlier and takes advantage of frontal photopolymerization (FPP) to generate 3-dimensional structures. This contact photolithography technique allows for the control of both lateral and vertical dimensions of patterns imaged on a negative polymer resist, which is then replicated on a transparent elastomer (PDMS). Assisted by flow simulations, we have devised a µF device geometry capable of drop formation, mixing of components, and drop acceleration and deformation (Figure 1).
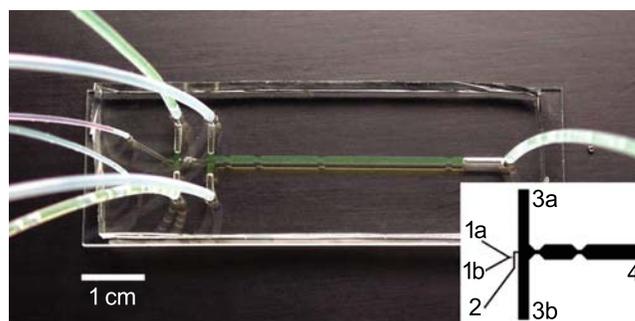


**Figure 1:** *Microfluidic prototype for measuring interfacial tension in immiscible fluids, displaying a combinatorial droplet mixer, acceleration junctions, and a series of extensional flow constrictions. This 3-dimensional device is fabricated using a novel rapid prototyping technique based on frontal photopolymerization and is sealed against a microscope glass slide. Inset: Schematic microchannel design. Fluids 1a and b are mixed together and injected as drops into immiscible stream 2. These drops are then fed by 3a and 3b into channel 4 for analysis and measurement. The constrictions in channel 4 accelerate and therefore stretch the drops. Multiple constrictions permit measurement at different interface age.*

A custom-built LabVIEW program drives fluid pumps, analyzes images in real time (Figure 3) and computes drop shape, velocity, and fluid extension rate. Following Taylor's classical theory for drop deformation in extensional flow fields, we compute the material rate of change of the drop deformation D (defined in Figure 2):

$$\tau \frac{d\mathsf{D}}{dt} = \mathsf{D}_{steady} - \mathsf{D} = \frac{5}{2\hat{\eta} + 3} \, \tau \dot{\varepsilon} - \mathsf{D} \ .$$

This rate is directly proportional to interfacial tension $\sigma$. Specifically, the drop relaxation time $\tau$ is:

$$\tau = \frac{(2\hat{\eta}+3)(19\hat{\eta}+16)}{40(\hat{\eta}+1)} \frac{\eta_c a_o}{\sigma}$$

where $a_o$ is the undeformed drop radius, $h_c$ is the continuous phase viscosity, $\dot{\varepsilon}$ is the shear rate, and $\hat{\eta}$ is the relative viscosity of the drop.
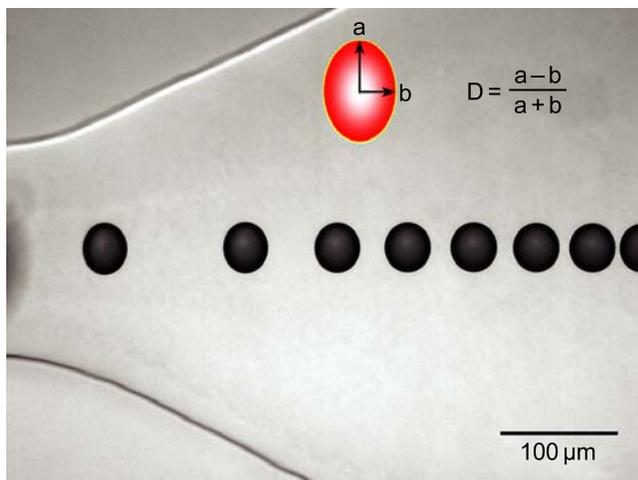


**Figure 2:** *Freeze-frame image of drops flowing left to right in an extensional flow gradient. When the drops leave the constriction (the channel walls appear as slanted lines in the left half of the image), the flow decelerates in proportion to the change in cross-sectional area. The drops, which are generated periodically in time, therefore, become closer together. This deceleration corresponds to a stretching in the transverse direction; note that the drops at the left side are stretched vertically, and their deformation decays as they pass to the right.*

The current measurement rate may exceed 100 data points/s and is dependent on drop formation and image acquisition rates.
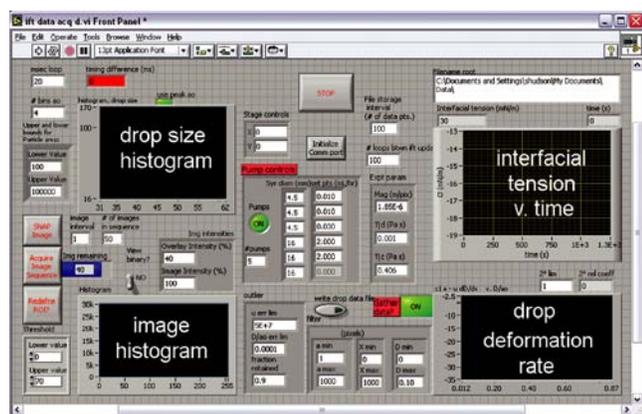


**Figure 3:** *LabVIEW interface used to control the instrument and record data.*
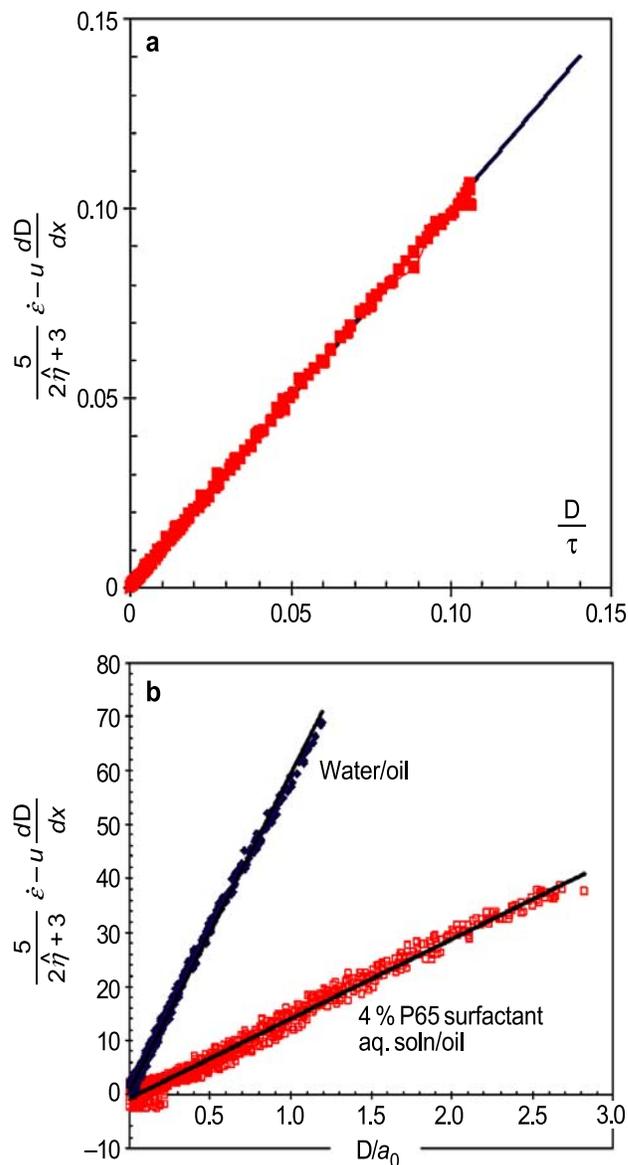


**Figure 4:** *a) Simulated and b) experimental analysis of drop deformation upon departure from the channel constriction. The radius $a_o$, deformation D and velocity u of the drops are measured directly by image analysis, at a rate of > 100 data points/s. The extension rate $\varepsilon$ is simply the gradient in the velocity $du/dx$. When the data is plotted in this way, the slope is directly proportional to the interfacial tension. For water in oil, the tension is $(31.8 \pm 0.8)$ mN/m, which is in accord with pendant drop measurement (32.0 mN/m). For the surfactant ($EO_{19}PO_{30}EO_{19}$) aqueous solution in oil, the tension is 7.2 mN/m. In this experiment, the interface age is approximately 1 s.*

## For More Information on this Topic

E.J. Amis, P.R. Start (Polymers Division, NIST); Focus Project Members: ICI National Starch; Procter and Gamble

J.T. Cabral, S.D. Hudson, C. Harrison, and J.F. Douglas, "Frontal Photopolymerization for Microfluidic Applications," *Langmuir*, in press.

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# Polymer Library Fabrication Techniques Using Microfluidic Technology

*Advanced material products incorporate highly designed polymer molecules, yet the effect of molecular parameters on end use properties is not understood. From both a scientific and an industrial perspective, there is a need for simple and economic synthetic methods that generate combinatorial polymer libraries that systematically vary molecular mass, architecture, and molecular composition. New methods at the NIST Combinatorial Methods Center (NCMC) enable the fabrication of polymer molecule libraries that are compatible with high-throughput measurement methods.*

## Kathryn L. Beers and Tao Wu



**Figure 1:** *a) CRP chip for producing well-defined polymeric materials tuned by flow rate and input stoichiometry; b) SEC data for polymers produced at different flow rates.*

For a large number of specialty polymers, the properties critical to their end use (*e.g.*, products ranging from personal care to nanotechnology applications) depend upon molecular variables such as chain sequence and composition, branching, and molecular mass. Often times, as in the case of the bicontinuous microstructures found in some block copolymers, the target variable space is narrow and difficult to define precisely. Tools exist to characterize these key properties in a high-throughput manner; however, there are few synthetic techniques that complement these measurement methods without capital-intensive automation. Moreover, in practice, current parallel polymer synthesis processes generally involve specimen volumes that are much larger than required for the screening tests, resulting in unnecessary chemical waste and over-use of expensive monomers.

As part of the polymer formulations project at NIST, new synthetic platforms are being developed for the fabrication of molecular gradient libraries that meet these challenges. Our approach leverages microfluidic technology to control and confine liquid chemical environments on the microscale. Using this technology, we have produced devices to achieve solution phase, surface-grafted, and suspension polymerizations in a manner that produces gradients in molecular properties in a controlled and addressable manner.

Figure 1 shows the first example of our new synthesis platform: a controlled radical polymerization (CPR) chip. Fabrication of the CPR chip uses conventional photolithographic techniques to pattern a thiolene-based optical adhesive between two glass slides, thus creating channel structures. Solutions of monomer, initiator, and catalyst are introduced through input ports at one end of the device and actively mixed with an enclosed spin bar. Controlled polymerization in a main channel is achieved through an atom transfer mechanism, where molecular weight is tailored by the ratio of monomer to initiator and the reaction time. By maintaining plug flow in the channel, controlling the stoichiometry of the reagents (input), and the flow rate of the solution through the channel, a polymer product with a predictable, continuous gradient in molecular weight and low polydispersity is produced. We validated polymerization kinetics in the CRP chip against published cases of synthesis carried out in large-scale reaction flasks.
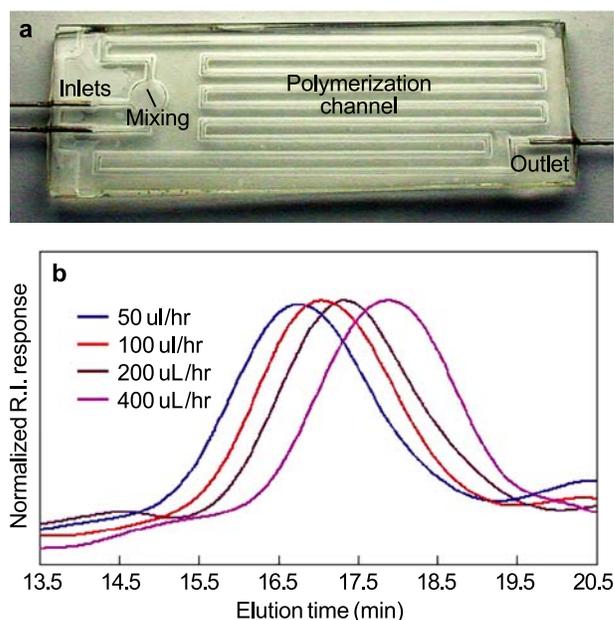
Whereas conventional techniques yield grams of a single material, the CRP chip produces microgram-scale material libraries that exhibit a systematic change in molecular properties. Accordingly, this technique is extremely powerful for optimizing materials with a narrow target molecular parameter space, or for developing new materials with expensive precursors, such as proteins and other biomolecules — all with minimal waste. Products of the CRP chip are neatly matched to the scale and design of NCMC methods to:

1) prepare gradient thin films for solid materials property measurements (*e.g.*, modulus, adhesion, microstructure); and

2) gauge solution properties (*e.g.*, viscosity, stability) through other fluidic devices being developed in the Center (see Polymer Formulations project in Advanced Manufacturing Processes).
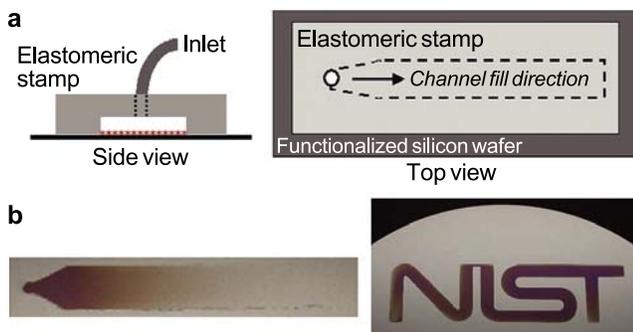
*Figure 2:* a) Schematic of microchannel confined surface initiated polymerization (µSIP) used to produce surface grafted polymer gradients. b) Image of a grafted polymer molecular mass gradient and a patterned substrate prepared using µSIP.

Another of our microfluidic devices exploits plug flow to achieve molecular gradients of surface grafted polymers. Microchannel confined surface initiated polymerization (µSIP; Figure 2) employs a shallow channel ($\approx$ 300 µm deep), formed through a patterned polydimethylsiloxane (PDMS) stamp, to confine a solution of monomer and catalyst over an initiator-functionalized silicon substrate. The result is a polymer grafted surface (brush) with geometry determined by the channel design and a gradient in molecular properties determined by the solution flow rate.

Several key features of µSIP illustrate its utility for combinatorial library fabrication.

1) The surface in contact with the PDMS stamp retains initiating capacity after the stamp has been removed, as do grafted polymers synthesized through an Atomic Transfer Radical Polymerization (ATRP) route. Accordingly, complex graft copolymer libraries can be built through sequential iterations of µSIP.

2) Utilizing multiple channels, it is possible to pattern the same surface with multiple brush configurations, as flow and stoichiometry conditions can be varied from channel to channel.

3) Confined gradients formed inside microchannels enable fabrication of grafted libraries of both statistical copolymers and gradient (tapered) block copolymers.

As a result, µSIP represents a significant improvement over existing techniques for grafting polymers from surfaces. Moreover, it enables fabrication of combinatorial substrates that could play a critical role in nanomaterials development, since many routes for nanofabrication (*e.g.*, self assembly) are extremely sensitive to substrate chemistry. Moreover, we envision µSIP to be a useful tool for nanometrology. For example, we intend to employ these techniques toward the fabrication of micropatterned substrates useful for the calibration of new scanned probe microscopy (SPM) methods

(see Combinatorial Gradient Reference Specimens for Advanced Scanned Probe Microscopy project under Nanometrology).

Our third device example concerns the preparation of polymer colloids and droplets via suspension polymerization in microfluidic channels (Figure 3). Indeed, these synthetic routes represent the most important methods used by industry. In this respect, our thiolene-based devices represent a major advance since they enable the creation of organic (hydrophobic) droplets in a hydrophilic (*e.g.*, water) matrix. This is a key requirement for reproducing necessary conditions for colloidal and suspension polymerization routes in microchannels, a major (unmet) challenge for channels fabricated from PDMS. Several preliminary devices have been designed to prepare and polymerize oil droplets in an aqueous continuous phase (Figure 3). In current work, we aim to polymerize organic phase droplets to form gradients of polymer microbeads.
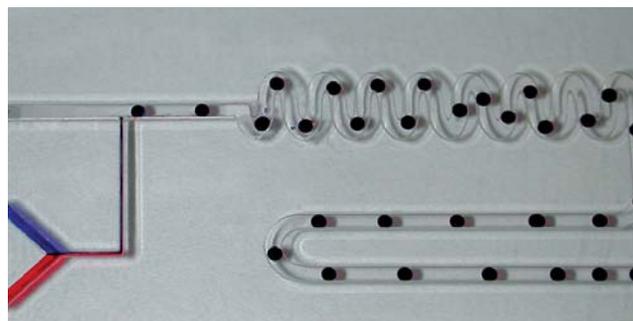


*Figure 3:* A device that produces, polymerizes and characterizes polymer colloids is one of the projects future directions. This device shows an important NIST-developed milestone, two-component toluene droplets suspended in an aqueous continuous phase.

Each of the three synthetic methods described above has unique advantages including small specimen volumes, the ability to make molecular gradients, and the type of polymers (solution, block, graft, colloidal) they produce. These methods are designed to interface with existing NCMC methods including solution blending, rheological and interfacial tension measurements, and gradient thin film deposition high-throughput solid characterization and microstructure analysis. As a part of the combinatorial and high-throughput toolset at NIST, the ability to prepare molecular gradients in a variety of forms is a fast, accurate, and inexpensive resource to prepare many important polymer libraries.

## For More Information on this Topic

K.L. Beers, T. Wu, C. Xu, Z.T. Cygan, Y. Mei, M.J. Fasolka, E.J. Amis (Polymers Division, NIST)

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# MALDI-MS Interlaboratory Comparison of Polymer Mixtures

*Polymer synthesis often results in impure products, containing multiple end groups, due to the synthesis process itself or the presence of impurities. Identification and quantification of these end groups and impurities is important because they influence polymer properties. An interlaboratory comparison of a mixture of two polystyrenes, one terminated with a proton, and the other terminated with a hydroxyl group, was performed using matrix-assisted laser desorption-ionization mass spectrometry (MALDI-MS). This interlaboratory comparison will be used to quantify the accuracy and repeatability of MALDI-MS in the identification of multiple end groups as a result of polymer synthesis.*

## Charles M. Guttman and William E. Wallace

A MALDI-MS interlaboratory comparison of mixtures of synthetic polymers of the same repeat unit and with closely matching molecular masses but with different end groups was sponsored by NIST. This interlaboratory comparison was designed to determine how well a group of laboratories engaged in MALDI-MS analyses of synthetic polymers agree on the percent composition of each polymer in the mixture. In an earlier interlaboratory comparison, NIST studied the molecular mass distribution (MMD) and the moments obtained by MALDI on polystyrene (PS) and compared the results with those obtained by classical methods. Interlaboratory comparisons enable us to gauge the needs of the community for standard methods and materials, to begin a dialog with the community on these needs, and to steer our own research. The interlaboratory comparison on mixtures of two polystyrenes with different end groups is of particular interest to industry where understanding and controlling the chemistry of reactive pre-polymers is a major concern.
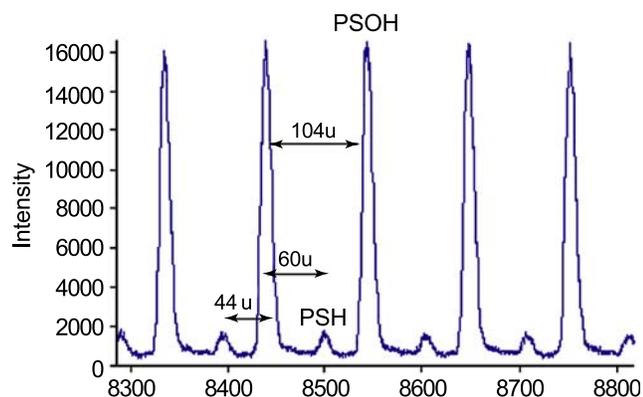
Five gravimetric mixtures of two polystyrenes with matched molecular masses but with different end groups, –H and –OH, were created. The challenge for the participants was, without knowing the gravimetric values, to determine the mass fraction of each polymer in each mixture. Difficulties to overcome included different ionization probabilities of the two polymers and finding small peaks in background noise for species that are in the minority in the mixture. Fourteen labs from 5 countries participated: 6 industrial, 4 academic, and 4 government laboratories.

The PS syntheses were both initiated with butyl initiator. One was terminated with H (PSH) and the other was terminated with $CH_2CH_2OH$ (PSOH). These end groups are separated by 44 u and 60 u in the mass spectrum and are well resolved (Figure 1). Five mixtures of these were made up with mass ratios between approximately 95:5 to 10:90 PSOH:PSH. Nuclear magnetic resonance (NMR) and Fourier-Transform infrared (FTIR) spectroscopies conducted at NIST confirmed the gravimetric mass ratio. The existence of a small amount of PSH in the as-received PSOH material was evident in our MALDI-MS analysis. NMR gave between (4 to 9) % PSH polymer in the PSOH-material. This is close to the value obtained from the initial MALDI-MS analysis performed at NIST.

Each participating laboratory was asked to perform MALDI-MS on each of the five mixtures using two distinct protocols: one using all-trans retinoic acid with defined concentrations of matrix:analyte:salt and a second protocol defined by the user as their preferred method for analyzing polystyrene. Each laboratory was asked to report two repeats of each protocol for each mixture to check for intralaboratory variability. Each laboratory was asked to report the estimated ratio of the mass of PSH to the mass of PSOH in each mixture and return data sets listing mass versus the integrated peak area of the mass spectra.

The analysis of the data revealed a strong variation among laboratories. This was seen in our first interlaboratory comparison as well. The effect of instrument manufacturer on the data was not significant. But the difference between acquiring mass spectra in the linear and the reflectron mode of operation resulted in significant variation in the end group fractions. The analysis of variance showed no significant influence of the sample preparation protocol on the fraction of PSOH in each mixture.

The accuracy of the instrument calibration of each laboratory was assessed by calculation of end group mass. In our first interlaboratory comparison, calibration varied more widely than anticipated. We would expect the calibration of most time-of-flight mass spectrometers in this mass range to be off by less than 3 u. Some laboratories showed calibrations off by



*Figure 1:* *MALDI mass spectrum of polystyrene mixture.*

over 40 u. Figure 2 shows that calibration was again an important issue in this interlaboratory comparison. The instrument calibration varied by as much as 20 u, even though the end groups were known.
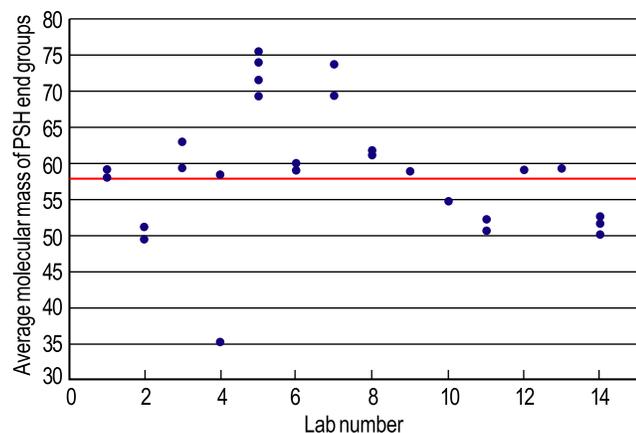


**Figure 2:** *The average molecular mass of PSH end groups for each laboratory. The red line represents the actual molecular mass of the end groups.*

Figure 3 shows a plot of the "Theoretical Mixture of PSOH" polymer fraction assuming 7 % PSH polymer in the PSOH material from the NMR data. The plot is compared to MALDI-MS data from some of the participating laboratories. The agreement is generally good, but the data show a wide range of variability among the laboratories. Deviation of the data from the expected percentages was found widest at the extremes of concentration of 95:5 and 10:90 PSOH: PSH, but even at the 50:50 ratio the deviation was as high as 10 %.
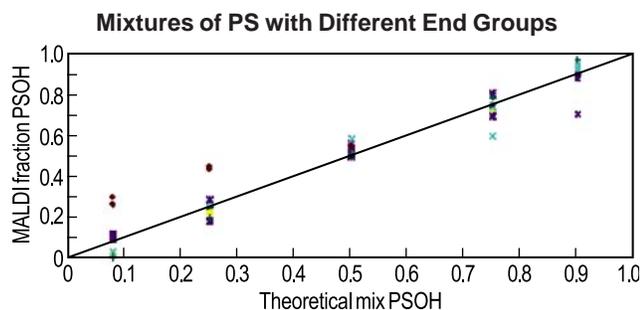


**Figure 3:** *The fraction of PSOH determined by MALDI compared with the gravimetric data.*

The agreement and standard deviation of data are shown in Table 1. The fraction of PSOH polymer in each mixture is given in the 2nd column. This column assumes the PSOH-material is 7 % PSH polymer and 93 % PSOH polymer. Seven percent is the midpoint of the range assigned by the NMR. It is seen from both Figure 3 and Table 1 that the agreement between the MALDI-MS and the gravimetric results for the fraction of PSOH polymer in each mixture is good when judged by the standard deviation of the MALDI results.

The key to "getting it right" in MALDI-MS, especially for Mix A and Mix E, is to optimize the instrument. This

*Table 1:* **The fraction of PSOH polymer by mass and determined by MALDI**

| | By Mass | MALDI Average | MALDI Std Dev |
|---|---|---|---|
| Mix A | 0.93 | 0.933 | 0.051 |
| Mix B | 0.716 | 0.746 | 0.086 |
| Mix C | 0.481 | 0.47 | 0.041 |
| Mix D | 0.284 | 0.259 | 0.051 |
| Mix E | 0.086 | 0.117 | 0.2 |

was seen in the higher variation in the fraction of PSOH determined for Mix A and Mix E, where a minor component may be lost in the noise. The result, which indicates significant variation in the fraction of PSOH for instrument mode, may be due to the resolution difference between reflectron and linear mode. In order to better understand the optimization of the MALDI-MS, we have begun to study the influences of the instrument and sample preparation parameters on the MALDI-MS signal. We are using an orthogonal fractional factorial design to study detector voltage, laser energy, delay time, and ion optic voltages, as well as matrix and polymer concentration. Once the effects of all parameters are understood, optimization will be easier to obtain.

These results also recapitulate the need for an unbiased, automated peak integration routine when the S/N is poor. We will continue to refine our MassSpectator software as a benchmark method to perform unbiased peak integration.

## For More Information on this Topic

S.J. Wetzel, K.M. Flynn, B.M. Fanconi, D.L. VanderHart (Polymers Division, NIST); S. Leigh (Statistical Engineering Division, NIST)

C.M. Guttman, S.J. Wetzel, K.M. Flynn, B.J. Fanconi, W.E. Wallace, and D.L. VanderHart, "International Interlaboratory Comparison of Mixtures of Polystyrenes with Different End Groups," *Proceedings of the 52nd ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, TN.

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S.J. Wetzel, C.M. Guttman, and K.M. Flynn, "The Influence of Matrix and Laser Power on the Molecular Mass Distribution of Synthetic Polymers obtained by MALDI," *Int. J. Mass Spectrometry*, in press.

# Extraordinary Transport Properties of Nanotube/Polymer Nanocomposites

*There has been intense interest in composites of polymers and carbon nanotubes (CNT) because of the large transport property (conductivity, elasticity, viscosity, thermal conductivity) changes exhibited by these additives for relative low CNT concentrations (≈ 1 % volume fraction). NIST's experience in the area of dielectric and rheological measurement, in conjunction with expertise in modeling, puts it in a unique position to lead the development of new processing concepts required by industry to utilize this important new class of materials.*

**Kalman B. Migler and Jack F. Douglas**

**Figure 1:** *Optical microscopy image of 1 % by volume MWNT/PP nanocomposite (obtained using a 100x objective) demonstrates good dispersion of the MWNT and reveals a polydispersity in nanotube length and shape. The MWNT volume fraction in this figure equals $\phi = 0.01$, which is close to the geometrical percolation concentration where the CNT network first forms and where the conductivity and stiffness of the nanocomposite increases by orders of magnitude (see Figure 2).*

The combination of extended shape, rigidity and deformability allows carbon nanotubes (CNT) to be mechanically dispersed in polymer matrices in the form of disordered network structures exhibiting a gel-like rheology. Our measurements on representative network-forming multi-wall carbon nanotube (MWNT) dispersions in polypropylene (PP) indicate that these materials exhibit extraordinary flow-induced property changes. Specifically, electrical conductivity $\sigma$ and steady shear viscosity $\eta$ both decrease strongly with increasing shear rate $\dot{\gamma}$, and these nanocomposites exhibit impressively large and *negative* normal stress differences, a rarely reported phenomenon in soft condensed matter. We illustrate the practical implications of these *non-linear* transport properties by showing that MWNTs *eliminate* die swell in our nanocomposites, an effect crucial for their processing.

The strong interest in CNT "nanocomposites" stems from their ability to affect thermal, electrical and rheological properties for relatively small concentrations of this type of additive. These additives have found manufacturing applications in electrostatic painting, protective coatings for electronic components, and flammability reduction. Utilization of CNT for more complex applications, however, requires an understanding of how processing conditions (mixing, molding, extrusion) influence nanocomposite properties.

Despite the high elastic modulus of CNT, their small cross-sectional dimensions and large aspect ratio allows them to bend substantially in response to inter-tube interactions under processing conditions. This bending leads to the formation of a disordered "web-like" structure (see Figure 1) of substantial mechanical integrity. The presence of a nanotube network interpenetrating the polymer matrix creates additional contributions to nanocomposite viscoelasticity that can have a radical effect on the processing characteristics of these materials.

In Figure 2, we characterize the large changes in viscoelasticity and conductivity for which polymer composites containing CNT are well known. *Simultaneous* measurements of $\sigma$ and the shear moduli ($G'$, $G''$) characterize the elastic and viscous properties of our composites. $G'$ can be thought of as a measure of "stiffness" and $G''$ provides a measurement of viscous resistance to deformation. The ratio ($G'/G''$) or "loss tangent" *(tan $\delta$)*, is a measure of the composite "firmness," and we compare this basic quantity to $\sigma$. We observe that both ($G'/G''$) and $\sigma$ increase with $\phi$ and that this variation becomes rapid for MWNT volume fraction $\phi$ in the range from 0.0025 to 0.01. We see that adding MWNT to the PP matrix increases the conductivity by an impressive seven orders of magnitude as a percolating network structure forms. $G'$ and $G''$ become frequency independent as $\phi$ is varied through the "gelation concentration," $\phi_c \approx 0.01$.

In order to manufacture MWNT nanocomposites into usable shapes, we must understand how the network structure acts to influence their processing behavior. The linear rheological and electrical transport properties (Figure 2) are strongly altered by flow, as

Figure 3 indicates. Notably, both the conductivity and the viscosity $\eta(\dot{\gamma})$ exhibit a strong *thinning*. The viscosity decreases over the full range of shear explored here, whereas the conductivity shows a plateau region at low shear. Moreover, a positive normal force $\Delta N$ is observed in our nanocomposite for $\phi \leq \phi_c$, where the matrix dominates the rheological response (Figure 3), but $\Delta N$ becomes large and *negative* for $\phi \geq \phi_c$, compensating the large $\Delta N$ exhibited by the matrix polymer. (A negative $\Delta N$ in nanotube dispersions was reported by Lin–Gibson, *et al.*) This has significant processing consequences.



**Figure 4:** *Comparison of PP extrudate with (A) and without (B) added nanotubes. The red dashed lines correspond to the die size.*
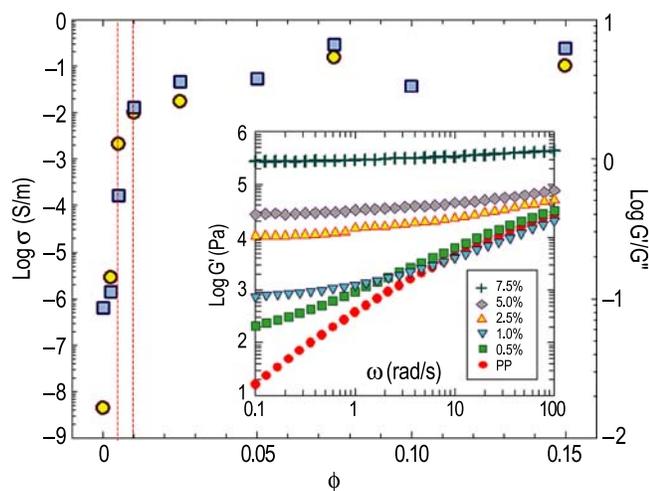


**Figure 2:** *Characterization of conductivity and viscolelasticity of MWNT/PP nanocomposites ($\phi = 0.025$; $T = 200\,°C$). Inset: Shear modulus as a function of frequency for a range of nanotube concentrations.*

Since the extrusion of the nanocomposite is a basic processing operation for which normal forces are known to be important, we extruded a nanocomposite sample ($\phi = 0.025$) and found that the cross-section actually shrinks upon extrusion (Figure 4). This striking effect is contrasted with the extrusion of pure PP where a nearly 6-fold increase in cross-sectional area is observed. Evidently, the CNT change the qualitative nature of the polymer flow.

The suppression of die swell of extruded polymers by adding a relatively small amount of MWNT ($\phi \approx 0.01$) offers a powerful tool for controlling dimensional characteristics and surface distortion in manufacturing composites. Our observations of strongly non-linear rheology under flow (shear thinning and large, negative normal stresses) imply that these fluids should exhibit other "anomalous" flow characteristics (*e.g.*, droplet distortion and thread break-up) that are quite unlike Newtonian fluids. Understanding these flow characteristics is crucial for their processing.

## For More Information on this Topic

S. Kharchenko, J. Obrzut, E. Hobbie (Polymers Division, NIST)

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S.B. Kharchenko, J.F. Douglas, J. Obrzut, E.A. Grulke, and K.B. Migler, "Extraordinary Flow Characteristics of Nanotube-Filled Polymer Materials," *Nature Materials*, in press.



**Figure 3:** *Normal stress measurements showing slightly positive normal stress for pure PP and increasingly negative normal stress as the MWNT fraction increases. Inset: Conductivity and viscosity as a function of shear rate for ($\phi = 0.025$; $T = 200\,°C$).*

# Advanced Manufacturing Processes

The competitiveness of U.S. manufacturers depends on their ability to create new product concepts and to speed the translation from concept to market while decreasing product cost. This is equally true for well-established "commodity" industries, such as automotive and aerospace, and rapidly growing or emerging industries, such as biotechnology and nanotechnology. For existing products, manufacturing is a critical step in reducing product cycle time. Rapid, low-cost development of manufacturing processes is needed to incorporate new materials into complex product shapes with higher performance at equivalent or lower cost as the competing, established materials and methods. For innovative product concepts, new materials with increasing functionality are needed to translate these concepts to reality.

To realize such improvements in materials and manufacturing, MSEL is developing robust measurement methods, models, standards, and materials and process data needed for design, monitoring, and control of manufacturing processes. A growing challenge is being able to design, monitor, and control such materials and manufacturing processes at size scales from nanometers to meters. The Advanced Manufacturing Processes Program focuses on the following high-impact areas:

- Combinatorial, high-throughput methods for materials ranging from thin films and nanocomposites to micro- and macroscale material structures;

- Industry-targeted R&D centered on unique measurement facilities in forming of lightweight metals for automotive applications, polymer processing, and high-speed machining;

- Innovative testbeds for emerging materials, including carbon nanotubes and fuel cells;

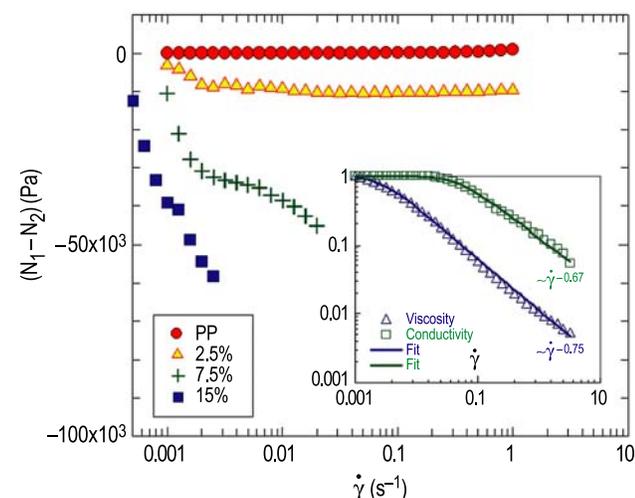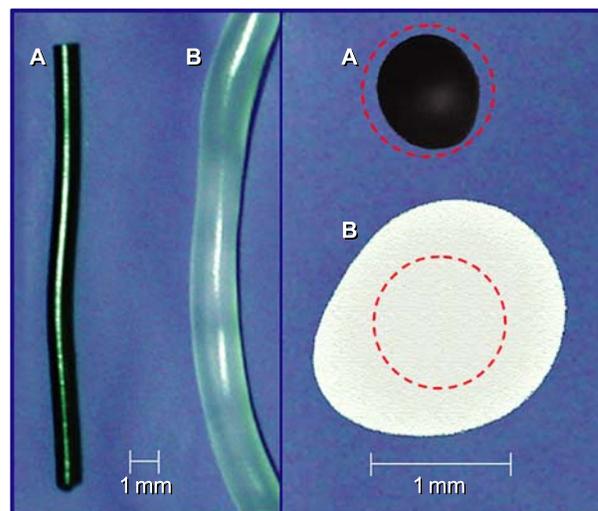- National traceable standards having a major impact on trade, such as hardness standards for metals and process standards for polymers; and

- Innovative, physics-based process modeling tools.

Our research is often conducted in close collaboration with industrial consortia and standards organizations. These collaborations not only ensure the relevance of our research, but also promote rapid transfer of our research to industry for implementation. Three projects focused on Advanced Manufacturing Processes are highlighted below.

## NIST Combinatorial Methods Center (NCMC)

The NCMC develops novel high-throughput measurement techniques and combinatorial experimental strategies specifically geared towards materials research.

These tools enable rapid acquisition and analysis of 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 NCMC lowers barriers to the widespread industrial implementation of this new R&D paradigm. MSEL uses a two-pronged strategy for accelerating the development and implementation of these approaches: an active intramural R&D program that demonstrates the ability of combinatorial methods to produce cutting-edge scientific research and an ambitious outreach activity; key to this effort is the validation of these approaches with respect to traditional "one at a time" experimental strategies.

## Forming of Lightweight Metals

Automobile manufacturing is a materials intensive industry that involves about 10 % of the U.S. workforce. In spite of the use of the most advanced, cost-effective technologies, this globally competitive industry has major productivity issues related to measurement science and data. Chief among these is the difficulty of designing stamping dies for sheet metal forming. An ATP-sponsored workshop ("The Road Ahead," June 20–22, 2000) identified production of working die sets as the main obstacle to reducing the time between accepting a new design and actual production of parts. This is also the largest single cost (besides labor) in car production. To benefit from weight savings enabled by new high-strength steels and aluminum alloys, a whole new level of formability measurement methods, models, and data is needed, together with a better understanding of the physics behind metal deformation. MSEL is working with U.S. automakers and their suppliers to fill this need.

## Polymer Processing

Polymers have become ubiquitous in the modern economy because of their processability, high functionality, and low cost. 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 our polymer research is on microfluidics and microscale processing, modeling of processing instabilities, and on-line process monitoring of polymers. 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. These measurements are carried out in close collaboration with interested industrial partners.

Contact: Carol A. Handwerker or
          Kalman Migler (Polymers Division)

# NIST Combinatorial Methods Center (NCMC)
## Pioneer and Partner in Accelerated Materials Research

*Combinatorial and high-throughput (C&HT) techniques hold great potential for making materials research more productive, more thorough, and less wasteful. However, significant barriers prevent the widespread adoption of these revolutionary methods. Through creative, cost-effective measurement solutions, and with an eye towards fruitful collaboration, the NIST Combinatorial Methods Center (NCMC) strives to ease the acquisition of C&HT techniques by the materials research community.*

### Cher H. Davis and Michael J. Fasolka

Now in its third year, the NIST Combinatorial Methods Center continues to be a sought after partner among industry, government laboratories, and academics interested in acquiring C&HT research capabilities for materials research. Indeed, the NCMC consortium currently includes 22 member institutions (see table) representing a broad cross-section of the materials research sector.

The NCMC is successful because it serves the combinatorial materials research community on several levels. Our foundation is the extensive suite of NCMC technologies, which provide measurement solutions to parties interested in acquiring C&HT capabilities. Many of these methods are described elsewhere in this report, as identified by the NCMC symbol (see top right corner).

Technology transfer efforts complement our methods foundation, as evidenced by the many institutions that have adopted NCMC techniques. For example, Air Products, Rhodia, National Starch (ICI), Dow, Procter and Gamble, and Eastman, plus many universities, have replicated NCMC devices in their laboratories. In this respect, NCMC *Focused Projects* are a new paradigm for NIST/industry partnership, which are extremely effective for both methods development and technology transfer.

> *"The focused project approach is particularly effective since it allows active collaboration with industry, allowing real needs to be addressed, and resulting technology transferred. The [NCMC] is at the leading edge of combi-based material science discovery, and this reflects both the quality of the research program and of the people."*
> — Dr. J. Carroll, ICI/National Starch, Strategic Technology Group

Under a Focused Project, NIST scientists and 2–3 member companies collaborate to develop a particular C&HT measurement solution. While the research is co-funded by industry members, we avoid the study of proprietary materials and all results are published; this allows the research to have the broadest impact. Currently, there are two Focused Projects. In the first, NIST is working with Procter and Gamble and National Starch (ICI) to produce HT microfluidic measurements of interfacial tension. The second Focused Project, sponsored by Intel and National Starch (ICI), will produce C&HT methods that gauge the performance of epoxy adhesives for flip chip electronics applications. Several other Focused Projects are in development.

New scientific endeavors (such as C&HT materials research) gain momentum when stake-holding parties are brought together. Accordingly, to advance the field, the NCMC invests itself in *community forming* activities aimed at information transfer and goal consolidation among institutions interested in C&HT research. Industry workshops play a major role in this endeavor, and in FY04 we hosted the 4th and 5th additions to the NCMC workshop series, focused on *Polymer Formulations* and *Processing and Characterization,* respectively.

> *"The NCMC provides a unique platform to exchange information and ideas with other member companies who form a part of this consortium."*
> — D. Bhattacharya, Global Coatings Application Development, Eastman Chemical Co.

Moreover, we have been very active in organizing symposia at national conferences. In FY04 alone, NCMC staff developed and organized multi-day symposia on C&HT methods for the Materials Research Society, the American Chemical Society, the Adhesion Society, and the Knowledge Foundation.

> *"I have heard nothing but praise from all who attended the recent NCMC conference. . .NIST did a superb job organizing the symposia, selecting thought-provoking topics, and leading good general discussions."*
> — Personal observation of J. Dias, ExxonMobil; Chair ACS PMSE

For more information on the NCMC, C&HT technologies, or post-doctoral research opportunities, see our website at **http://www.nist.gov/combi**.

| NCMC Members (*New in FY2004): | |
| --- | --- |
| 3M | Honeywell International |
| Accelrys* | Hysitron International* |
| Air Force Research Lab | Intel* |
| Air Products & Chemicals | ICI/National Starch & Chemicals |
| Akzo Nobel | Michelin |
| Atofina Chemicals* | PPG Industries |
| BP* | Procter & Gamble |
| BASF | Rhodia |
| Bayer Polymers | Sealed Air Corp* |
| Dow Chemical Company | Symyx* |
| Eastman Chemical* | Univ. of Southern Mississippi |
| ExxonMobil Research | Veeco/Digital Instruments* |

### Contributors and Collaborators

K.L. Beers, C.M. Stafford, A. Karim, E.J. Amis, The Multivariant Measurement Methods Group (Polymers Division, NIST)

# Polymer Formulations: Rapid Prototyping Technology for Polymeric Materials Development

*Industrial development of complex mixtures of materials known as "formulations" has traditionally relied upon empirical data and technical intuition, resulting from years of trial and error studies. We accelerate product discovery and optimization by providing new testing platforms that use high-throughput and combinatorial methods to rationally explore formulations variable space. These techniques, which have proven powerfully effective in drug and catalyst discovery, are now adapted to the myriad of materials measurements to which complex mixtures are typically submitted.*

## Kathryn L. Beers and João T. Cabral

Commercially available combinatorial and high-throughput (C&HT) fluid handling and measurement capabilities have enabled tremendous progress in industrial product development; however, the platforms are often costly and time-consuming to implement. The approach adopted by most manufacturers has been to build these automated platforms that mimic the development process for a specific material in a narrow application. This greatly increases data acquisition rates, but it is challenging to adapt this system-specific infrastructure to changing R&D needs. In response, our research aims to develop new methods for the manipulation and measurement of complex polymeric fluids, thereby providing flexible and inexpensive alternatives to robotics-driven instrumentation.

To improve the versatility of high-throughput formulations testing, we employ microfluidic technology to build a toolset of complementary library fabrication and test methods. The preparation of devices is fast and modular, allowing for rapid prototype development
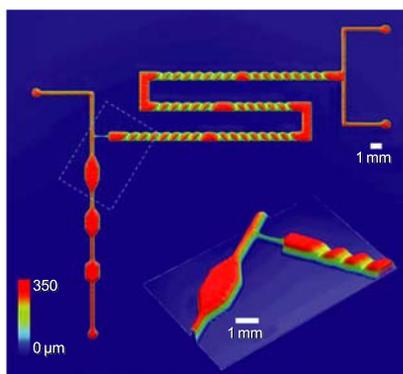


**Figure 1:** *Profilometry image of a fluidics device master prepared by patterning an optical resin. 3-D channel structure is possible due to the frontal polymerization mechanism of the resin.*

and increased flexibility. Our fabrication method is an adaptation of existing procedures that uses an optical resin with good solvent resistance and obeys a frontal polymerization mechanism, which enables us to prepare quasi-three-dimensional channel structures (Figure 1).

This year, we have built and demonstrated several methods of preparing polymer libraries in microfluidic devices (see Technical Highlights: Polymer Library Fabrication Techniques Using Microfluidic Technology). The libraries produced are designed to feed directly into the thin film gradient tools previously developed in the NCMC as well as the fluid measurement capabilities currently being built in our lab.
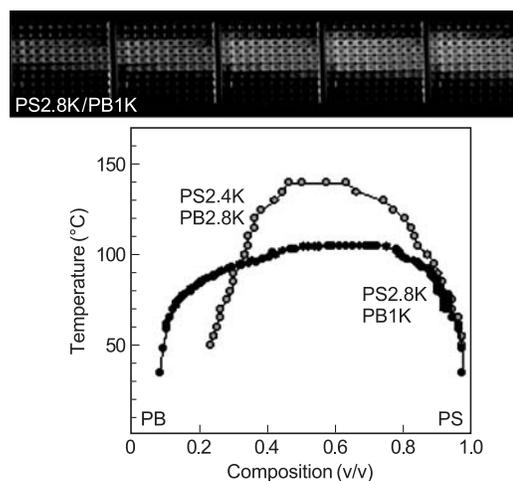


**Figure 2:** *High-throughput cloud point curves (graph) determined from uniform temperature sweeps of an array of blend compositions in a prototyped sample plate (top images).*

Complex fluid capabilities developed this year to complement our library fabrication include a high throughput microfluidic device for measuring interfacial tension (see related article in this report), a combinatorial magneto-driven rheometer, and a small angle light scattering (SALS) instrument for high throughput screening of polymer blends and solutions. The SALS instrument builds upon our work demonstrating high throughput cloud point mapping of polymer blends using sample libraries prepared in prototyped arrays (Figure 2).

## Contributors and Collaborators

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# Carbon Nanotube Processing

*We are developing new metrologies for quantifying the dispersion and orientation of carbon nanotubes in polymer melts and solutions. This will open the door to innovative processes and in-line characterization methods that will, in turn, empower novel approaches in materials science and engineering, creating a pathway toward the realization of a modern generation of materials and applications for carbon nanotubes.*

## Erik K. Hobbie and Barry J. Bauer

Carbon nanotubes exhibit remarkable physical properties, and there is considerable interest in using them as nanoscale building blocks for a new generation of novel materials. Despite this promise, fundamental issues related to the dispersion, fractionation, and orientation of individual carbon nanotubes remain unresolved, and bulk processing schemes do not yet exist. In fact, techniques for measuring these parameters in nanotubes are primitive. In light of these issues, we have established a program to enable proficient nanotube processing by quantifying the response of carbon nanotube suspensions and melts to changes in such parameters as composition, aspect ratio, shear stress, and dispersant.

The manufacture of nanotube-based devices and composites typically entails suspending them in an aqueous or molten polymeric media and subjecting them to shearing stresses. We have completed a comprehensive set of measurements detailing the response of nanotube suspensions to imposed flows. These experiments have been conducted over a wide range of shear rates, concentrations, and tube type (single or multi-wall). By combining optical methodologies with neutron scattering, the influence of flow on nanotube clustering, orientation, and dispersion has been elucidated.

Typical optical measurements are shown in Figure 1a, which shows scaled birefringence as a function of a scaled shear rate (Peclet number), where the left inset (red scale bar) is a SEM image of the multi-wall nanotubes (MWNT), and the right inset (blue scale bar) is an AFM image of a single-wall nanotube (SWNT) bundle (scale bar = 50 nm). The measured order parameter has been scaled onto the data, and the line is a power-law fit. Figure 1b shows an analogous plot of the birefringence, where the left inset is an optical micrograph of a MWNT (scale bar = 5 μm), and the right inset is a SANS pattern for a SWNT suspension (scale bar = 0.06 nm$^{-1}$). The scaling shown in Figure 1 confirms theoretical predictions of the importance of hydrodynamic interactions in the semi-dilute regime. One intriguing result is a segregation by tube length in
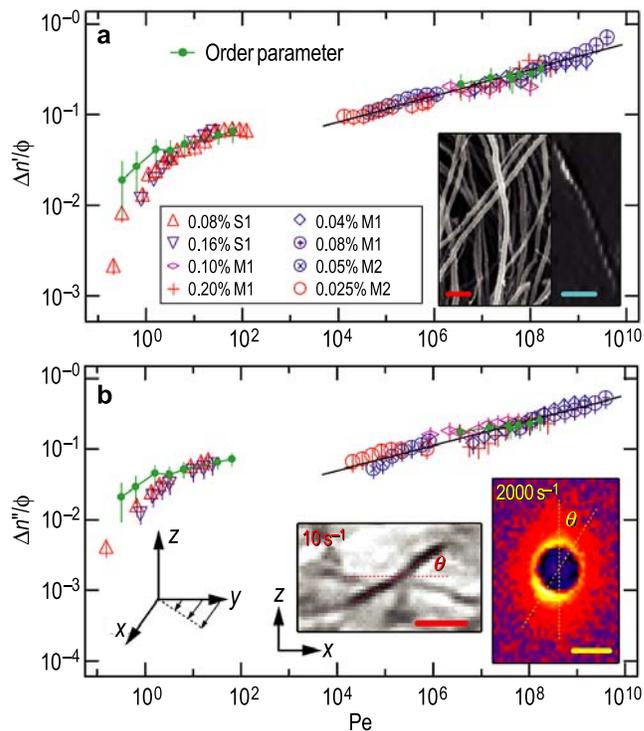


**Figure 1:** *Scaled birefringence ($\Delta n'$) and dichroism ($\Delta n''$) as a function of Peclet number for a variety of carbon nanotube suspensions. ($\phi$ is the volume fraction.)*

the shear cell; this suggests a path towards the goal of the production of monodisperse nanotubes.

A "grand challenge" in nanotube research is to break up the clusters and "ropes" that naturally form so that isolated single-wall tubes are realized, which can be utilized in applications. Numerous recipes for dispersing the nanotubes have been proposed, but there is little quantification of the resulting suspensions and no powerful method for comparing different techniques.

We are employing neutron scattering to establish base-line standards for nanotube dispersion and orientation using a variety of functionalization and dispersion methods. These measurements will resolve a number of controversial and outstanding questions regarding form and structure in single-walled carbon nanotube suspensions, including persistence length and phase behavior.

## Contributors and Collaborators

D. Fry (Polymers Division, NIST); H. Wang (Michigan Tech)

# Processing Flows and Instabilities

*As polymer processing is carried out under highly non-equilibrium conditions, it is difficult to assess the state of the polymer without in-situ real-time measurements. Our program develops and applies in-situ measurement technology to problems chosen on the basis of input from our industrial partners. This year's focus has been on the state of dispersion of nanoclay-polymer composites, as well as on additives to control the extrusion process.*

## Anthony Bur and Kalman Migler

In the marketplace of commodity polymers, much of the value added is due to processing operations. Indeed, the ability to precisely control product quality often determines the economic viability of a product. Due to the highly non-linear and non-equilibrium processes that occur during large-scale processing operations, it is generally not feasible to obtain accurate determinations of the relevant process state that would allow precision control. Thus, most of the quality control is engineered into the manufacturing process during the R&D stage.

Our program has built numerous collaborative relationships with the upstream industries, such as materials producers, additive suppliers, and instrument manufacturers to further industry's ability to monitor processing parameters. We have developed a variety of on-line instruments which can characterize critical parameters of the polymer during processing such as its temperature, velocity field, molecular orientation and morphology of dispersed components. This year we focused on two projects: the behavior of polymer additives during processing; and techniques to assess the state of dispersion of clay in polymer nanocomposites.

Additives are frequently mixed into polymeric materials in minute quantities in order to make them processable into the typical products well known to consumers, such as plastic sheets, pipes, and wire insulation. However, the basis for the effectiveness of these additives remained unknown because the existing tools available to measure their behavior in the manufacturing process were rather crude. We utilized the optical phenomena of Frustrated Total Internal Reflection (Frus-TIR) to directly visualize the behavior of fluoropolymer additives in polyethylene melts.

From visualization of the additive coating process, we developed a semi-quantitative model which predicts the coating efficiency as a function of additive droplet size and shear rate. A collaboration between NIST, DuPont Dow Elastomers, The University of Minnesota,

and The University of Maryland is now using this Frus-TIR technique to test for the critical factors that influence the coating efficiency.
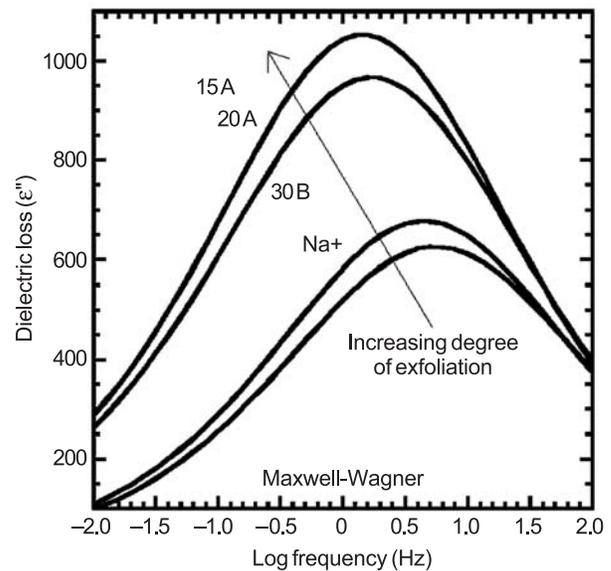


**Figure 1:** *Use of dielectric spectroscopy to assess the state of dispersion of a nanoclay composite. Nylon 11 compounded with four different clays.*

The second focus was to measure the dispersion of nanoclay additives using an on-line dielectric cell. This cell is effectively a slit die with interdigitated electrodes glazed onto one wall. Past work has shown that it can also be used to carry out rheological and optical measurements. The program achieved its goal of finding the signature of exfoliation in the spectra of the dielectric measurements (see Figure 1). Further, the state of exfoliation was measured from two complementary methods: the changes in the optical fluorescence when certain dyes were incorporated into the clay; and changes in the transparency of the material as a function of exfoliation. This last method is particularly inexpensive and may be of use to end-users. These measurements correlated well with the traditional laborious off-line techniques (transmission electron microscopy and x-ray).

## Contributors and Collaborators

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# Quantitative Polymer Mass Spectrometry

*Traditional measures of molecular mass (and the standards derived from them) provide either absolute values for only one moment of the distribution or relative values for the entire distribution. As we discovered from our two recent industry workshops, producers and users of synthetic polymers, analytical laboratories, and standards developing organizations, need a method (and standards derived from it) for absolute molecular mass distribution determination. Mass spectrometry is being developed as such a method. Both Type A ("random") and Type B ("systematic") uncertainties must be included in determining the uncertainty budget for mass spectrometry.*

## William E. Wallace

In mass spectrometry, methods exist to calibrate the mass axis with high precision and accuracy. In contrast, the ion-intensity axis is extremely difficult to calibrate. This leads to large uncertainties in quantifying the content of mixtures. This is true whether the mixture is composed of different oligomeric species of the same polymer (*i.e.*, the molecular mass distribution), of polymers with the same repeat unit but having different end groups (*e.g.*, pre-polymers), or polymers having different repeat units (*i.e.*, copolymers). The aim of this project is to calibrate the ion intensity axis. This task has been divided into three parts: sample preparation/ion production, instrument optimization, and data analysis.

Matrix-assisted laser desorption/ionization (MALDI) is used to create intact gaseous macromolecular ions. We have begun to study the MALDI ion-creation process using two-dimensional combinatorial libraries where the analyte:matrix ratio is varied in one dimension and the analyte:salt ratio is varied in the other. We add a factorial design methodology to optimize the instrument parameters at each composition using the signal-to-noise ratio. Instrument parameters to be optimized included laser energy, several critical ion optics voltages, detector voltage, as well as analyte:matrix ratio and matrix material. From this, it was discovered that the detector voltage was the single most important factor, followed by the laser energy. Additionally, we continue to develop the MassSpectator computer code to perform unbiased processing of the data.

To gain greater insight into the complex mechanisms of ion creation, the MALDI process was studied as a function of sample temperature. The common MALDI matrix 2,5-dihydroxybenzoic acid (2,5-DHB) was used due to the extensive literature on its physical properties. Due to the high vapor pressure of 2,5-DHB, single crystals were necessary to minimize the surface-to-volume ratio and thereby decrease the sublimation rate.



*Figure 1: A 2,5 DHB single crystal on the sample stage. The bright yellow feature is the near UV laser spot. Notice the light pipe effect as visible radiation escapes from the ends of the sample. The sample is approximately 3 mm long.*

It was observed that a steep rise in ion production occurs at 90 ºC, achieved a maximum between 120 ºC to 130 ºC, then decreased sharply to a minimum at 130 ºC to 140 ºC, and returned to a second maximum value at 150 ºC. Above 150 ºC, useful information could not be obtained because of rapid volatilization of the sample into the vacuum. The overall trend in ion production is well described by a recent two-step theory of the laser desorption/ionization process, which takes into account the temperature-dependent effects of plume expansion. It was observed that thermal dehydration, condensation, and decarboxylation reactions increase the volume of gas released under laser ablation at high temperatures. The resultant higher local pressure at the crystal surface was found to have a profound effect on gas-phase ion formation with higher pressures leading to lower ion production.

## Contributors and Collaborators

M.A. Arnould, B.J. Bauer, W.R. Blair, H.C.M. Byrd, B.M. Fanconi, K.M. Flynn, C.M. Guttman, D.L. VanderHart, S.J. Wetzel (Polymers Division, NIST); A.J. Kearsley, P.M. Ketcham (Mathematical and Computational Sciences Division, NIST); J.J. Filliben, J. Lu (Statistical Engineering Division, NIST); S.A. Audino, J.E. Girard, Z. Vakili (American University); R. Knochenmuss (Novartis); N. Sari (CARB); Y. Brun (DuPont)

# Polymer Standards

*Producers, processors, and users of synthetic polymers use polymer standards for calibration of instruments, assessment of laboratory proficiency, test method development, and materials improvement. NIST assists in the standards process by providing standard reference materials (SRM®), reference materials (RM), and reference data. Activities include recertifying SRM®s and RMs as stock is depleted, determining opportunities for production of new SRM®s and RMs, producing new SRM®s and RMs and building databases of relevant data pertaining to SRM®s and RMs.*

## Bruno Fanconi, Charles Guttman, and John Tesk

## Recertification of SRM® 1476

SRM® 1476, a branched polyethylene, was originally issued as a melt flow rate standard. It was discontinued because insufficient material remained for recertification as a melt flow rate standard. During its availability, SRM® 1476 was also used in studies of branching in polyethylene, a desirable molecular characteristic for certain types of products. Although chemists now have methods to produce a variety of branch structures, measurement methods to quantify the critical aspects of the branch architecture are lacking. Owing to the available molecular data on SRM® 1476, manufacturers of chromatographs include small quantities of the original SRM® 1476 with purchases of their instruments for comparative measurements. NIST has received inquiries from manufacturers, researchers and resin producers about making the remaining supply of SRM® 1476 resin available, not as a melt flow rate standard, but as an aid in chromatographic measurements. The remaining supply of SRM® 1476 resin was sufficient for this purpose. Hence, recertification of SRM® 1476 resin for chromatographic measurements was completed in FY 2004. Although the new SRM is not intended as a melt flow rate standard, it remains certified for this purpose to assure continuity with the original material.

## Reference Scaffolds for Tissue Engineering

At the November 19, 2003 meeting of ASTM International Committee F04.42 — Tissue Engineered Biomaterials, a task force was initiated for the development of reference scaffolds for tissue-engineered medical products (TEMPs). Reference scaffolds had been identified at a NIST workshop as the most needed reference material for TEMPs. The task force will conduct measurements to characterize test scaffolds that will be supplied to its members; the results will be used to determine the most useful characterizations to employ when the reference scaffolds are produced. Scaffolds of known porosity, interconnectivity, surface and bulk chemistry, physical and mechanical properties, and cellular reactivity are needed. Initially, the focus will be on characterizing porosity (pore volume and pore size distribution), connectivity, and interconnectivity of pores and work toward consistent, unambiguous understanding of terminology. Scaffolds that consist of a regular array of cubic pores, such as with 600 μm pore-edge dimensions and consistent interconnections, were identified for the task force's initial study. Micro-x-ray Computed Tomography (μ-CT) was used for preliminary evaluation of scaffold designs manufactured by different processes, materials, dimensions, and pore size. On this basis, two designs were chosen for distribution to the 17 laboratories participating in the ASTM activity. Laboratory evaluations of these designs will ensure that the characteristics needed for the reference scaffolds will be well defined and that their measurements will produce consistent results when the reference scaffolds are produced. The reference scaffolds will be available for distribution to researchers and developers of scaffolds for tissue engineering applications. Initial measurements by NIST showed that μ-CT would be an important measurement method for distinguishing scaffolds with acceptably consistent features.
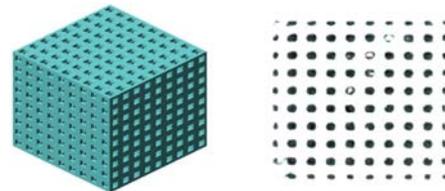


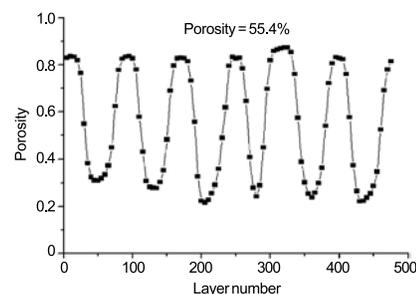***Figure 1:*** *Cubic scaffold with cubic pores (left) and μ-CT scaffold slice (right).*



***Figure 2:*** *Porosity as a function of depth of μ-CT slice (layer).*

## Contributors and Collaborators

J. Dunkers, F. Wang, M. Chiang, M. Cicerone, K. Flynn, W. Blair, J. Maurey, S. Wetzel (Polymers Division, NIST); M. Yaszemski, E. Jabbari, L. Lu (Mayo Clinic); D. Dean, M. Cooke (Case Western Reserve University)
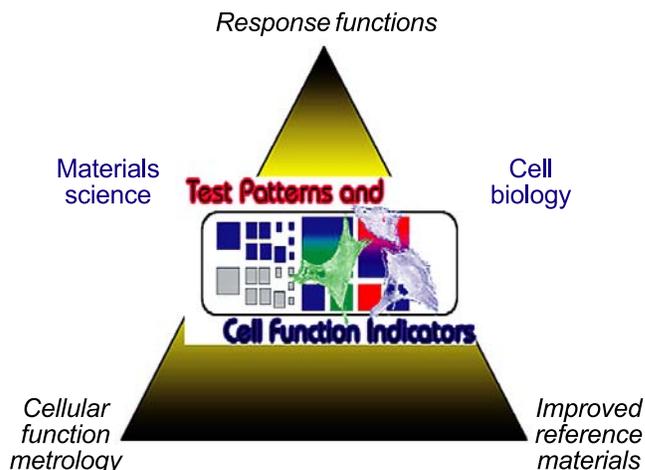
# Biomaterials

New materials and devices are radically changing the treatment of injury and disease, yet it is clear that within this rapidly evolving segment of the materials industry, a basic measurement infrastructure does not exist. The Biomaterials Program develops measurement methods, standards, and fundamental scientific understanding at the interface between the materials and biological sciences. For 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. Three primary foci exist within this program: biocompatibility, biomaterials characterization, and materials measurements applied to biological systems.

Whether the medical issue involves implanting a hip- or knee-joint prosthesis, a synthetic bone graft, or a tissue engineering scaffold into the human body, one primary issue is biocompatibility. Using our expertise in materials science, we have developed suitable Reference Materials (RM) for investigating biocompatibility and implant suitability. Research has focused on measuring cellular response to powders and bulk materials that are candidates for implants; recently, we produced a realistic wear particle Standard Reference Material (SRM® 2880) for bioactivity testing.

Work on quantitative methods of biomaterials characterization includes assays for adhesion, viability, proliferation, and differentiation of bone cells, 3-dimensional structural/functional imaging of tissue in-growth, and biochemical assays to quantify inflammatory responses to synthetic materials. The focus of this effort is bridging the gap between fundamental knowledge and the product development needs in industry. For example, in collaboration with the Chemical Science and Technology Laboratory, we are developing measurement methodologies and reference materials to assess interactions in complex systems of living cells with synthetic materials. The expected outcome of this work includes reference substrates that induce specific cellular responses, and engineered DNA vectors to act as fluorescent reporters of cellular responses.

Another example of our effort to bridge this gap is our collaboration with the dental industry, which is primarily composed of small manufacturers with limited R&D capability. Collaborations with the American Dental Association Foundation (ADAF) develop improved materials and materials measurements techniques, patent and license these inventions, and, most importantly, provide a technical foundation. 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. We also collaborate with the ADAF to develop metrology for the biocompatibility of synthetic bone grafts.

In this era of interdisciplinary research, we provide an added dimension. By taking a physical/mechanical approach to how cells function, respond, and remodel in interaction with synthetic materials, we provide skill sets typically absent in the biomedical community. Mechanical properties issues also arise when considering synthetic bone grafts and tissue engineering scaffolds. Complementing traditional bulk mechanical property measurements, combinatorial approaches are being developed to identify compositions and surface features that affect properties such as biocompatibility and mechanical durability.

Our mechanical property metrology extends further to biological systems that span the range from individual neurons and muscle cells to complete pulmonary arteries. This necessitates the development of unique mechanical testing platforms and application of a materials science approach to understanding integrated properties. Recently, we have developed a bioreactor capable of applying biaxial stresses and allowing monitoring of the stress and strain of a two-dimensional scaffold sheet during tissue growth.

Fundamental to the Biomaterials program is recognition of the need for an integrated systems approach. Collaborations among and between project teams are critical to progress against the ambitious goals of this program.

Contact: Eric J. Amis (Polymers Division)

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# Structure-Property Relationships in Dental Nanocomposites

*Polymeric dental materials are finding increasing applications 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 in collaboration with the American Dental Association Health Foundation Paffenbarger Research Center, NIST is providing the dental industry with a fundamental knowledge base that will aid in the prediction of clinical performance of dental materials.*

## Joseph M. Antonucci and Elizabeth Wilder

Inorganic fillers of various types, sizes and shapes are commonly used to modify polymer properties. In resin-based dental composites, fillers are added to enhance the modulus, hardness and strength of the polymer phase while also reducing its coefficient of thermal expansion and volumetric contraction during polymerization. In order to achieve composites with optimal properties, it is also necessary to provide an effective, high-quality interfacial phase that will make the filler both interactive and reinforcing with respect to the polymeric matrix phase.

Recent developments in nanotechnology have spurred interest in nano-size fillers and additives for dental materials. The interactions that occur between the disparate polymer matrix and inorganic filler phases are increasingly important to elucidate for nano-fillers due to their high surface area. Surface treatments of the nano-sized fillers, designed to generate desirable interfacial phases upon polymerization, assume even greater importance in nanocomposites compared to conventionally sized materials.

In this project, we investigate two types of nanofillers: (1) a pure silica particulate surface-treated

with blends of two silane agents, and (2) a well-characterized amorphous calcium phosphate (ACP) particulate modified by exposure to the organogelator dibenzylidene sorbitol (DBS). Before treatment, both of these fillers exist as complex aggregates that are difficult to incorporate into dental resins.

The objective of our research with the nano-sized silica filler was to explore how the interfacial chemical structural variations arising from using a blend of two silane agents (Figure 1), one reactive (MPTMS) with the resin and the second non-reactive (OTMS), influence certain critical properties of the composites. It was found that processability, as measured by the facility of introducing the silica into the resins, was improved if the silane system contained OTMS. With equal parts by mass of MPTMS and OTMS, at least the same degree of reinforcement, measured by a biaxial flexure or 3-point flexural test, was achieved. The dual silane treatment also allows for the formulation of nanocomposites with higher filler contents.
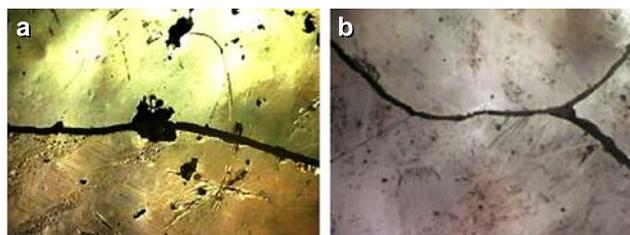


**Figure 2:** *Fractured ACP composite with: a) 0 % and b) 8 % mass fraction DBS.*

The second part of this project was aimed at determining the effect of DBS networks on shrinkage, stress development and mechanical properties of a bioactive composite utilizing ACP as the filler phase. DBS is capable of self-assembling into nano-scale fibrillar networks in a variety of dental monomers. The addition of DBS-reduced pore defects (Figure 2), increased biaxial flexure strength and reduced polymerization shrinkage and stress. These results suggest that dual silanization techniques and the use of organogelators may provide facile ways to enhance critical properties of polymeric dental composites and related materials.

## Contributors and Collaborators

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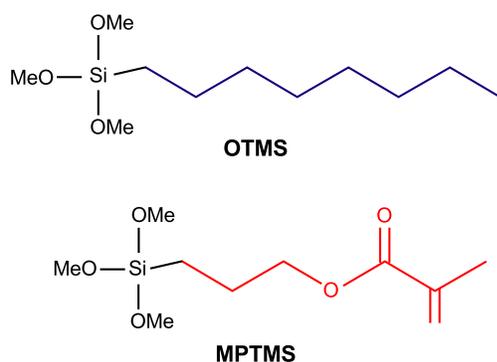


**Figure 1:** *Structure of (top) octyltrimethoxysilane(OTMS) and (bottom) methacryloxypropyltrimethoxysilane (MPTMS).*

# Multi-Modal Imaging and Quantitative Data Reduction Methods for Regenerative Medicine

*This project develops methods for determining the viability of tissue engineered medical products (TEMPs) through the use of in-vitro imaging coupled with data reduction techniques. These techniques are vital for distilling the voluminous amount of imaging data down to selected metrics of interest relating to TEMP viability. We illustrate this approach by using various imaging techniques, along with 3D image quantitation, to establish relationships between cell proliferation and scaffold microstructure.*

**Joy P. Dunkers and Forrest A. Landis**

## TEMP Imaging: Collinear Optical Coherence/ Confocal Fluorescence Microscopies

We use collinear optical coherence microscopy (OCM) in conjunction with one photon confocal fluorescence microscopy (CFM) as a multifunctional technique for characterization of TEMPs. OCM with its unparalleled combination of resolution ($\approx 1$ µm) and sensitivity ($> 100$ dB) is well-suited for imaging TEMPs. CFM has proven to be an extremely powerful technique for understanding cell viability, differentiation, and protein expression in tissue engineering and provides complementary information to the structural characterization provided by OCM.

Figure 1 shows OCM/CFM imaging data on a polymer scaffold. The OCM channel images changes in refractive index. In the image, the scaffold is shown in red and pores in black. The scaffold was seeded for 56 d with osteoblasts and subsequently the nuclei were stained. The presence of cells was detected using CFM (shown in yellow). From this image, it is clear that the cells are highly confluent along the surface of most of the scaffold including the pore walls but do not yet completely fill the pores. The image size is 500 µm $\times$ 500 µm $\times$ 100 µm.
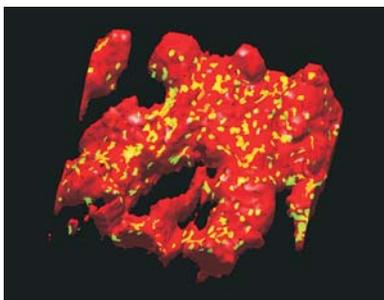


**Figure 1:** *OCM/CFM image of a polymer scaffold.*

## Data Reduction Method: 3D Image Quantitation

We have developed methods to compute critical quantities from the imaging data, which can then be related to cell response. We have implemented algorithms that calculate pore volume, pore size distribution and structural anisotropy from 3D imaging data. Quantities such as pore connectivity and tortuosity are also expected to be influential, and algorithms are currently being developed.

## Data Reduction Method: Immersive Visualization

Immersive visualization (IV) is a "virtual-reality" experience that literally puts you in the middle of your data. This is particularly advantageous when there are multiple types of volumetric data to be displayed simultaneously. IV allows one to see the entire data set at once and manipulate it in real time, which facilitates both qualitative and quantitative evaluation. Figure 2 shows a scientist exploring a TEMP imaging data set with a tool (arrow) in an immersive environment.
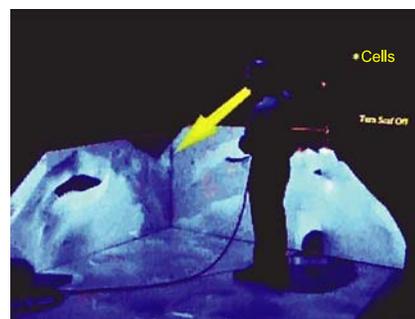


**Figure 2:** *A scientist exploring a TEMP imaging data set in an immersive environment.*

## Impact

Our collinear OCM/CFM work has been highlighted by the biomedical community:

"Two Imaging Techniques Work Better Than One," *Biophotonics International*, January 2004.

"Microscopes Provide New View for Tissue Engineering," *Medical News Today*, December 10, 2003.

## Contributors and Collaborators

J. Stephens, M. Chiang, X. Wang, M. Cicerone, J. Cooper (Polymers Division, NIST); J. Devaney, J. Hagedorn, S. Satterfield (Mathematical and Computational Sciences Division, NIST)

# Tissue Engineering Scaffolds

*Design issues relating to bioactive devices for regenerative medicine reflect the complexity of biological and materials issues, and their interactions. Regulatory issues also reflect this complexity. Quantifiable, reliable metrics that are relevant to success of tissue engineering (TE) constructs in properly supporting cell and tissue growth are needed to reduce the impact of this complexity. We are helping to define and develop these metrics.*

## Marcus T. Cicerone

The current efforts on this project are divided into two main areas: porosity measurements and useful definitions of porosity and chondrocyte response to dynamic environments. We are preparing to embark on another area — transferring results of cell-surface compatibility studies in 2D to 3D scaffolds. In each of these areas, we are emphasizing the use of unique volumetric imaging capabilities in the Polymers Division. We also apply real-time PCR (polymerase chain reaction) and other more common methods, such as histology.



**Figure 1:** *Histology (panels a and b) showed an increase in ECM (sulfated proteoglycan) production for the dynamically cultured scaffolds as compared to the static culture scaffold. Real-Time PCR (panel c) showed the expression of genes for collagen type II and aggrecan under dynamic conditions and only aggrecan under static conditions.*

## Chondrocyte Response

Links have been established between a chondrocyte's dynamic environment and composition of the extracellular matrix (ECM) it produces. We are developing measurement tools to help determine how the dynamics of the environment is sensed by the cell, and stimulus levels required for engineering cartilage with specific ECM compositions. This work is in collaboration with top researchers at the National Institutes of Health's (NIH) National Institute of Arthritis and Musculoskeletal and Skin Diseases (NIAMS).

Our working hypothesis is that physical deformation of chondrocytes influences ECM composition in the cartilage produced by both an intracellular transduction mechanism and increased perfusion of nutrients. This has been tested by applying variable pulsitile fluid stresses to chondrocytes encapsulated in poly(ethylene glycol) dimethacrylate gels. Cellular responses and matrix production are characterized by histological techniques, optical coherence tomography (OCM), and real time PCR. We are developing spectroscopic imaging methods that will aid in non-invasive determination of ECM composition.

Output of this work will be presented at the "Musculoskeletal Biology & Bioengineering Gordon Research Conference" and the "Polymer Network Conference" (both 2004). We also have a manuscript in preparation for *Journal of Orthopedic Research*.

## Porosity

It is generally agreed that "porosity" of tissue scaffolds is an important parameter; however, there is a general lack of agreement as to precisely what aspect of "porosity" is important, or how best to measure it.

We have initiated a collaborative project through ASTM (Task Force F04.42.06) to identify aspects of scaffold porosity that are most relevant and to come to consensus on how these aspects should be quantified. Seventeen laboratories throughout the world have joined us in this activity, which will be carried out in several stages, ultimately leading to the development of a reference scaffold for porosity measurements.

Output of this work thus far has included an ASTM draft guide for scaffold characterization (in preparation). Also, this work has been reported at the "Society of Biomaterials Meeting" and "World Biomaterials Meeting," both in 2004.

## Contributors and Collaborators

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# Combinatorial Methods for Rapid Screening of Biomaterials

*Current methods for biomaterials development involve one-specimen-at-a-time characterization which is costly and time-consuming. In order to accelerate development, we have created a suite of high-throughput and combinatorial methods for rapidly screening and characterizing new biomaterials. Specifically, new methods for rapidly characterizing cell response to polymer crystallinity, composition, and surface chemistry have been developed.*

## Carl G. Simon, Jr. and Newell R. Washburn

Combinatorial and high-throughput methods hold the potential to accelerate research and development in any field of scientific study. In the Polymers Division, we are trying to lead the way in the application of these approaches to the characterization of biomaterials. Towards this end, we have utilized gradient technology to create libraries with varying material properties focusing specifically on *surface energy, polymer crystallinity,* and *polymer composition*.

*Surface energy* is a fundamental material property that affects cell interactions. This response may be through a direct cell-material interaction, but more often is an indirect effect where surface energy dictates protein adsorption, which subsequently dictates cell response. An automated stage is used to move a silanized glass slide beneath a UV lamp to create a gradient in oxidation from differential exposure to the UV light. Water contact angles for this gradient surface varies from 30 ° to 90 °. Cell behavior is assessed on the gradients, providing a unique tool to probe the fundamental correlations between cell response and surface energy.
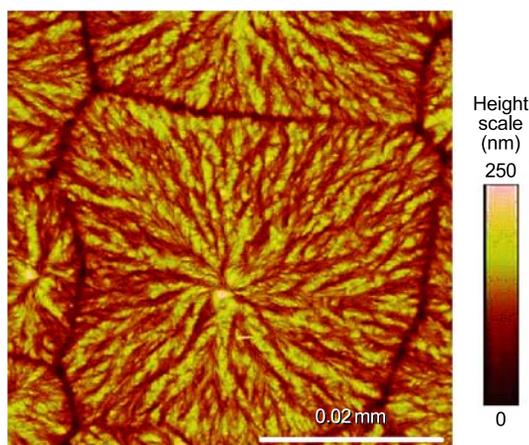


*Figure 1: Atomic Force Microscopy (AFM) height image of a poly(L-lactic acid) spherulite.*

*Polymer crystallinity:* Surface topology can strongly influence the performance of tissue-engineered medical products. Crystalline polymers used in biomedical applications, such as poly(ε-caprolactone) and poly(L-lactic acid) (PLLA), can have either a rough or a smooth surface depending upon processing. To create a gradient in surface topology, polymer solutions are first spread onto glass substrates to yield smooth, amorphous, thin films. The films are placed on a temperature gradient stage such that one end is held below the glass transition temperature ($T_g$) at ambient temperature and the other end is heated above the $T_g$ to 100 °C. This produces gradients in crystallinity along the PLLA films where the room temperature-end remains smooth and amorphous while the 100 °C-end becomes crystalline and roughened. When combined with cell culture, we have a high-throughput method for studying cell response to the surface roughness that results from polymer crystallinity.

*Polymer composition:* Manufacturing industries have historically used polymer blending as an inexpensive method to create new materials with desirable properties. Blending can optimize modulus, strength, morphology, and crystallinity. For these reasons, blending is also receiving attention from the tissue engineering community. A gradient library of two polymers is created using a three-syringe pump system and a translation stage. The library is a strip-shaped film, and its composition is measured by Fourier Transform Infrared (FTIR) microspectroscopy. A gradient in composition spans the long axis of the film being PLLA-rich on one end and PDLLA-rich on the opposite end. Cells are cultured on the gradients to yield a high-throughput method for screening cell response to polymer blends.

The project accomplishments have been presented at six different symposia and in two journal articles, one of which was in the top-ranked tissue engineering journal, *Biomaterials*. Four other articles have been submitted or are in preparation. Finally, these activities were highlighted under "Government News" in *Biomaterials Forum* which is a quarterly news bulletin circulated by the Society for Biomaterials amongst its 1500 members.

## Contributors and Collaborators

F.W. Wang, E.J. Amis (Polymers Division, NIST); N. Eidelman (American Dental Association, NIST); Y. Deng (Ceramics Division, NIST); K.M. Yamada (NIDCR/NIH); J. Kohn (Rutgers University); R. Gross (Polytechnic University)

# Materials for Electronics

The U.S. electronics industry faces strong international competition in the manufacture of smaller, faster, more functional, and more reliable products. Many critical challenges facing the industry require the continual development of advanced materials and processes. The NIST Materials Science and Engineering Laboratory (MSEL) works closely with U.S. industry covering a broad spectrum of sectors including semiconductor manufacturing, device components, packaging, data storage, and assembly, as well as complementary and emerging areas such as optoelectronics and organic electronics. MSEL has a multidivisional approach, committed to addressing the most critical materials measurement and standards issues for electronic materials. Our vision is to be the key resource within the Federal Government for materials metrology development and will be realized through the following objectives:

- Develop and deliver standard measurements and data;

- Develop advanced measurement methods needed by industry to address new problems that arise with the development of new materials;

- Develop and apply *in situ* as well as real-time, factory floor measurements, for materials and devices having micrometer- to nanometer-scale dimensions;

- Develop combinatorial material methodologies for the rapid optimization of industrially important electronic materials;

- Provide the fundamental understanding of the divergence of thin film and nanoscale material properties from their bulk values;

- Provide the fundamental understanding of materials needed for future nanoelectronic devices, including first principles modeling of such materials.

The NIST/MSEL program consists of projects led by the Metallurgy, Polymers, Materials Reliability, and Ceramics Divisions. These projects are conducted in collaboration with partners from industrial consortia (*e.g.*, International SEMATECH), individual companies, academia, and other government agencies. The program is strongly coupled with other microelectronics programs within the government such as the National Semiconductor Metrology Program (NSMP). Materials metrology needs are also identified through the International Technology Roadmap for Semiconductors (ITRS), the IPC Lead-free Solder Roadmap, the National Electronics Manufacturing Initiative (NEMI) Roadmap, the Optoelectronics Industry Development Association (OIDA) Roadmap, IPC (the International Packaging Consortium), and the National [Magnetic Data] Storage Industry Consortium (NSIC) Roadmap.

In each of these areas, MSEL researchers have made substantial contributions to the most pressing technical challenges facing industry, from new fabrication methods and advanced materials in the semiconductor industry, to advanced packaging materials, to magnetic data storage. Below are just a few examples of MSEL contributions over the past year.

## Advanced Gate Dielectrics

To enable further device scaling, the capacitive equivalent thickness (CET) of the gate stack thickness must be 0.5 nm to 1.0 nm. This is not achievable with existing $SiO_2$/polcrystalline Si gate stacks. Given the large number of possible choices for these new layers, the only feasible approach to understanding the complex materials interactions that result at the gate dielectric/substrate and gate dielectric/metal gate electrode interfaces is through the application of combinatorial methodologies. This same methodology and apparatus are applicable to a wide variety of problems in the electronic materials field.

## Sub-100 nm Nanofabrication

The continual decrease in feature size has been the driving force for advances in the semiconductor industry. Current structures have 90 nm dimensions with planned nodes at 65 nm and 35 nm structures. Advanced measurements of the patterning materials (photoresists), are needed to enable future large scale manufacturing of smaller devices. MSEL utilizes advanced x-ray and neutron tools to provide insight into the feasibility and optimization of these important processes.

## Advanced Metallization

Electrodeposited copper is rapidly replacing aluminum for on-chip "wiring" because of its lower electrical resistivity, superior electromigration behavior, and the ability to fill fine features without the formation of seams or voids. As feature dimensions go below 100 nm, difficulties in maintaining performance are anticipated. These issues are addressed through a combination of modeling and experimental efforts.

## Test Methods for Embedded Passive Devices

Significant advantages arise if passive devices are integrated directly into the circuit board as embedded passive devices rather than discretely attached with automated assembly. New metrology methods were developed to address the needs of the electronic industry. Two test methods were completed and have received wide acceptance by industry as new methods to accelerate the development of embedded passive device technology.

Contact: Martin L. Green or
        Eric K. Lin (Polymers Division)

# Characterization of Porous Low-k Dielectric Constant Thin Films

*NIST provides the semiconductor industry with unique on-wafer measurements of the physical and structural properties of nanoporous thin films. Several complementary experimental techniques are used to measure the pore and matrix morphology of candidate materials. The data are used by industry to select candidate low-k materials. Measurement methods that may be transferred to industrial laboratories, such as x-ray porosimetry, are developed. New methods are being developed to measure patterned low-k samples and to assess the extent of porous structure modification caused by plasma etch.*

**Eric K. Lin and Wen-li Wu**

The future generation of integrated circuits requires porous low-k interlayer dielectric materials to address issues with power consumption, signal propagation delays, and crosstalk that decrease device performance. The introduction of nanometer scale pores into a solid film lowers its effective dielectric constant. However, increasing porosity adversely affects other important quantities such as physical strength and barrier properties. These effects pose severe challenges to the integration of porous dielectrics into the device structure.

There is a need for nondestructive, on-wafer characterization of nanoporous thin films. Parameters such as the pore size distribution, wall density, porosity, film uniformity, elemental composition, coefficient of thermal expansion, and film density are needed to evaluate candidate low-k materials. NIST continues to develop low-k characterization methods using a combination of complementary measurement methods including small angle neutron and x-ray scattering (SANS, SAXS), high resolution x-ray reflectivity (HRXR), x-ray porosimetry (XRP), SANS porosimetry, and ion scattering. To facilitate the transfer of measurement expertise, a recommended practice guide for XRP was completed and will be available for industrial customers.

In collaboration with industrial and university partners, we have applied existing methods to new low-k materials and developed new methods to address upcoming integration challenges. A materials database developed in collaboration with International SEMATECH is used extensively by SEMATECH and its member companies to help select candidate materials and to optimize integration processing conditions. This year, we also addressed the effects of the ashing/plasma etch process on the low-k material during pattern transfer. Often, surfaces exposed to ashing/plasma densify and lose terminal groups (hydrogen or organic moiety) resulting in increased moisture adsorption and, thus, increased dielectric constant. HRXR measurements enable quantification of the surface densification or pore collapse in ashing-treated and/or plasma-treated blanket films.
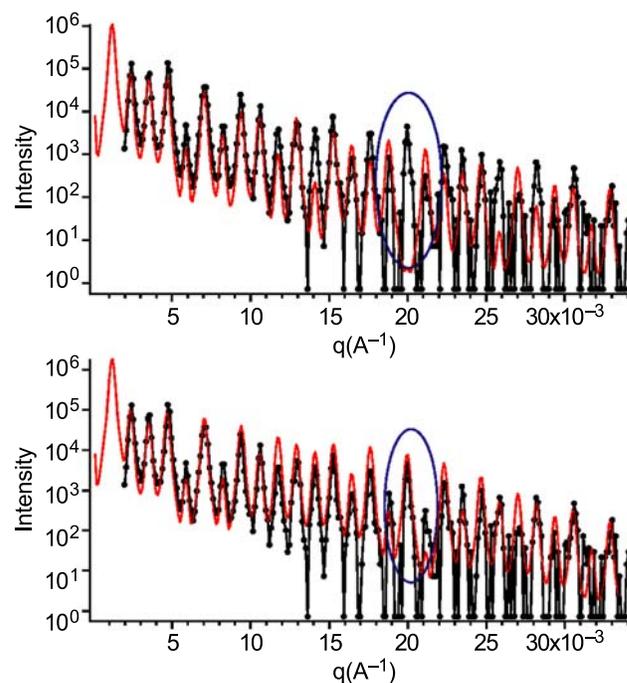


**Figure 1:** *SAXS data of a test line grating created in a porous low-k film. Experimental data — solid symbol; model fit — red line. The top data was fit with a uniform cross-section whereas the bottom data was fit with a dense skin layer. Regions outlined by blue circle highlight the difference between these two models.*

A new method using SAXS was also developed to investigate the effect of plasma etch on patterned low-k films. Any densification of the sidewall may be observable by x-ray scattering from the cross-section of a patterned nanostructure. Preliminary SAXS work was carried out at Argonne National Laboratory using line gratings of low-k material. The feasibility of this approach is shown in Figure 1 where a surface layer densification is needed to fit the SAXS data.

## Contributors and Collaborators

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# Polymer Photoresists for Next-Generation Nanolithography

*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.*

## Vivek M. Prabhu



**Figure 1:** *NEXAFS instrument and spectra illustrating a homopolymer enrichment at the film surface for a model 157 nm photoresist blend. The mismatch in surface versus bulk composition illustrate interfacial limitations for sub 100 nm structures.*

Photolithography is the driving technology used by the microelectronics industry to fabricate integrated circuits with ever decreasing sizes. In addition, this fabrication technology is rapidly being adopted in emerging areas such as optoelectronics and biotechnology requiring the rapid creation of nanoscale structures. In this process, a designed pattern is transferred to the silicon substrate by altering the solubility of areas of a polymer-based 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 shorter wavelengths of light requiring photoresist films less than 100 nm thick and dimensional control to within 2 nm.

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 that can significantly affect the patterning process.

This year, we have continued to apply and advance unique measurement methods to provide structural measurement of fabricated nanoscale structures and 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 x-ray and neutron scattering (SAXS, SANS), near-edge x-ray absorption fine structure spectroscopy (NEXAFS), combinatorial methods, solid state nuclear magnetic resonance (NMR), quartz crystal microbalance (QCM), fluorescence correlation spectroscopy (FCS), and atomic force microscopy (AFM).
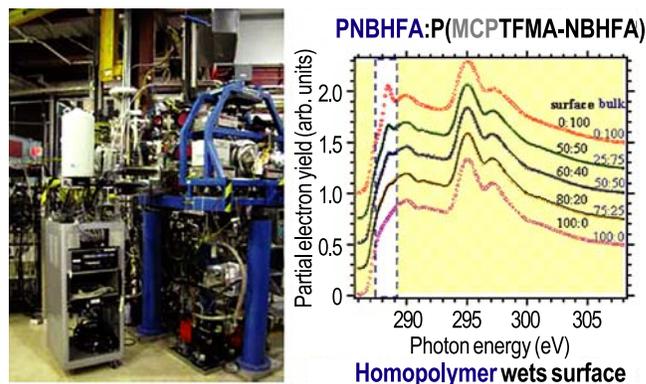
Accomplishments for this past year include: advancement of photoresist–liquid interfaces for immersion lithography and developer distribution in ultrathin films (see highlight); photoresist component segregation (see Figure 1); quantification of the post-exposure bake time on the reaction–diffusion of photoacid 3D deprotection volume; first measurement of immersion and exposure dependence of the surface composition of base additives in 193 nm resist films; identification of key anti-reflective coating (ARC) components responsible for profile control problems and residual layer formation at the ARC-resist interface; quantification of environmental sensitivity by *in-situ* processing using NEXAFS; and quantification of the effects of developer and additives on the final resolution of lithographic features using a model reaction–front bilayer geometry.

International SEMATECH has selected NIST in an effort to apply these fundamental measurements to identify materials sources of the fabrication limits of advanced photoresists.

## Contributors and Collaborators

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# Organic Electronics

*The field of organic electronics has dramatically emerged in recent years as an increasingly important technology encompassing a wide array of devices and applications including embedded passive devices, flexible displays, and sensors. Device performance, stability, and function critically depend upon charge transport and material interaction at the interfaces of disparate materials. We develop and apply non-destructive measurement methods to characterize the electronic and interfacial structure of organic electronics materials with respect to processing methods, processing variables, and materials characteristics.*

## Eric K. Lin and Jan Obrzut

Organic electronic devices are projected to revolutionize integrated circuits through new applications that take advantage of low-cost, high-volume manufacturing, nontraditional substrates, and designed functionality. The current state of organic electronics is analogous to the early stages of the silicon electronics industry with the concurrent development of multiple material platforms and processes, and a lack of measurement standardization between laboratories. A critical need exists for new diagnostic probes, tools, and methods to address new technological challenges.

Organic electronics presents fundamentally different measurement challenges from those identified for inorganic devices. The adoption of this technology will be advanced by the development of an integrated suite of metrologies to correlate device performance with the structure, properties, and chemistry of materials and interfaces. We are developing measurement methods to provide the data and insight needed for the rational and directed development of emerging materials and processes.

This year, we have addressed three areas covering a spectrum of active organic electronic materials: dielectric measurements for embedded passive devices, measurements of moisture permeation rates through barrier films for organic light-emitting diode displays, and measurements of the orientation and structure of organic semiconductors for transistor applications.
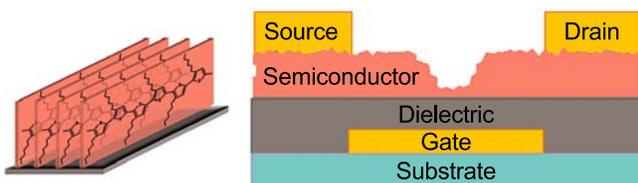
To meet the metrology needs for embedded passive devices, two new measurement methods were successfully developed and will find widespread use within industry (see Highlight). A NIST-developed *Test Method for Dielectric Permittivity and Loss Tangent of Embedded Passive Materials from 100 MHz to 12 GHz* was accepted and recommended as a standard test method. In addition, a new test was developed and applied for testing passive materials at high electric fields and voltages.

For organic light-emitting diode displays, a key measurement challenge is the quantification of the moisture permeation rates through a barrier coating. Any moisture able to penetrate the coating compromises the performance of the device. There is a need to measure moisture permeation rates as low as $10^{-6}$ g/m$^2$ d. In collaboration with Vitex Systems, Inc., neutron and x-ray reflectivity measurements demonstrated the capability of measuring these low permeation rates in addition to providing spatial detail about the transport of water within the barrier material itself.

Finally, near-edge x-ray absorption fine structure (NEXAFS) spectroscopy was applied to several classes of organic electronics materials to investigate the electronic structure, chemistry, and orientation of these molecules near a supporting substrate. NEXAFS provides a powerful and sensitive method to probe the interfacial structure that is critical to the performance of these devices. For example, it was found that several organic semiconductor molecules preferentially align "edge-on" rather than "face-down" on solid substrates.



*Figure 1: Schematic diagrams of the local structure of poly 3-hexylthiophene, an organic semiconductor, near an interface (left) and the architecture for an organic transistor (right).*

## Contributors and Collaborators

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# Nanoimprint Lithography

*Nanoimprint lithography (NIL) has emerged as a viable next generation lithography (NGL) capable of transferring physical patterns smaller than 5 nm into a polymeric film.*[1] *The production of nanoscale structures enabled by NIL raises new metrology challenges, as the ability to pattern now exceeds the ability to measure and/or evaluate material properties. The objective of this project is to develop high-resolution metrologies that facilitate the development of NIL.*

## Christopher L. Soles and Ronald L. Jones

NIL has recently emerged as one of the leading NGL candidates for the semiconductor industry. The 2003 update of the *ITRS Semiconductor Roadmap* identifies NIL as a strong candidate lithography for the 45 nm technology node. *Silicon Strategies* included *Molecular Imprints, Inc*. (Austin, TX) and *Nanonex* (Princeton, NJ), two major NIL tool companies, in their "60 Emerging Start-ups" list for 2004. Going beyond CMOS, MIT's *Technology Review* selected NIL as one of the "10 Emerging Technologies That Will Change the World."[2] The cost efficient and high-resolution nanopatterning of NIL will also be beneficial in emerging technologies such as optical communications, data storage, bio devices, nano-electromechanical systems (NEMS), micro-electromechanical systems (MEMS), and sensors, by enabling low-cost nanofabrication.

The NIL concept is elegantly simple. A master pattern with sub-100 nm features is fabricated into a hard material (Si, quartz, Ni, etc.) using high-resolution (but slow) patterning, such as e-beam lithography. The patterns are then transferred into a resist by stamping the hard master mold into a softer polymer or monomer film. The pattern is "set" into the resist film with either heat, to facilitate flow into the mold features, or by using a monomeric (liquid-like) film that cross-links in the mold. These imprints can be repeated multiple times using a single master, greatly reducing the cost of ownership.
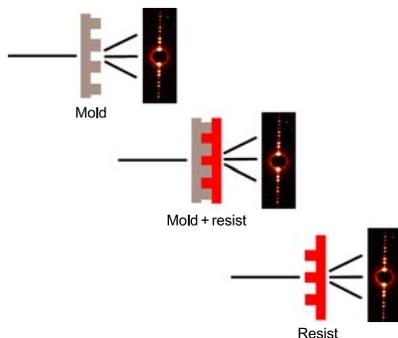


**Figure 1:** *CD-SAXS quantification of the nanoimprint process.*

One of the greatest challenges facing NIL is to quantify the fidelity of pattern transfer; traditional shape metrologies struggle when feature sizes approach 5 nm. We are developing critical dimension small angle X-ray scattering (CD-SAXS) to quantify 3-D pattern shape, with *sub-nm* resolution. Since CD-SAXS uses high-energy X-rays that penetrate Si and most mold materials, we can quantify pattern shape in the master mold, on the mold in contact with the resist, and in the final pattern (*i.e.*, fidelity of pattern transfer), as depicted in Figure 1.
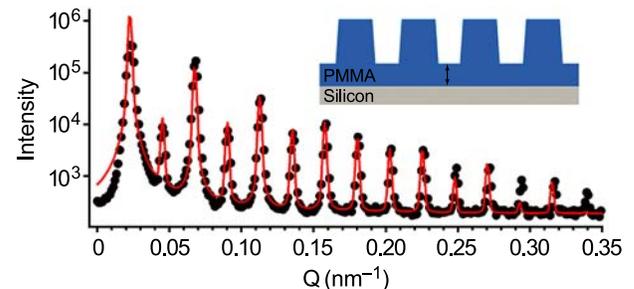


**Figure 2:** *CD-SAXS data (intensity versus scattering vector) for parallel lines and spaces imprinted into a PMMA film.*

Figure 2 illustrates CD-SAXS data for parallel lines and spaces imprinted into a poly(methyl methacrylate) (PMMA) film. The data are in black, while the red line is a fit to a trapezoidal cross section. By tilting the sample and fitting several data sets, we determine that the pattern pitch is $(253 \pm 1)$ nm, the average line width is $(146 \pm 1)$ nm, the trapezoid side-wall angle is $(4.2 \pm 0.5)$ °, and line height is $(180 \pm 1)$ nm.

By providing such accurate structural information, we enable the quantitative evaluation and improvement of imprint processes. Furthermore, we are also developing complementary mechanical and physical property measurements for imprinted polymeric nanostructures. Understanding the unique properties that arise in these nanostructures is crucial to engineering functional and robust polymeric devices at the nanoscale.

## References

1. M.D. Austin, *et al.*, *Appl. Phys. Lett.* **84**, 5299 (2004).

2. *Technology Review*, Feb, 42–44 (2003).

## Contributors and Collaborators

# Nanometrology

The burgeoning field of nanomaterials extends across the full range of traditional material classes, including all forms of metals, polymers, and ceramics. No previous materials technology has shown so prodigiously a potential for concurrent advances in research and industry as does the field of nanomaterials in mechanical devices, electronic, magnetic, and optical components, quantum computing, tissue engineering and other biotechnologies, and as-yet unanticipated exploitations of as-yet undiscovered novel properties of nanoscale assemblies of particles. Already, there is growing excitement surrounding the ability of some molecules or particles to self-assemble at the nanoscale to form new materials with unusual properties. Nanometrology, *i.e.*, the ability to conduct measurements at these dimensions, to characterize the materials, and to elucidate the structure and nature of these new and novel assemblies, is a requisite and fundamental cornerstone that must be established securely if this technology is to flourish.

NIST is uniquely positioned to lead the development of the measurement methods, instrumentation, standards, and reference materials that, together, will form the metrological infrastructure essential to the success of nanotechnology.

The MSEL Nanometrology Program incorporates basic measurement metrologies to determine material properties, process monitoring at the nanoscale, nanomanufacturing and fabrication techniques, and structural characterization and analysis techniques such as advanced imaging and multiscale modeling. The Program comprises 22 projects in the Ceramics, Materials Reliability, Metallurgy, and Polymers Divisions, and includes structural characterization using neutron scattering at the NIST Center for Neutron Research (NCNR). The projects cover a wide range of measurement and characterization methods grouped into the areas of mechanical property measurement, chemical and structural characterization and imaging, fabrication and monitoring of nanoprocesses and events, and modeling of nanoscale properties. In each area, we work to advance basic measurement capabilities and lead the intercomparison, standardization, and calibration of test methods. The newly completed Advanced Measurement Laboratory at the NIST Gaithersburg site provides an incomparable environment for accurate nanoscale metrology.

In the area of mechanical property measurement, we are developing and standardizing techniques for determining nanoscale elastic properties (elastic moduli, Poison's ratio, and internal stress), plastic deformation, density, adhesion, friction, stiction, and tribological behavior. Work in nanoindentation, used extensively in determining mechanical properties of thin films and nanostructures, focuses on developing traceable calibration methodologies and standard test methods. We also use atomic force acoustic microscopy, surface acoustic wave spectroscopy, and Brillouin light scattering to measure the mechanical properties of thin films. In addition, we are developing micro- and nano-scale structures and test methods to measure strength and fracture behavior of interfaces and materials having very small volumes.

The chemical and structural characterization and imaging utilize neutron and x-ray beam lines at three facilities: the NCNR; the National Synchrotron Light Source at Brookhaven National Laboratory; and the Advanced Photon Source at Argonne National Laboratory. Innovative scattering and spectroscopy methods are advancing our ability to obtain a wide range of chemical and structural information at the nanoscale, including chemical bond identification and orientation, polyelectrolyte dynamics, and equilibrium structures. In collaboration with three other NIST laboratories, we are developing electron microscopy and spectroscopy instrumentation for quantitative, 3D chemical imaging at the nanoscale. Other characterization projects include work on gradient reference specimens for the calibration of advanced scanning probe microscopy, and the application of carbon nanotubes as physical probes of cell membranes.

Efforts in the fabrication and monitoring of nanoscale processes and events include the study of electrochemical and microfluidic methods for fabricating nanostructures, novel approaches to nanocalorimetry for the study of interfacial reactions, *in situ* observations of nanoparticle and nanotube dispersion and alignment, and advanced instrumentation for nanotribology experiments.

Finally, we have extensive efforts in the theory, modeling, and prediction of material properties and behavior extending from nanoscale to macroscale dimensions. Modeling efforts include large-scale finite element methods, multiscale Green's function methods, classical atomistic simulations, first principles, and quantum mechanical calculations using density functional theory. Often, several modeling methods must be combined into one study to accurately describe the material behavior; thus, we pay great attention to the correct interfacing between models operating at different length scales, to ensure that our models properly capture the physics of both components and total systems.

Contact:  Douglas T. Smith, Stephen M. Hsu, or
Michael J. Fasolka (Polymers Division)

# Combinatorial Adhesion and Mechanical Properties: Axisymmetric Adhesion Testing

*Axisymmetric adhesion tests promise a powerful means to quantify adhesive performance with the simultaneous ability to visualize debonding mechanisms. However, industrial adoption of these techniques has been slow, since traditional axisymmetric testing equipment does not allow rapid assessment of product performance over a large parameter space. In response, we are developing instruments that permit high-throughput (and high value) measurements of adhesion across combinatorial libraries.*

## Aaron M. Forster and Seung-ho Moon

Adhesion is governed by surface interactions and the mechanical properties of the adhesive. Axisymmetric adhesion (ASA) measurements, such as JKR[1] methods and "probe tack" tests, provide powerful means for quantifying these contributions to adhesion, while providing visual insight into the mechanisms by which adhesives fail. However, current ASA instruments are geared towards serial testing of single specimens. This "one-at-a-time" paradigm is incompatible with industry research, which increasingly requires methods to rapidly and thoroughly measure large numbers of adhesive formulations. Our objective is to produce ASA measurement instruments that operate in a high-throughput manner, while retaining the high-value data these methods produce. These tools enable the rapid identification of structure–property relationships critical for adhesive performance, thereby assisting industry in developing new adhesive formulations. This report describes two of the high-throughput ASA instruments that have been built to address these issues.

The JKR method employs a hemispherical lens that is pressed into a specimen. Tracking the lens/specimen contact area versus load or lens displacement yields the work of adhesion. Our instrument, the Multilens Combinatorial Adhesion Test (MCAT) employs an array

of microlenses to conduct multiple JKR-type adhesion tests in parallel. By simultaneously tracking the contact radii of each element of the lens array, up to 400 measurements of the work of adhesion are collected in the time required for a single traditional JKR test (see Figure 1). When MCAT is used in conjunction with gradient combinatorial specimen libraries, each lens measures a different adhesive system. We recently benchmarked MCAT measurements of the work of adhesion between glass and silicone against single lens JKR tests, with excellent agreement.
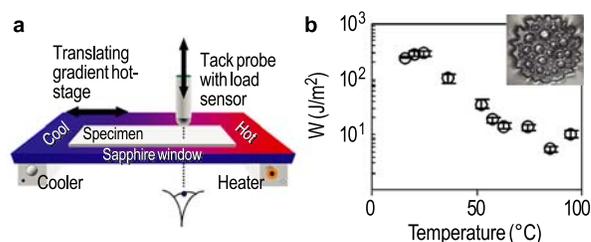


*Figure 2: a) Schematic of CPT adhesion test instrument. b) Adhesion energy (W) of a model PSA vs. temperature. Inset: Image of probe/sample contact shows debonding of the PSA.*

The adhesion of viscoelastic materials, such as pressure sensitive adhesives (PSAs), is not described well by JKR-type tests. Probe tack tests provide quantitative adhesion measurements for viscoelastic systems with simultaneous visualization of debonding events. We developed a new combinatorial probe tack (CPT) test for the measurement of PSA formulation performance (Figure 2). A key feature of the instrument, a gradient hot-stage, enables rapid assessment of temperature effects. Temperature is an important processing parameter and environmental factor for PSAs. Our CPT testing of PSAs (Figure 2) rapidly provides quantitative adhesion energy data and debonding images as a function of temperature. The device design significantly reduces experimental uncertainties associated with fabrication of multiple samples, and reduces the overall measurement time significantly, while maintaining high-quality, rich datasets. We are currently refining the CPT instrument and testing its use towards a variety of applications such as UV-cured PSAs and epoxy systems.

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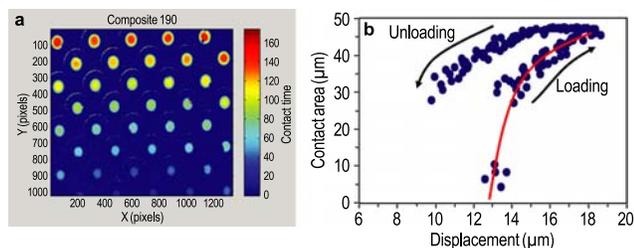


*Figure 1: a) Contact area map of MCAT lens array. Each circle represents data for a separate measurement. b) Contact area vs. displacement data for a single lens array element. The red line is the fit to JKR theory, which yields the work of adhesion.*

## Contributors and Collaborators

A. Chiche, C.M. Stafford, W.L. Wu, W. Zhang (Polymers Division, NIST)

# Combinatorial Adhesion and Mechanical Properties: Innovative Approaches to Peel Tests

*Peel testing is the primary tool industry uses to gauge adhesive performance, but current peel test methods involve "one-at-a-time" analysis of single specimens. Our research aims to accelerate adhesive performance testing by developing devices and measurement strategies that meld the peel test construct with combinatorial and high-throughput (C&HT) methods.*

## Christopher M. Stafford and Martin Y.M. Chiang

As part of the mission of the NIST Combinatorial Methods Center (NCMC), we are developing C&HT peel-test methods that enable rapid assessment of adhesion within the large parameter space associated with adhesive formulation and processing. This report describes two milestones we have met in this endeavor.

Our first achievement involves a NIST-developed experiment design for measuring adhesion of a polymer layer to an underlying substrate in a combinatorial manner. This test method utilizes the peel-test geometry to investigate the interfacial failure between a thin polymer film and a silicon substrate as a function of annealing time and temperature, as well as the substrate surface energy. Combinatorial libraries are generated by using the existing NCMC gradient toolkits: a polymer film is coated onto a substrate containing a surface energy gradient, and this sample is subsequently exposed to an orthogonal temperature gradient.[1] To further extend the parameter space available in this study, we incorporated annealing time as a third dimension. This requires fabricating multiple identical samples and successively annealing each sample for longer times. By applying the Williams–Landel–Ferry (WLF) time-temperature superposition, we can construct a master curve (failure map) detailing the transition from adhesion (bonded) to failure (debonded)
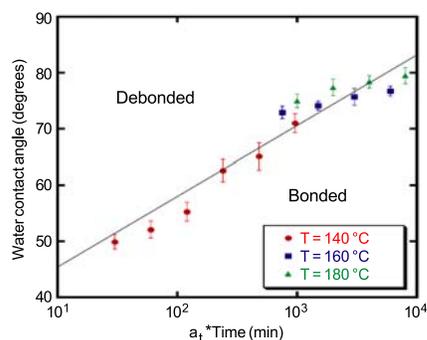


*Figure 1: Master adhesion map delineating critical surface energy conditions for adhesion vs. a reduced time-temperature function, $a_t$.*

as a function of substrate surface energy, annealing time, and annealing temperature (see Figure 1). This defines an operating window of temperature, time, and surface energy to ensure proper adhesion of a thin polymer film to the material of interest.
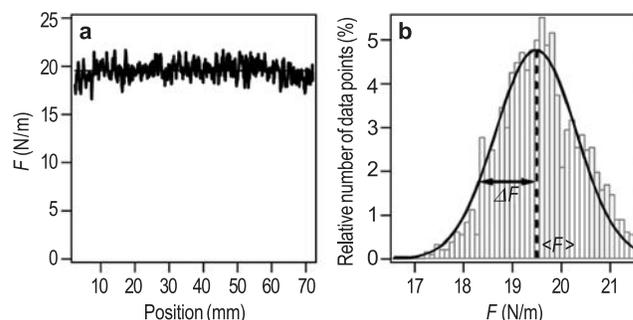


*Figure 2: a) Force vs. distance curve for a typical peel test; and b) distribution curve of the force data.*

Our second achievement addresses a challenge in applying the peel test to combinatorial specimens: the lack of ample statistical information that is the foundation of this type of measurement. For example, a conventional peel test conducted under constant conditions results in a fluctuating force to be averaged. Applying a continuous gradient of sample properties or test conditions in the peel direction implies that each data point (force) corresponds to a given test condition, thus prohibiting the average force to be calculated for a given condition. To address this issue, we have developed a simple statistical treatment that allows a relationship between the uncertainty of the force and the domain size to be established. This treatment ultimately will dictate the number of data points required to obtain acceptable uncertainties in the measurement.

These studies demonstrate how combinatorial approaches can be applied to characterize adhesion using a peel test blueprint. In doing so, we have designed a new statistical tool to assist in defining the gradient step size (discrete gradients) or gradient steepness (continuous gradients) that allows ample statistical information to be obtained.

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## Contributors and Collaborators

# Gradient Reference Specimens for Advanced Scanned Probe Microscopy

*Engineering of nanomaterials, biomaterials, and nano-electromechanical systems hinges on techniques for imaging complex nano-structures. In this respect, new Scanned Probe Microscopy (SPM) methods promise nano-scale mapping of chemical, mechanical, and electro-optical properties, but these techniques generally only offer qualitative information. Through a suite of reference specimens fabricated with a combinatorial design, we aim to calibrate image data from emerging SPM methods, thereby advancing these nanometrology tools.*

## Michael J. Fasolka and Duangrut Julthongpiput

Recent years have seen the development of a new generation of SPM techniques, which intend to measure chemical, mechanical, and electro–optical properties on the nanoscale. However, contrast in new SPM images is difficult to quantify since probe fabrication can be inconsistent and probe/sample interactions are not understood. Our research at the NIST Combinatorial Methods Center (NCMC) aims to provide a suite of reference specimens for the quantification of next generation SPM data. By design, our specimens will gauge the quality of custom-made SPM probes, calibrate SPM image contrast through "traditional" surface measurements (*e.g.*, spectroscopy, contact angle) and provide information for understanding complex probe/sample interactions. Our specimens are produced with bench-top microfabrication routes and combinatorial gradient methods developed by the NCMC. Here, combinatorial methods are key since they enable the fabrication of specimens that vary properties that govern SPM image contrast in a systematic, independent manner. Moreover, as opposed to traditional reference specimens, combinatorial samples provide not one, but a multitude of calibration conditions.

Figure 1 illustrates principles of our specimen design through a specific case useful for quantifying chemically sensitive SPM techniques such as friction-force SPM,
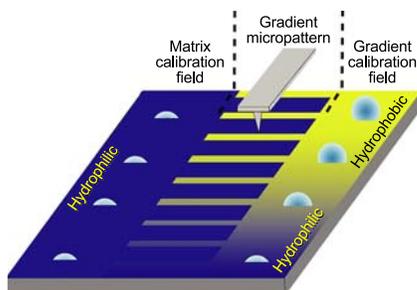
or Chemical Force Microscopy, which employs a custom-made probe. The crux of this specimen is a "gradient micropattern" ($\nabla$-$\mu$p): a series of micron-scale lines that continuously change in their chemical properties (*e.g.*, surface energy) compared to a constant matrix. Two "calibration fields" adjacent to the $\nabla$-$\mu$p directly reflect the chemistry of the lines and the matrix. Thus, traditional measurements (*e.g.*, contact angle) along the calibration fields (1) gauge local chemical differences in the $\nabla$-$\mu$p and thereby (2) calibrate contrast in SPM images acquired along the $\nabla$-$\mu$p.
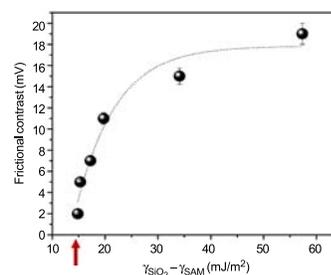


**Figure 2:** *Preliminary calibration curve relating friction force SPM image contrast to differences in surface energy ($\gamma$), as determined from a single gradient reference specimen. The minimum contrast point (red arrow) illuminates the sensitivity of the probe.*

Figure 2 demonstrates use of this specimen for calibrating friction force SPM image contrast. We fabricate this specimen via microcontact printing of a chlorosilane self-assembled monolayer (SAM) on a $SiO_2$ matrix. The chemical gradient is achieved via a graded UV-ozonolysis of the SAM. The plot abscissa gives the difference in friction force (contrast) between the lines and matrix for SPM images collected along the $\nabla$-$\mu$p. The ordinate expresses the corresponding surface energy ($\gamma$) data (from contact angle measurements) collected along the calibration fields. Thus, from a single specimen we create a comprehensive calibration curve that relates SPM friction force to differences in surface energy. Moreover, the plot neatly illuminates the smallest $\gamma$ difference sensed by the probe (red arrow), which is useful for gauging the quality of custom-made probes.

Currently, we are refining this reference specimen design, and we are developing similar designs for other advanced SPM methods.

## Contributors and Collaborators

K. Beers (Polymers Division, NIST); D. Hurley (Materials Reliability Division, NIST); T. Nguyen (Materials and Construction Research Division, BFRL); S. Magonov (Veeco/Digital Instruments)



**Figure 1:** *Schematic illustration of our gradient reference specimen for chemically sensitive SPM techniques.*

# Wet Nanomanufacturing

*Wet nanomanufacturing is the generation of novel nanostructures and the control of chemical reactions (and signals) **in a fluid environment**; this requires effective techniques and efficient material measurements. Therefore, we aim to develop sophisticated fluid-handling devices for directing material assembly, controlling material transport, and measuring material properties.*

## Steven D. Hudson

Flow control is essential for fluid measurement and manufacturing applications. The type and strength of flow are often crucial for producing the desired structure and properties when assembling advanced materials. Using recent advances in microfluidic technology, we have developed a miniature tool without moving parts that mimics the function of a four-roll mill, a rheological and processing instrument.[1] Several microchannels converge to the measurement zone, where micro-particle-image velocimetry was used to map the flow field. By adjusting the relative flow rates, the full range of planar linear flows could be produced. This includes simple shear, which is inaccessible in the four-roll mill.



***Figure 1:*** *Carbon nanotube clusters suspended in the microfluidic trap in extensional flow in the horizontal direction. The cluster at right has fractured from the main one. Also, an individual tube that has broken from the cluster is visible at the far left (arrow). Individual tubes have also been trapped and examined in flow.*

Most importantly, this new device works as a trap, so that particles and other objects can be examined in flow. Using this and related devices, clusters of carbon nanotubes suspended in fluids have been examined (Figure 1). In addition, extension and alignment of individual wormlike micelles has been measured as a function of flow strength and duration.

To achieve certain flow characteristics for particular measurement applications, other microchannel geometries have been and are being developed. Specifically, a device for measuring cell and tissue viability, and mechanical response, is being assembled. Also, a new instrument system for measuring interfacial tension has been developed.

Although microchannels are effective for these important functions, reaching a smaller scale efficiently, requires a new approach. Miniaturization towards nanochannels is usually not practical, because it necessitates very high pressures. At these smaller scales, membranes mediated by pores (as found in living systems) are likely to be efficient means to control the transport of material in metrological and nanomanufacturing processes.
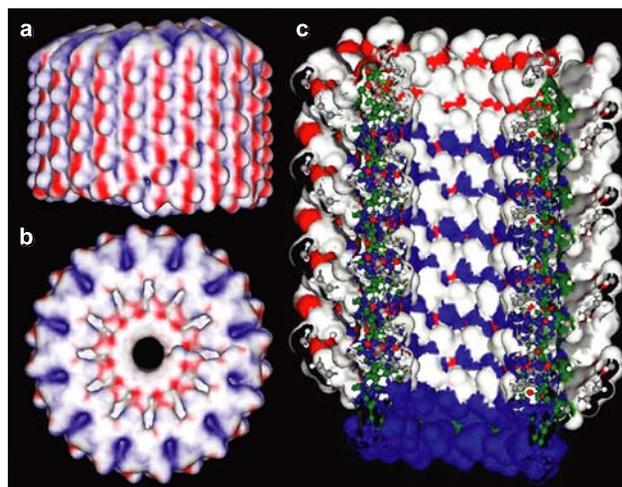


***Figure 2:*** *Molecular model of the artificial membrane pore viewed from: a) the side, b) top, and c) in cross section.*

One such membrane pore (Figure 2) assembled by supramolecular chemistry has been characterized recently.[2] Determination of Fourier components (amplitude and phase) by transmission electron microscopy demonstrated that the supramolecular assemblies are tubular, with an inner diameter of 1.4 nm. Proton conduction through these channels has been measured to be comparable to the transmembrane protein channel gramacidin. Directed assembly of other artificial transmembrane channels will be explored.

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## Contributors and Collaborators

# Characterization of Counterion Association with Polyelectrolytes: Novel Flexible Template Behavior

*Polyelectrolytes differ in chain dynamics and equilibrium structure from neutral polymers due to long-range electrostatic interactions. This manifests into strongly interacting solutions for both synthetic and biopolymers, as observed by associative behavior and multi-mode relaxations. Origins of these relaxations require new experimental methods probing the local structure and dynamics.*

## Vivek M. Prabhu and Eric J. Amis

Polymeric templates are found throughout nature most commonly in the nucleic acid base-pairing of DNA. This special hydrogen bond template has currently been explored for design of novel nanostructured materials. New routes to self-assembled or template-assisted assembly using externally supplied fields such as electric, flow, magnetic, and patterned substrates must overcome Brownian motion as well as structural correlations between and among molecules. For polyelectrolytes, such as DNA, the long-ranged electrostatic interactions also contribute to the solution structure in addition to the local and directional hydrogen bond associations. The distribution and dynamics of the counterion species about a polyelectrolyte serve as a starting point to understand the interactions governing controlled assembly and complement the often-studied polymer structure point-of-view.

We have established, using neutron scattering experiments performed at the NIST Center for Neutron Research (NCNR), the remarkable ability for counterions to essentially conform to linear flexible polyelectrolytes. This was accomplished by direct measure of the counterion partial static and dynamic structure factor highlighting the coupled polymer and counterion association for model synthetic materials shown below.
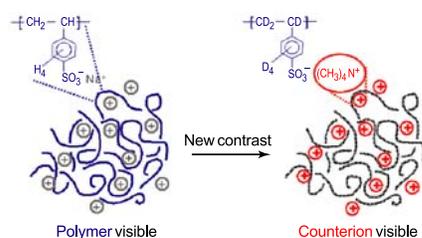
Small-angle neutron scattering (SANS) was used to characterize the equilibrium structure, while neutron spin echo (NSE) spectroscopy was used to examine the dynamics occurring at length scales between (60 and 3) nm and time scales between 45 ps to 100 ns.
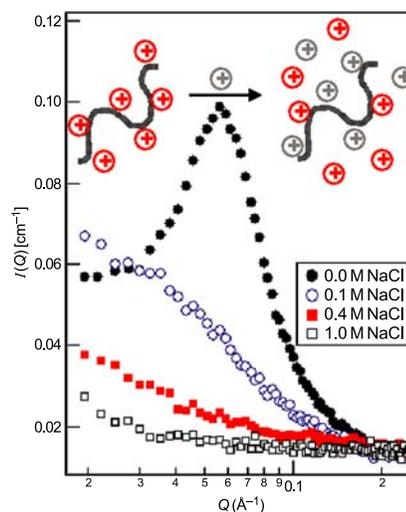


**Figure 1:** *"Visible" organic counterions associate with the negatively charged chain at low salt and are displaced by added "invisible" sodium ions for fixed polymer concentration of 24.9 $gL^{-1}$.*

An example of the counterion correlations is shown by the SANS structural peak in Figure 1. The peak illustrates the counterion correlations mediated by the chain. By tuning the range of the electrostatic interactions with added NaCl, an "invisible" salt, the influence is two-fold: (1) the electrostatics are screened, and the solution returns to neutral-like behavior; and (2) at higher salt concentrations, the $Na^+$ displace the visible $h$-$TMA^+$ counterions as shown in the accompanying schematic. Although the polymer template is no longer observed, its influence is still observed with a "visible" salt.

The counterion dynamics are length scale dependent and slow down near the correlation peak. This behavior illustrates that the polyion-counterion motions are coupled at the nanoscale. Hence, the role of counterions also serves as a design criteria in assembling structures. Unique labeling has provided a new viewpoint of charged polymer solution structure and dynamics. This project aims to characterize the role of charged polymer topology with branched materials, networks, and gels on the coupled dynamics to assess the parameters governing template-assisted assembly. Modern simulation and theoretical insight will assist in understanding these challenges for nanoscale assembly.

## Contributors and Collaborators

D. Bossev, N. Rosov (NIST Center for Neutron Research)

# Safety and Reliability

While various structural failures have captured national attention over the years, the events of September 11, 2001 generated a greatly increased awareness of vulnerabilities in our national infrastructure. The extent of these vulnerabilities depends to a large degree on the performance of materials in situations outside of the original design considerations. It is now recognized that a critical and urgent national need exists to establish the behavior of materials under such extreme loadings, and to disseminate guidance and tools to assess and reduce future vulnerabilities.

The goal of providing a technical basis for cost-effective changes to national practices and standards, coupled with a need for an integrated effort drawing on capabilities and expertise of a broad collaborative team, has lead to the development of the Safety and Reliability Program within MSEL. This program draws on the expertise of several divisions in MSEL and across NIST.

Project selection is guided by an identification and assessment of the particular vulnerabilities within our materials-based infrastructure, and focusing on those issues which would benefit strongly by improved measurements, standards, and materials data. Ultimately, we intend to moderate the effects of acts of terrorism, natural disasters, or other emergencies, all through improved use of materials.

Our vision is to be the key resource within the Federal Government for materials metrology development as realized through the following objectives:

- Identify and address vulnerabilities and needed improvements in U.S. infrastructure;

- Develop and deliver standard measurements and data;

- Develop advanced measurement methods needed by industry to address new problems that arise with the development of new materials;

- Support other agency needs for materials expertise.

This program responds both to customer requests (primarily other government agencies) and to the Department of Commerce 2005 Strategic Goal of "providing the information and framework to enable the economy to operate efficiently and equitably." For example, engineering design can produce safe and reliable structures only when the property data for the materials is available and accurate. Equally important, manufacturers and their suppliers need to agree on how material properties should be measured.

The Safety and Reliability Program works toward solutions to measurement problems on scales ranging



from the macro to the micro, in three of the Laboratory's Divisions (Materials Reliability, Metallurgy, and Polymers). The scope of activities includes the development and innovative use of state-of-the-art measurement systems; leadership in the development of standardized test procedures and traceability protocols; development of an understanding of materials in novel conditions; and development and certification of Standard Reference Materials (SRMs). Many of the tests involve extreme conditions, such as high rates of loading, high temperatures, or unusual environments (*e.g.*, deep underwater). These extreme conditions often produce physical and mechanical properties that differ significantly from the handbook values for their bulk properties under traditional conditions. These objectives will be realized through innovative materials, property measurement and modeling.

The MSEL Safety and Reliability Program is also contributing to the development of test method standards through committee leadership roles in standards development organizations such as the ASTM International and the International Standards Organization (ISO). In many cases, industry also depends on measurements that can be traced to NIST Standard Reference Materials (SRM®).

In addition to the activities above, all three 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 on metallurgical issues involving pipelines and dams, advising the Department of the Interior on the structural integrity of the U.S.S. Arizona Memorial, and collaborating with both the Department of Transportation and the Department of Energy on pipeline safety issues.

Contact: Thomas A. Siewert, Frank W. Gayle, or Chad R. Snyder (Polymers Division)

# Ballistic Resistance of Polymeric Materials

*Ballistic-resistant body armor has been credited with saving more than 2,500 lives, but new materials are constantly being developed, and there currently exists no method for evaluating armor over time to ensure the continued effectiveness of the protection.  The objective of this project is to prevent catastrophic failure of personal body armor by developing a standard test method for reliability of the active polymeric materials that comprise them.*

## Chad R. Snyder and Gale A. Holmes

This research is focused primarily on two goals: (1) to link chemical structure and fiber mechanics to ballistic performance; and (2) to identify chemical mechanisms underlying reduction of ballistic performance, such as UV degradation and hydrolysis. Currently, one of the most promising models linking fiber mechanical properties to ultimate ballistic resistance is the work of Cunniff and Auerbach.[1] From a dimensional analysis study, these researchers concluded that the principal fiber property of interest in relating the ballistic performance of any armor system material to any penetrator, independent of system areal density, is the $(U^*)^{1/3}$ parameter, which is the product of fiber specific toughness and strain wave velocity and is expressed in m/s, *i.e.*,

$$(U*)^{1/3} = \left[ \frac{\sigma \varepsilon}{2\rho} \left( \frac{E}{\rho} \right)^{1/2} \right]^{1/3} \quad (1)$$

where $\sigma$ is the fiber ultimate axial tensile strength, $\varepsilon$ is the fiber ultimate tensile strain, $\rho$ is the fiber density, and $E$ is the linear elastic fiber modulus.  This model has recently been given a firmer theoretical framework by Phoenix and Portwal.[2]
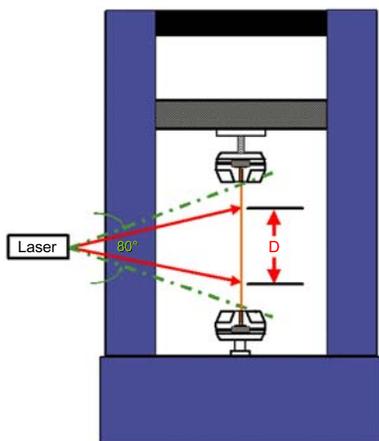


**Figure 1:** *Single fiber fragmentation testing instrument.*

Most tests of ballistic fiber strength are performed on yarns rather than single fibers.  However, obtaining yarns from vests currently in service tends to be very invasive and decreases the strength of the vest.  Obtaining single fibers is far less invasive and, therefore, provides a potential mechanism for monitoring vests while in service without comprising the integrity of the vests.  Because of recent research in our laboratory into polymer composites, there are a number of instruments available to conduct tests on single fibers.  One such instrument is an automated single fiber fragmentation testing machine (see Figure 1), which allows us to obtain stress, strain, and modulus.  In the past, resin samples containing a single carbon or glass fiber were put into the machine.  For this project, we have developed a method to characterize isolated fibers without a resin matrix.
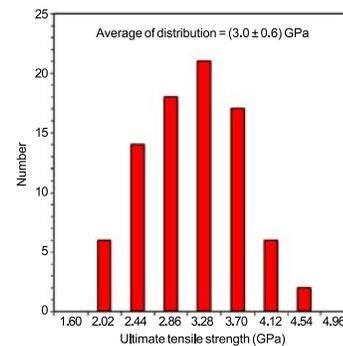


**Figure 2:** *Single fiber data obtained on single E-glass fibers.*

To verify the capability to measure isolated ballistic fibers, we have recently completed measurements on isolated glass fibers (Figure 2).  The results are within the predicted limits, and testing is ongoing on single ballistic fibers.  To address the influence of chemical structure on ballistic fiber performance and durability, model compounds are being prepared to identify any UV and/or hydrolytic degradation pathways of the fibers through mass, infrared, and nuclear magnetic resonance  spectroscopies.

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## Characterization and Measurement — Internal Capabilities/Method Development

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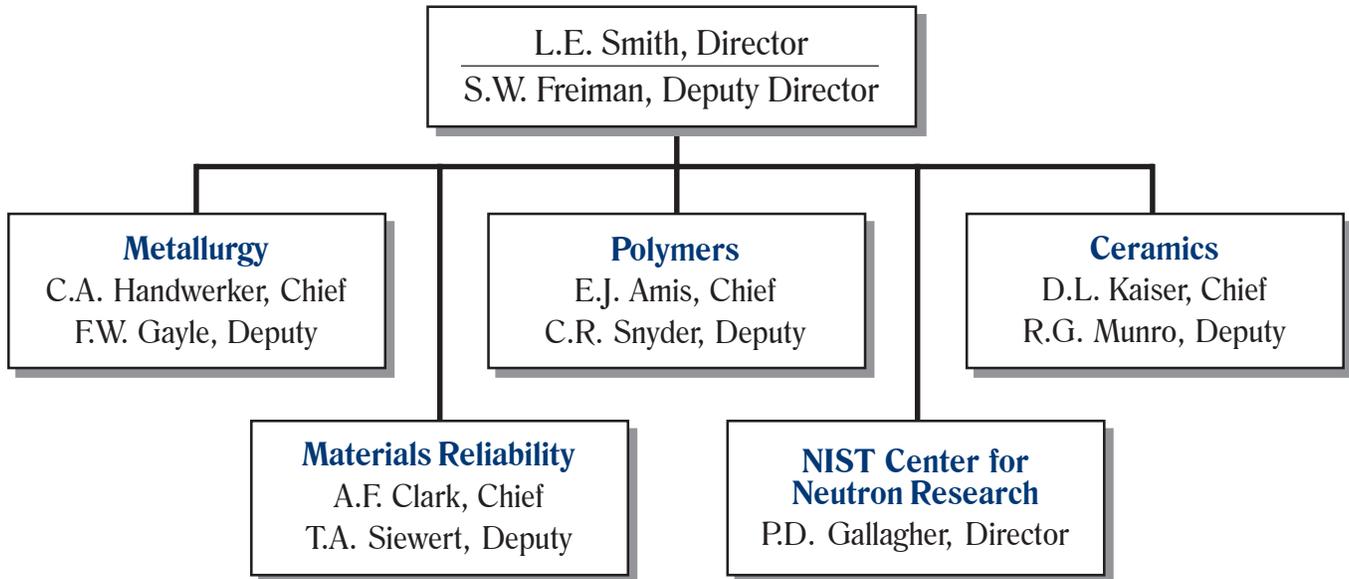
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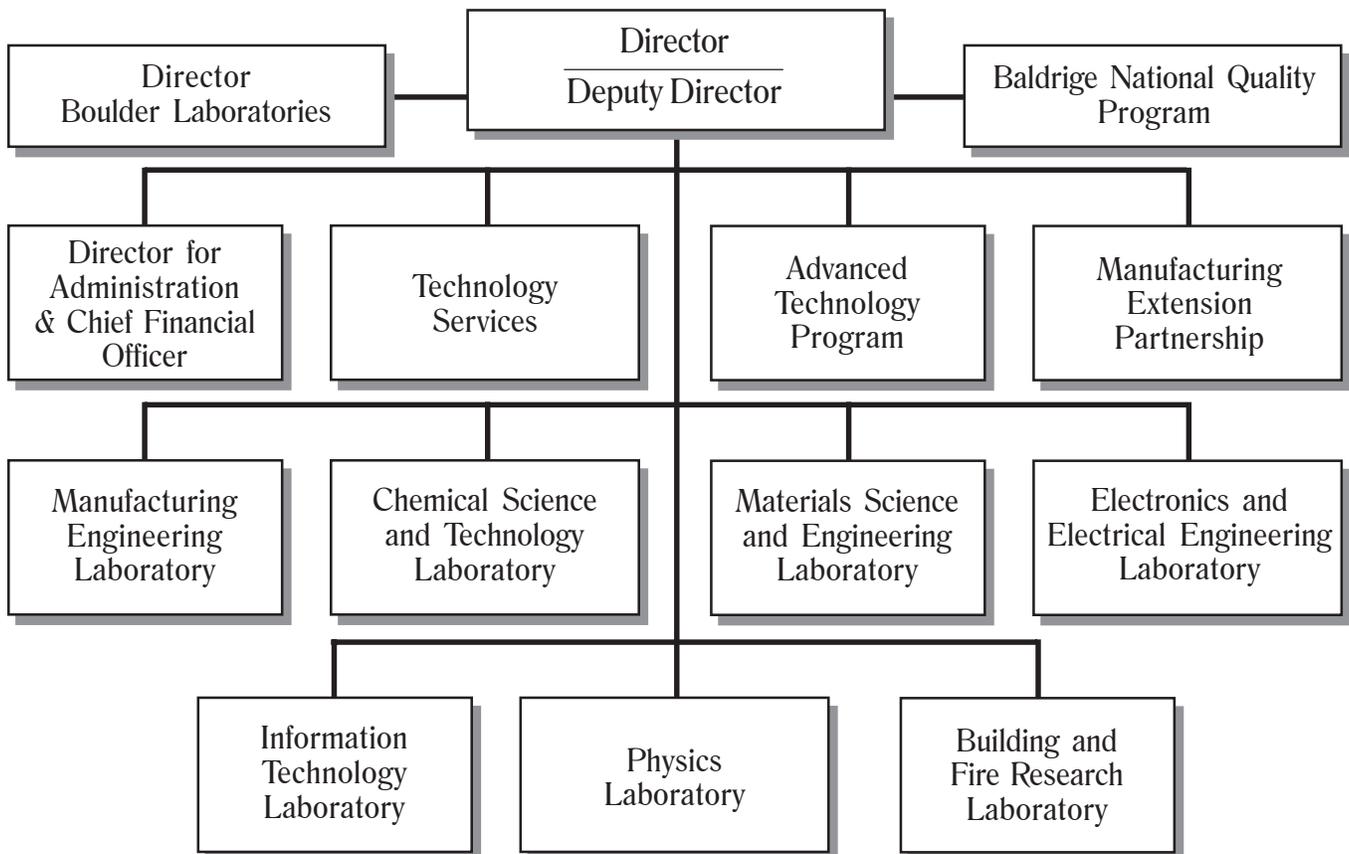>Polymer thin films and blends

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# Organizational Charts

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Manufacturing Engineering Laboratory

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