

POLYMERS Division



MATERIALS SCIENCE AND ENGINEERING LABORATORY

FY 2006 PROGRAMS AND ACCOMPLISHMENTS

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**National Institute of
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James Turner
Acting Director

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of Commerce**
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Secretary



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Eric J. Amis, Chief

Chad R. Snyder, Deputy Chief

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Table of Contents

Executive Summary	1
Technical Highlights	
Cell Morphology and Migration Linked to Substrate Rigidity	2
Chemical Heterogeneity in Chemically Amplified Photoresists: FTIR Measurements and the Effect on Film Dissolution	4
Combinatorial Platform for Measuring the Effect of Substrate Heterogeneities	6
Comparative Metrologies for Evaluating Single Wall Carbon Nanotube (SWNT) Dispersion	8
Numerical Optimization of Complex Instrumentation.....	10
Platform for Characterizing Defects in Magnetic Nanoparticles	12
Advanced Manufacturing Processes	15
NIST Combinatorial Methods Center: <i>A Pioneer and Partner in Accelerated Materials Research</i>	16
Polymer Formations: <i>Soft Materials Measurements on a Chip</i>	17
Quantitative Polymer Mass Spectrometry	18
Biomaterials	19
3D Tissue Scaffolds.....	20
Combinatorial Methods for Tissue Engineering	21
Dental Polymers and Composites: <i>Developing a Test Suite for Total Materials Characterization</i>	22
Metrology for Biomechanical Effects on Cell/Material Interactions	23
Materials for Electronics.....	25
Dimensional Metrology with Small Angle X-Ray Scattering.....	26
Organic Electronics	27
Polymer Photoresists for Next-Generation Nanolithography	28

Table of Contents

Nanometrology	29
Carbon Nanotube Materials:	
<i>Achieving the Gold Standard in Quality and Characterization</i>	30
Combinatorial Methods for Nanomaterials and Nanometrology	31
Defects in Nanostructured Materials	32
Mechanics of Complex Interfaces:	
<i>Libraries for Probing Interfacial Adhesion</i>	33
Nanoimprint Lithography	34
Self-Assembly for Soft Nanomanufacturing	35
Safety and Reliability	37
Ballistic Resistance of Polymeric Materials	38
Polymers Division FY06 Annual Report Publication List	39
Polymers Division	49
Research Staff	50
Organizational Charts	59



Executive Summary

I am pleased to yet again report to you the results of a strong year for the Polymers Division. Our staff and research collaborators continue to be acknowledged for their work in important areas, and in my summary this year, I would like to note some of the recognitions received this year.

As an agency of the Department of Commerce, the National Institute of Standards and Technology focuses on work, often in collaboration with industry, to foster innovation, trade, security, and jobs. This year, our efforts have been recognized by an award specifically related to service to industry. The Secretary of Commerce awarded the Department of Commerce Silver Medal for the development of innovative measurement methods for the structure and properties of nanoporous low- k thin films needed in next-generation IC's to **Barry J. Bauer, Christopher L. Soles, Da-Wei Liu, Ronald L. Jones, Eric K. Lin, and Wen-li Wu**. Silver Medals are awarded for work that demonstrates exceptional performance characterized by superlative contributions that have a direct and lasting impact within the Department of Commerce.

Two Bronze Medals were also awarded within the Division by the NIST Director. **Jan Obrzut** received his for leadership in development and demonstration of an accurate broadband dielectric measurement for frequencies where earlier methods were inadequate; and **Christopher L. Soles** received his for innovative applications of incoherent neutron scattering to measure the dynamics of glassy materials. Bronze Medals are awarded for outstanding contributions that increase the efficiency and effectiveness of NIST.

Complementing these awards for service to industry, several scientists and engineers were acknowledged for their outstanding scientific careers. In a White House ceremony on July 26, 2006, **Christopher L. Soles** was awarded the 2005 Presidential Early Career Award for Scientists and Engineers (PECASE), the nation's highest honor for professionals at the outset of their independent research careers. Chris was recognized for his development of measurement methods and scientific insight into confined nanostructured materials. Annually, two NIST researchers are nominated for PECASE. Chris is the fourth Polymers Division scientist to win this honor with the previous awardees Sharon Glotzer (1998), Eric Lin (2001), and Michael Fasolka (2004).

At the 2006 Annual March meeting of the American Physical Society (APS), **Steven D. Hudson** was named a Fellow of the Society for excellence in structural studies of supramolecular and polymeric materials and the quantitative description of droplet and particle dispersion under quiescent and flow conditions. Steve joins seven

other current Polymers Division scientists and dozens of Division alumni as APS fellows.

Annually, our report provides a sample of the outstanding research from the Polymers Division. 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.

This also represents my last report to you as Chief of the Polymers Division. With the start of the 2007 fiscal year, I moved to our laboratory office as Deputy Director of Materials Science and Engineering. I have thoroughly enjoyed my 11 years working with the outstanding team of talented and dedicated scientists in this premier organization. Our research continues to push the scientific boundaries and fulfill the NIST mission. It is with heartfelt appreciation that I thank the staff of the Division and our many alumni for their support as we have grown and learned together. I am especially grateful to the members of my management team, Chad Snyder, Eric Lin, Alamgir Karim, Kalman Migler, Mike Fasolka, Marc Cicerone, and Dawn Bradley, for their dedication, willingness to challenge the status quo, and respect they show to our goals. The same can be said for the many great individuals who make up the Division staff, our collaborators, and the NIST management. I know this team will continue to grow as they give their support to Eric Lin as the new Division Chief. Together we will continue the tradition of excellence of the NIST Polymers Division.

Eric J. Amis
Chief, Polymers Division



Polymers Division Management Team. Clockwise from Left: Kalman Migler, Eric Lin, Chad Snyder, Eric Amis, Alamgir Karim, Mike Fasolka, and Marc Cicerone.

Cell Morphology and Migration Linked to Substrate Rigidity

Appropriate cell migration is critical to many areas of biology, and to guiding outcomes in Tissue Engineering. Also, cell morphological changes affect the formation of cell adhesion and phenotypic expression. Cells have been shown to change morphology and migrate in response to a wide number of external stimuli, including chemical, mechanical, and electrical. We have developed a model that links cell morphology and migration to substrate mechanical properties.

Martin Y.M. Chiang

Cells cultured, *in vivo*, on substrates show activity that is influenced by substrate mechanics in the following ways:

(1) Cells respond to variation in substrate rigidity. Certain types of cells on stiffer substrates have less rounded morphologies and are more likely to extend into branched morphologies than the same cells on softer substrates (Fig. 1a). In contrast, some experimental studies show that other cell types extend into more branches on softer substrates and exhibit no preference to branching on stiffer ones (Fig. 1b).

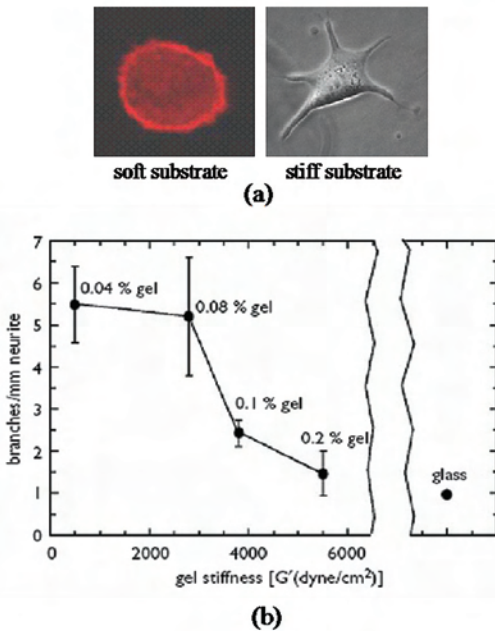


Figure 1: Morphological change (stability).

(2) When cells, cultured on a substrate, are subjected to a uniaxial cyclical substrate stretch, the cells tend to elongate perpendicular to the direction of stretch (Fig. 2).

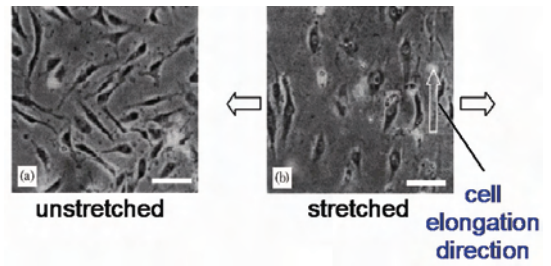


Figure 2: Orientation stability.

(3) Cells tend to migrate towards stiffer regions on a substrate with a stiffness gradient, which is known as durotaxis, although reverse durotaxis (migration towards less stiff regions) has also been observed.

Guided by the aforementioned experimental observations, we have developed a mathematical model of cell-substrate adhesion that connects cell morphology and migration with the mechanical properties of the extracellular environment. The model is based on the hypothesis that morphology of a cell adhering to a substrate is driven by the competition between strain energies (in the cell and substrate) and interfacial energy (work of adhesion at the cell periphery). The stability of a given cell morphology is given by the total energy of the cell/substrate system based on strain and interfacial energies.

The total free energy (E_{tot}) is expressed as the sum of the strain energy in the cell and substrate (E_1) and interfacial energy at the cell periphery (E_2). The ratio of these energies is given the designation β :

$$\beta = E_1/E_2$$

In Fig. 3, the graph on the right hand side of the figure displays E_{tot} as a function of perturbation mode for several values of β . Here, β is varied by changing substrate rigidity. The image insets correspond to the most

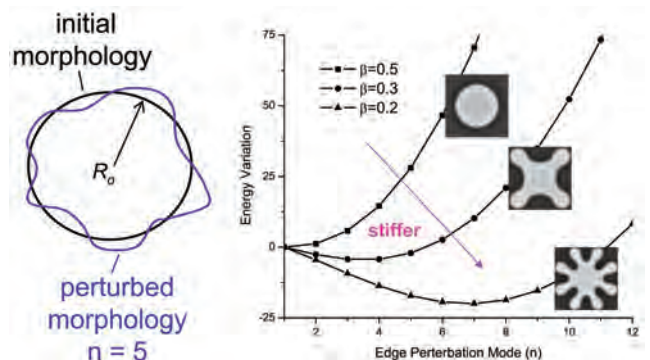


Figure 3: Left-An initially circular cell (solid line) undergoing a morphological perturbation of harmonic form (dotted line). Right-The energy variation as a function of perturbation mode (or number of lobes) n for different values of β due to changes of the substrate rigidity.

stable configuration of the cell predicted using phase-field simulation that includes geometric nonlinearity.

In agreement with experimental observations reported in the literature, our model has demonstrated the hypotheses that the morphological stability of an adherent cell to substrate is governed by the minimal total free energy in the cell/substrate system. The morphological changes of a cell can be rationalized as the consequence of competition between interfacial and elastic energies in the total free energy of cell/substrate system. Thus, the cell changes into its energetically favorable shape by the assembling/disassembling of focal adhesions distributed around the cell periphery. The interfacial energy between the cell and substrate stabilizes the cell morphology while the strain energy from intracellular and extracellular forces destabilizes it. The competition results in a “resonant” window that refers to the range of the stiffness ratio (μ^s/μ^c , substrate to cell) over which the cell is in interaction with the substrate (Fig. 4). With this interaction, the cell and substrate can be mutually compliant. Consequently, it becomes energetically favorable for the cell to undergo significant morphological changes. More importantly, the results from our analysis indicates that the change of trend in morphological stability (the inflection point, Fig. 5) corresponds to $\mu^s = \mu^c$. Therefore, controlled experiments can be planned to estimate the cell stiffness by observing this change (as shown in Fig. 4.)

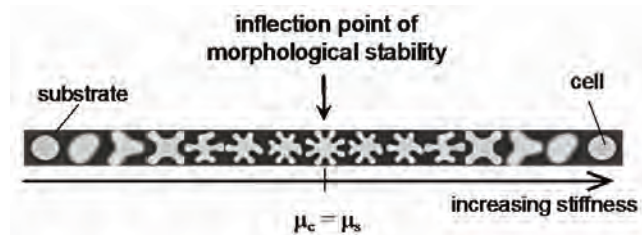


Figure 4: Schematic representing how cell morphology changes in response to substrate rigidity.

Within the framework of our phase-field model, cell migration and orientation are due to the variation of substrate stiffness and durotaxis is viewed as a *progressive* minimization of the total free energy in a cell/substrate system. Our analysis indicates that the cell migrates not only from softer towards to stiffer regions of the substrate, but that the reverse is possible under certain conditions. The occurrence of durotaxis or reverse durotaxis phenomena depends on the relative rigidity between the cell and substrate.

Our study provides insights into the dependence of cell morphology and migration on substrate mechanics; it can be used to rationalize discrepancies on the trend of morphological changes reported in the literature as well as cell locomotion due to the stiffness variation of a substrate. Finally, the study provides a guide in measurement science for cell stiffness and can be extended

to explore cell morphology and migration in a more complex native environment subjected to other external stimuli.

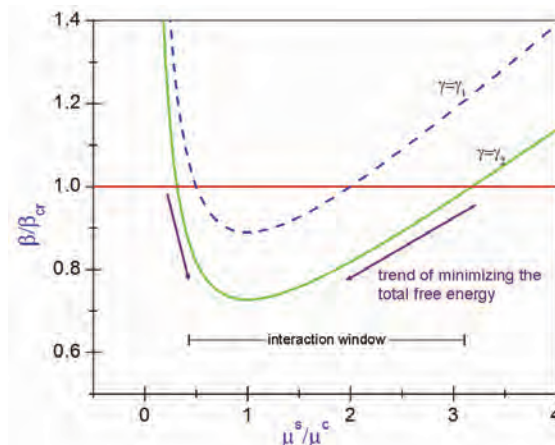


Figure 5: The variation of normalized β as a function of rigidity ratio, μ^s/μ^c , for various interfacial energies, γ_1 and γ_2 ($\gamma_1 > \gamma_2$), corresponding to different cell/substrate systems. β , the ratio of the interfacial energy density to strain energy density of the cell/substrate system. The decrease of β gives rise to morphological instabilities.

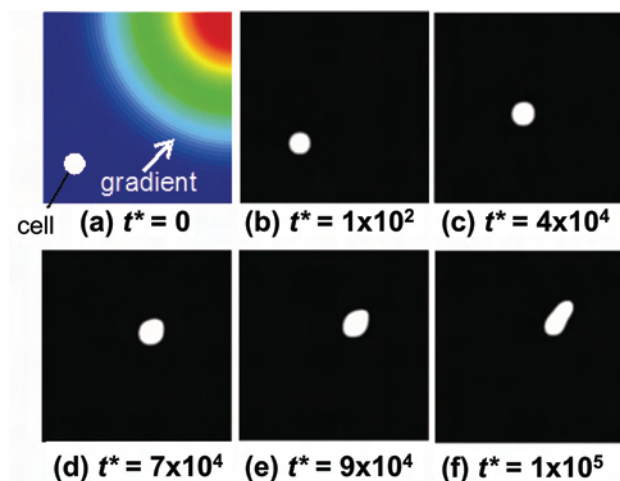


Figure 6: A typical evolution path of the cell from the initial stage to final stage of the simulation. A circular cell initially located on the softer region of substrate with a stiffness gradient (a). The cell migrates from the substrate surface with lower stiffness to higher stiffness (b-f). When the cell migrates to a region on the substrate surface with a critical stiffness, the cell morphology becomes unstable and changes from the original shape to a “potato”-like shape (f). This phenomenon is attributed to a consequence of the competition between energies for the morphological change and the migration.

For More Information on This Topic

M.Y.M. Chiang, J.P. Dunkers, and M.T. Cicerone
(Polymers Division, NIST)

Chemical Heterogeneity in Chemically Amplified Photoresists: FTIR Measurements and the Effect on Film Dissolution

The semiconductor industry roadmap indicates that excessive line-edge roughness (LER) in photoresists at sub 45 nm half pitch is a critical problem with no known manufacturable solutions. It has been broadly accepted that the chemically heterogeneous structure in the photoresist is due to the reaction-diffusion process used to alter the solubility of exposed areas of the material. However, few measurements of this structure have been successful. In this work, we demonstrate that Fourier-Transfer Infrared (FTIR) spectroscopy measurements can be used to parameterize the degree of heterogeneity in polymer thin films, and to illustrate its effect on the response of the polymer to an aqueous base developer solution.

Vivek M. Prabhu

The semiconductor industry roadmap indicates that excessive line-edge roughness (LER) in photoresists at sub 45 nm half pitch is a critical problem with no known manufacturable solutions. LER is believed to result from the heterogeneous distribution in the deprotection product at the line edge of the latent image. The optical image quality of the exposure and the distribution of the subsequently generated photoacid catalysts is a key factor to LER. This heterogeneous deprotection distribution results in local differences in solubility in the developer solution, where highly deprotected chains dissolve, and those with insufficient deprotection remains in the film. A quantitative measure of the degree of heterogeneity in the deprotection reaction product is needed to identify and enable design strategies to reduce materials sources of LER. Direct experimental observation of the degree of heterogeneity is difficult because of the small size scale, and the limited contrast between protected and deprotected chains.

Here, we developed a method to characterize the degree of heterogeneity in thin polymer films using FTIR on materials that exhibit hydrogen bonding. Carboxyl groups are well known to form dimers that induce a band shift in C=O IR spectra relative to the monomer state. Since hydrogen bonding (dimer) can only occur with adjacent C=O groups, and the films are processed well below the glass transition, the local distribution in chemical composition generated by deprotection reaction can be deduced from the ratio of hydrogen bonded to free C=O groups. As a reference point, we use the fraction of hydrogen-bonded C=O groups when the

sites are randomly distributed. If the measured fraction exceeds this limit, dimer clusters are expected and the positive deviation from the homogeneous limit is indicative of the degree of heterogeneity. These results can help understand correlations between compositional heterogeneity and the roughness observed upon the dissolution (development) of resists in aqueous bases.

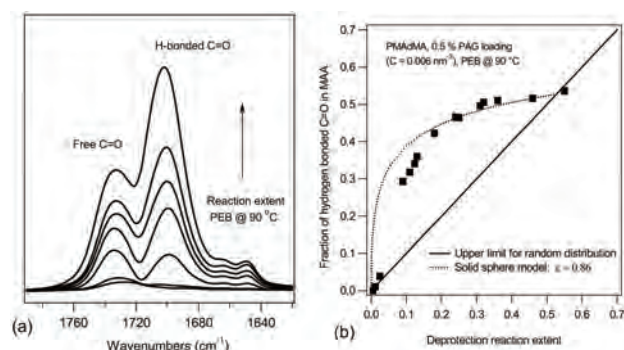


Figure 1: (a) Evolution of C=O stretching bands of MAA groups with reaction extent in PMAdMA samples. (b) Change of fraction of hydrogen bonded C=O in MAA groups with deprotection reaction extent.

Figure 1a shows the IR spectrum of methacrylic acid (MAA) in a partially deprotected poly(methyladamantyl methacrylate) (PMAdMA) film with different extents of reaction. If we define a ratio of the hydrogen bonded C=O to the total C=O in MAA, F_{bond} , we can obtain a continuous change of this ratio with the extent of reaction of the film (Figure 1b). Here, F_{bond} is calculated from the area under the IR peaks corresponding to hydrogen bonded and free C=O, respectively. The degree of heterogeneity within the film is defined relative to the ideal homogeneous structure with a random distribution of components.

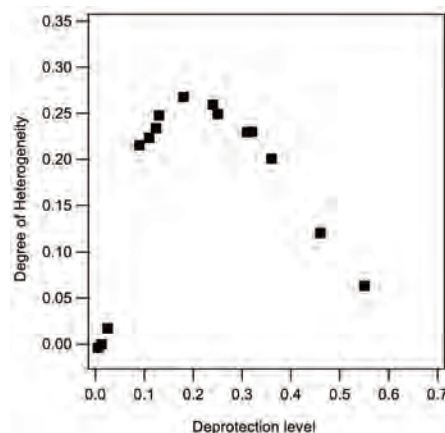


Figure 2: Degree of heterogeneity vs. deprotection level in PMAdMA film for photoacid concentration $C = 0.006 \text{ nm}^{-3}$

We calculate the degree of heterogeneity (DH) and the dependence of DH on deprotection level as shown in Fig. 2. It can be seen that the DH is small at very low and very high deprotection level, but is maximized at a deprotection level of approximately 0.20 to 0.25. These trends arise because the system heterogeneity is dominated by one component at low or high deprotection levels, and the contrast from the uniform phase is small.

The heterogeneity measured from FTIR strongly affects the response of a thin film to an aqueous base solution as a function of the average composition of the polymer as it changes during an acid catalyzed deprotection reaction.

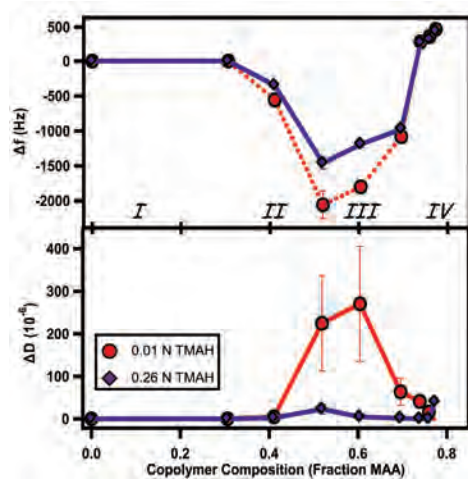


Figure 3: Polyelectrolyte quasi-equilibrium phase behavior determined from the long-time QCM response in frequency (Δf) and dissipation (ΔD).

Quartz crystal microbalance (QCM) with energy dissipation measurements are used to monitor changes in the crystal resonance frequency (film swelling) and its dissipation (related to its mechanical response). Four different regimes of film behavior were identified when equilibrated with aqueous hydroxide solutions (Figure 3). In Regime I, there is no film swelling between compositions ($0 < f_{MAA} < 0.3$); at higher average degrees of protection ($0.3 < f_{MAA} < 0.5$), Regime II is characterized by film swelling only; in Regime III ($0.5 < f_{MAA} < 0.7$), partial dissolution of a swollen film is observed; and finally, in Regime IV ($f_{MAA} > 0.7$), nearly complete dissolution is observed.

The different responses of the films to the aqueous solution are a function of the copolymer composition and the distribution of the methacrylic acid within the polymer films (Figure 4). At short reaction (bake) times, the photoacid diffuses and reacts to a limited extent, forming domains of reacted photoresist that do not overlap. At this early stage, Regime I, the hydrophobic continuum of protected polymer, prevents penetration of water. The methacrylic acid content is inaccessible

to the solution. With longer reaction time, diffusion and reaction of the photoacid molecules increases the methacrylic acid content, which eventually forms a connected or percolated network. The percolated character of these groups provides pathways for solute transport throughout the film, enabling the hydroxide ions to induce film swelling by titrating methacrylic acid groups. The film swelling is enabled by the percolated distribution of deprotection domains, while the degree of swelling is controlled by the ionizable group content.

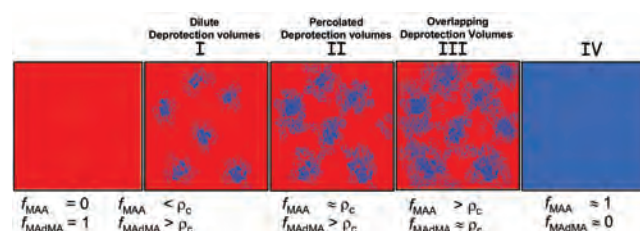


Figure 4: Schematic of the deprotection morphologies of the four regimes and relationship to the average f_{MAA} (and f_{MADMA}) and percolation threshold (ρ_c).

These data raise an interesting question about the origin of the stability of the swollen films. For most polymer gels, film stability during swelling is due to the existence of cross-link junctions formed covalently or by physical entanglement of high molar mass chains. However, the system here does not have any chemical cross linking, and the molar mass of the polymers is below the entanglement molar mass. The stability of our swollen films is attributed to physico-chemical junctions formed by the continuum of hydrophobic (methacrylamantyl) groups. The formation of these junctions is analogous to the aggregation of hydrophobic/hydrophilic copolymers in aqueous solution.

The combination of FTIR and QCM measurements provides new insights into the mechanisms of development which are being incorporated into photoresist models of latent-image formation and dissolution. In future work, we plan to extend these results to the gradient latent image line-edge to understand the polyelectrolyte effects at the liquid-photoresist interface by *in situ* neutron reflectivity.

For More Information on This Topic

B.D. Vogt, S. Kang, V.M. Prabhu, E.K. Lin, S.K. Satija, K. Turnquest, and W. Wu, *Macromolecules* **39**, 8311 (2006).

A. Rao, S. Kang, B. D. Vogt, V. M. Prabhu, E. K. Lin, W. L. Wu, M. Muthukumar, W. D. Hinsberg, *Langmuir* **22**, 10009 (2006).

Combinatorial Platform for Measuring the Effect of Substrate Heterogeneities



To the developers of thin films for coatings, electronics, and nanotechnology, substrate heterogeneities can be the boon of a chemical pattern that drives self-assembly, or the bane of a defect that causes film fail-ure. We have recently developed a combinatorial method for measuring a key under-examined factor in thin film behavior: the “strength” of substrate chemical heterogeneities. Our approach merges soft-lithography and gradient techniques to design a mi-cropatterned library with gradually diminishing chemical contrast. As we demonstrate for the case of polymer film dewetting, our graded test patterns illuminates functional ranges and critical phenomenon in film behavior.

Michael J. Fasolka and Duangrut Julthongpiput

Surface chemical heterogeneities are essential to the performance and behavior of substrate supported polymer films. For example, from a quality control standpoint, substrate chemical heterogeneities can be defects that drive instabilities, and thus failure, in polymer film products such as barrier coatings, electronics packaging, and resist systems. Alternately, patterned chemical heterogeneities on a substrate can be advantageous, since they can template structures in an overlying film for micro- and nano-manufacturing aims.

With respect to both of these themes, a critical parameter is the *strength* of heterogeneity, i.e., the magnitude of chemical differences expressed by the substrate. However, the effect of this factor is difficult to quantify and examine in a methodical manner. In response to this need, we have developed a breakthrough combinatorial library for measuring the effect of differences in surface chemistry, or surface energy.

Our combinatorial test substrates consist of a pattern of micrometer-scale lines that exhibits a continuous gradient in surface energy differences against a constant surface-energy matrix (Fig. 1). The library is fabricated through a vapor-mediated soft lithography of an octyldimethylchlorosilane self assembled monolayer (SAM), which is then treated with a graded ultraviolet (UV)-ozonolysis. The substrate matrix material is SiO₂. The library design includes two calibration strips that express the changing and static surface energy of the SAM pattern lines and matrix, respectively. The surface energy contrast, $\Delta\gamma = \gamma_{\text{SiO}_2} - \gamma_{\text{SAM}}$, along the pat-

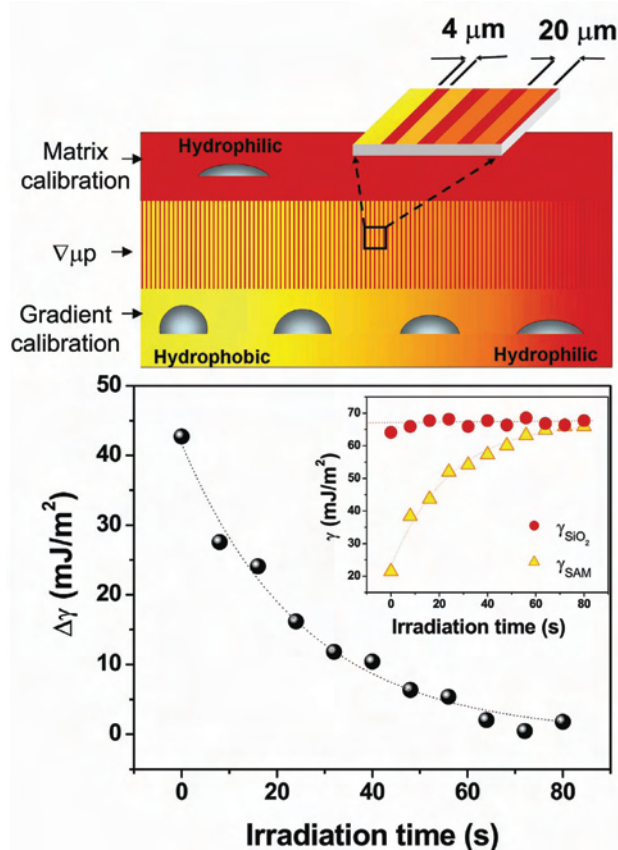


Figure 1: Schematic illustration (top) and calibration (bottom) of the gradient micropattern ($\Delta\mu\text{p}$) library of surface chemical heterogeneities. The inset graph shows γ data from the calibration regions.

terned region can thus be determined by contact angle measurements along these calibration regions. In these libraries, $\Delta\gamma$ diminishes from $\approx 45 \text{ mJ/m}^2$ to 0 mJ/m^2 (i.e., a homogeneous surface).

Previously we described how gradient micropattern ($\Delta\mu\text{p}$) libraries can be used to quantify emerging nanometrologies, such as chemical force microscopy [*Nanoletters* **5**, 1535 (2005)]. This year, we illustrated the utility of $\Delta\mu\text{p}$ libraries for mapping thin film phenomenon. As a demonstration case, we examined the dewetting of a polystyrene (PS) deposited on the micropattern. The film was 35 nm thick and annealed at 60 °C for 12 h.

As summarized in Fig. 2, the $\Delta\mu\text{p}$ enables systematic evaluation of the film dewetting as $\Delta\gamma$ diminishes, and illuminates critical surface energy conditions associated with this behavior. The top of Fig. 2 shows a mosaic of optical micrographs used to assess the dewetted film morphology across the library. An automated optical

microscope was used to capture this fully contiguous set of images. Figure 2a-d shows four strips of optical microscopy data taken from this array. The top and bottom of each strip respectively show the matrix and SAM calibration regions. As expected from homogeneous areas, the dewetted film exhibits polygonal arrangements of droplets, the scale of which remains constant along the matrix, but which increases as γ decreases along the SAM region.

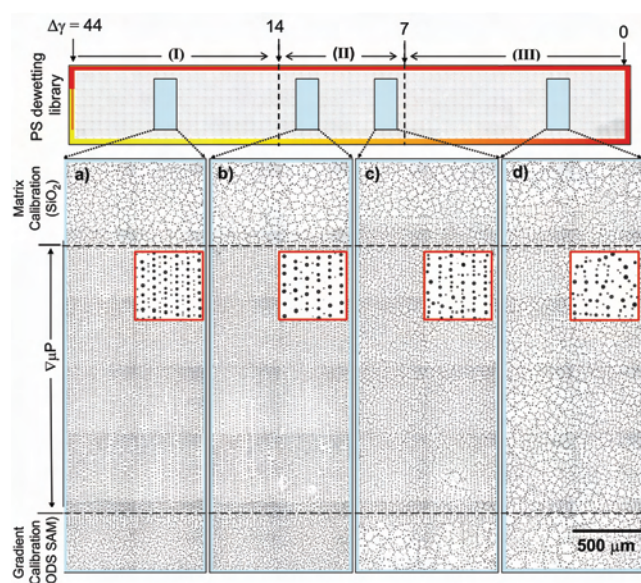


Figure 2: PS film dewetting from a $\Delta\mu_P$ library. Top: Contiguous optical micrographs over the entire library. Bottom (a-d): images detailing the transition from pattern-directed to isotropic dewetting, delineated as Regions I-III. Red insets are $250\ \mu\text{m} \times 250\ \mu\text{m}$. (ODS SAM = *n*-octyldimethylchlorosilane self-assembled monolayer)

Middle sections of Fig. 2a-d show dewetting along the $\Delta\mu_P$. Highlight images (red border) detail representative droplet morphologies in each strip. The $\Delta\mu_P$ library reveals three regimes of behavior. The borders of these regimes can be delineated with precise $\Delta\gamma$ values because the library is calibrated, and due to the detail provided by comprehensive optical microscopy measurements.

In Region I, where $\Delta\gamma > 14\ \text{mJ/m}^2$, we observe a *pattern-directed* dewetting. Region I is characterized by ordered arrays of PS droplets which are distributed along the center of both the matrix and SAM portions of the pattern. In Region III, where $\Delta\gamma < 7\ \text{mJ/m}^2$, isotropic dewetting occurs. In this region, film dewetting is not affected by the substrate pattern, and the droplet morphology closely resembles the polygonal arrangements observed in the calibration regions. A crossover between these limiting behaviors is exhibited in Region II ($7\ \text{mJ/m}^2 < \Delta\gamma < 14\ \text{mJ/m}^2$) where droplets gradually lose registry with the underlying pattern. More detailed analysis in this region (not shown) indicates

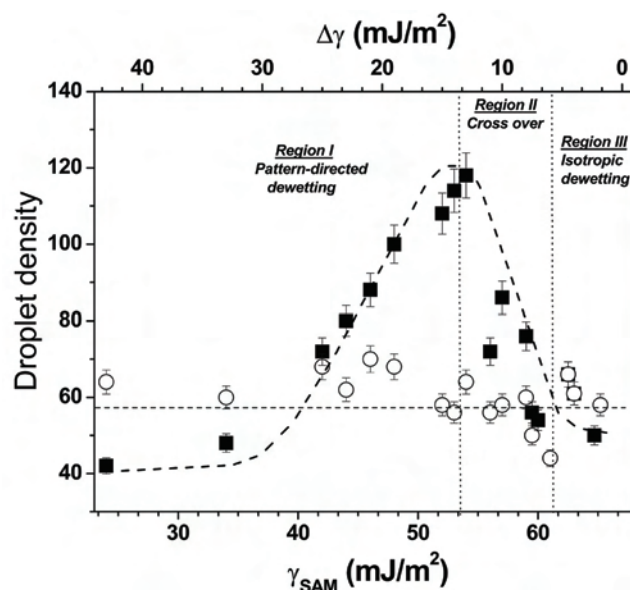


Figure 3: Summary of droplet density data derived from images in Figure 2. Three regimes of droplet behavior are indicated in the figure.

that this crossover is largely due to competition between the kinetics of isotropic and pattern-driven dewetting. By comprehensively mapping dewetting behavior, the $\Delta\mu_P$ illuminates functional ranges and critical values of substrate chemical heterogeneity for film applications. For example, the library shows that for self-assembly of PS droplet arrays, the optimum pattern strength is in the range of $14\ \text{mJ/m}^2 < \Delta\gamma < 20\ \text{mJ/m}^2$. Likewise, to avoid heterogeneity-driven dewetting, surface energy differences on the substrate need to be less than $7\ \text{mJ/m}^2$ in magnitude.

In FY06, we reported this work through an invited lecture at the *American Chemical Society* fall meeting, and at the *2006 International Waterborne Coatings Symposium*.

For More Information on This Topic

A. Karim, J. Douglas, E. Amis (Polymers Division, NIST). For more information on the NIST Combinatorial Methods Center, see www.nist.gov/combi.

Comparative Metrologies for Evaluating Single Wall Carbon Nanotube (SWNT) Dispersion

Despite claims of SWNT dispersion throughout the literature, there is currently no consensus on an absolute measure, nor has there been a methodical comparison of different approaches that might serve as a foundation for such a measure. We demonstrate that small-angle neutron scattering (SANS) provides the most direct measure of dispersion. Near-infrared fluorescence spectroscopy, proposed to be sensitive to the bundling or clustering of SWNTs, similarly exhibits a definitive measure. In contrast, optical absorption spectroscopy and resonant Raman scattering have limited sensitivity. Our study represents the first controlled comparison of currently accepted metrics for evaluating SWNT dispersion, and serves as a useful point of reference for any of the four techniques.

Jeffrey A. Fagan and Erik K. Hobbie

Single wall carbon nanotubes (SWNTs) exhibit remarkable physical properties, and have the potential for profound impact over a broad range of technologies, from first generation applications such as conducting and mechanically reinforced plastics, to more advanced applications such as fuel cells, microelectronic components, flat panel displays, and biochemical sensors. In many of these applications, efficient dispersion of SWNTs at the individual nanotube level will be a prerequisite for optimal performance. Sources of imperfection in dispersing individual SWNTs are most likely bundles, defined here as the lengthwise aggregation or “roping” of tubes, and aggregates, the fractal-type networking of tubes in a floc.

Of all the measurement techniques currently used to evaluate SWNT dispersion in solutions and composites, small-angle scattering is perhaps the simplest to interpret and understand. This technique directly probes two-point correlations in composition, and can thus distinguish true form scattering due to individual SWNTs from the structural scattering that arises from nanotube aggregates and bundles. Other more readily available methods, however, have also recently been used to evaluate SWNT dispersion, typically by focusing on subtle effects such as those that tube-tube interactions have on the optical signatures associated with transitions between electronic states in SWNTs of different chirality. Most notably, these techniques include optical absorption spectroscopy, near-infrared (NIR) fluorescence spectroscopy, and resonant Raman scattering. To extract maximum information from these optical techniques, the sensitivity of each to the level of SWNT dispersion must be known, especially as the limit of individually dispersed tubes is approached.

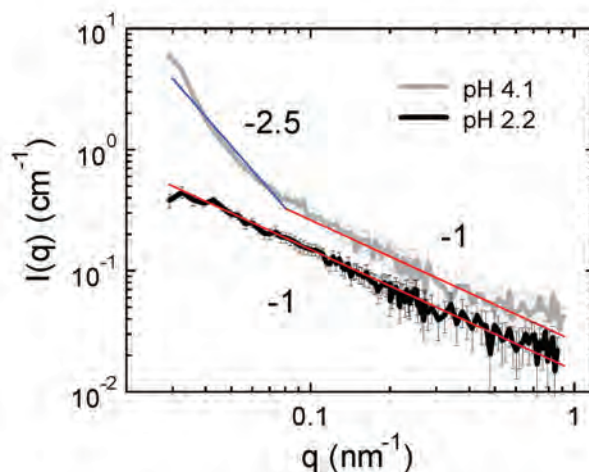


Figure 1: SANS intensity as a function of scattered wave vector for SWNT-PAA composites cast from ssDNA stabilized SWNTs in unbuffered (pH 2.2) and buffered (pH 4.1) aqueous 240k PAA solution, where the red lines denote a power law with an exponent of -1, and the blue line a power law with exponent -2.5. The black trace has been shifted down slightly for clarity by a constant multiplication factor of 1.77. Error bars denote two standard deviations in the total experimental uncertainty.

Despite claims of SWNT dispersion throughout the literature, there is currently no consensus on an absolute measure, nor has there been a methodical comparison of different approaches that might serve as a foundation for such a measure. For this purpose, we have prepared model polymer composites composed of single-stranded deoxyribonucleic acid (ssDNA) stabilized SWNTs dispersed in polyacrylic acid (PAA) for an evaluation of the different metrologies currently used to assess SWNT dispersion. By varying the pH of the precursor PAA-SWNT solution, a systematic variation in SWNT aggregate dispersion is evaluated by scattering and optical spectroscopy. Small-angle neutron scattering (SANS) provides the most direct measure of dispersion. Near-infrared fluorescence spectroscopy, proposed to be sensitive to the bundling or clustering of SWNTs, similarly exhibits a definitive measure. In contrast, optical absorption spectroscopy and resonant Raman scattering have limited sensitivity. Our study represents the first controlled comparison of currently accepted metrics for evaluating SWNT dispersion, and serves as a useful point of reference for any of the four techniques.

SANS profiles from the two composite samples are shown in Fig. 1. For fully dispersed linear objects, we would expect a power law of -1. The unbuffered composite exhibits this power law over the entire q range measured, corresponding to rigid-rod behavior over a range of length scales between (6 and 200) nm. In comparison, the buffered composite exhibits a distinctive

upturn in scattering at low- q , approximately proportional to a power law with an exponent of -2.5 , which is characteristic of nanotube clustering. The difference is both striking and conspicuous, directly demonstrating ideal nanoscale SWNT dispersion in the unbuffered composite, as well as the ability to tune dispersion through adjusting the pH of the precursor PAA solution.

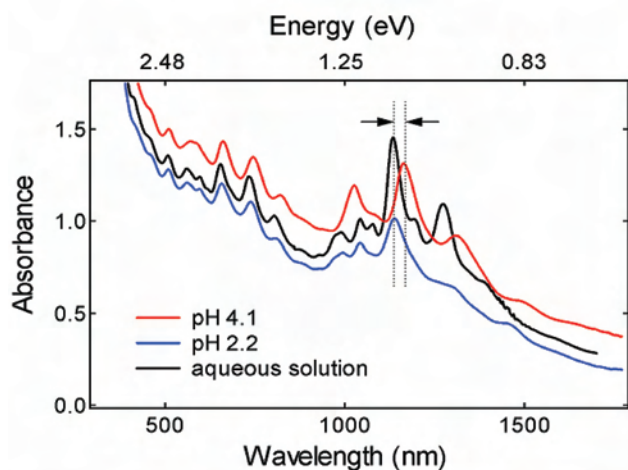


Figure 2: UV-Vis-NIR absorbance as a function of wavelength for the same SWNT-PAA composites, where the solid/black trace denotes the spectra of the same concentration of ssDNA wrapped SWNTs in pure aqueous suspension (pH 7).

Figure 2 shows a comparison of the ultraviolet-visible-near-infrared (UV-Vis-NIR) absorption spectra obtained from the two composites, along with that from the initial aqueous (pH 7) ssDNA stabilized SWNT suspension. The relative intensity of the peaks corresponding to the excitonic transitions for SWNTs of specific chirality in the NIR region of the spectrum are reduced from aqueous solution to buffered composite to unbuffered composite. The second difference between samples is a redshift in the position of the dominant absorption peak from 1134 nm in the aqueous solution and unbuffered composite to 1163 nm in the buffered composite. The changes in the peak structure leading to a broader and redshifted absorption in the buffered sample compared to the unbuffered one supports the SANS results that enhanced dispersion is achieved for the unbuffered composite.

Fluorescence spectroscopy is also a sensitive measure of SWNT dispersion, since SWNT bundling quenches the NIR fluorescence associated with the narrow band gap of the semiconducting SWNT species. A comparison of the fluorescence maps for the unbuffered and buffered PAA composites, shown in Fig. 3, illustrates a pronounced difference in their spectral emissions. In contrast, resonant Raman scattering from the SWNT radial breathing mode (Fig. 4) shows very little difference between the two samples. In combination,

these two observations point to fully debundled SWNTs that have aggregated in the pH 4.1 composite.

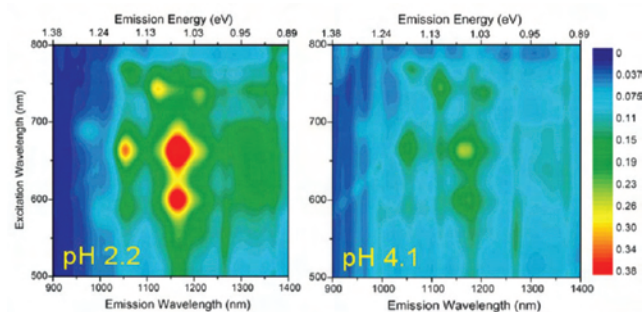


Figure 3: Comparison of NIR fluorescence plots for the SWNT composite samples. Despite equal SWNT concentration and near equal film thicknesses, the fluorescence of the unbuffered film is substantially larger.

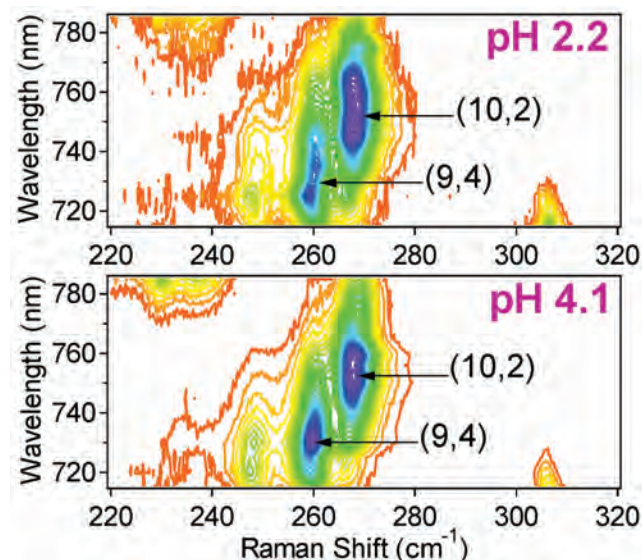


Figure 4: Radial breathing mode resonant Raman scattering for the two SWNT composites.

From this comparison, SANS provides the most direct measure of nanotube dispersion, followed by near-infrared fluorescence spectroscopy. Resonant Raman scattering and optical absorption spectroscopy are useful, but the limits of these techniques for assessing the relative level of dispersion need to be clearly understood, as they provide measures with more subtle changes in signal. From our results, the independent use of any of these techniques can be improved in its interpretation.

For More Information on This Topic

J.A. Fagan, E.K. Hobbie, K.B. Migler, B.J. Bauer
(Polymers Division, NIST)

Numerical Optimization of Complex Instrumentation

A novel approach has been created for the selection of optimal instrument parameters that yield a mass spectrum which best replicates the molecular mass distribution of a synthetic polymer. The application of implicit filtering algorithms was shown to be a viable method to find the best instrument settings, while simultaneously minimizing the total number of experiments that need to be performed. This includes considerations of when to halt the iterative optimization process at a point when statistically significant gains can no longer be expected. This work represents part of an effort to develop an absolute molecular mass distribution polymer Standard Reference Material® by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry.

William E. Wallace

Typical analytical instrumentation optimization is performed by the analyst by simply applying the “factory settings” or by “optimizing by eye.” This is because an exhaustive search of the parameter space for modern instrumentation with many adjustable parameters is prohibitively time consuming. However, a variety of little-known mathematical methods exist that enable the experimentalist to optimize instrument settings without performing an exhaustive search. Broadly classified, these methods are all forms of numerical optimization. When the topology of the search space is very complex, for example, when it has great sensitivity to one or more parameters (as mass spectrometers often do), the methods used are part of the field of non-linear programming. They are called non-linear because some (or all) of the instrument parameters do not have a linear relationship between parameter value and measurement response. A simple example is laser intensity in MALDI-TOF mass spectrometry and its effect on signal-to-noise ratio where a relatively sharp threshold is observed experimentally. When the measurement outcomes (which in the present case are mass spectra) contain random noise, the mathematical methods are termed stochastic numerical optimization. Stochastic methods are important in mass spectrometry because all mass spectra have noise, this noise varies as the instrument parameters are adjusted, and the noise will often change across the spectrum. Measurement noise presents a significant challenge to any optimization method especially for cases where signal to noise is not the measurand to be optimized. Nevertheless, numerical optimization methods offer experimentalists a way to tune the instrument parameters to achieve the desired goal without having to

search all possible parameter combinations. To measure the absolute molecular mass distribution of a synthetic polymer, it would be ideal to locate a region in parameter space where the instrument response function was uniform across the entire mass range. Finding the instrument response function is necessary to calibrate the intensity axis of the mass spectrum; that is, to go from mass spectrum to molecular mass distribution. If the instrument response function is uniform, then the relative peak areas in the mass spectrum correspond directly to the relative abundances of individual n-mers in the sample. A uniform instrument response function would be a line of zero slope; that is, it would have a derivative of zero. If not uniform, the instrument response function could slowly vary across the mass range, preferably linearly with mass. The optimal conditions are those that give the simplest (or flattest) instrument response function; that is, the one with the smallest derivative.

To measure the instrument response function, a gravimetric mixture was made of three low polydispersity polystyrenes that were very close in average molecular mass. The optimal instrument settings were those that provided the closest match between the total integrated peak intensity of each of the three polymers with the known gravimetric ratios. Note that there is no guarantee (or even assumption) that the optimal instrument settings that give the flattest instrument response function will also yield optimal signal to noise ratios. In fact there is no reason to believe that a search for the instrument settings that optimize the response function will not lead into a region where the mass spectra become so noisy as to make peak integration impossible. Thus, to find the optimal instrument settings, we used stochastic gradient approximation methods. These methods have proven to be extremely robust in cases where the measured data are very noisy.

Optimization is performed by defining an objective function $J(x)$ where x is a vector consisting of the instrument parameters. In our case, the objective function was the sum of the squared differences between the amount of each polymer in a mixture created gravimetrically, and the amount of each polymer in the mixture found by mass spectrometry. When this function is zero, the gravimetric concentrations match the concentrations found by mass spectrometry, and the instrument is optimized. The function $J(x)$ is a noisy function with respect to the parameter vector x , due to the inherent statistical noise in the mass spectra. This complicates the task of numerically locating the minimum of $J(x)$. The fact that each evaluation of $J(x)$ requires an experiment, and subsequent interpretation of experimental

results, means that there is a high cost for each function evaluation. This further complicates any numerical procedure that seeks to minimize $J(x)$. Finally, there are values of the vector x (for example, out of range instrument parameter settings), for which $J(x)$ cannot be evaluated. One method for minimizing noisy functions that seeks to approximate the gradient of the objective function is called implicit filtering. Broadly speaking, this method uses a very coarse grained step-length to build a finite difference approximation to the gradient of $J(x)$. This gradient is then used to generate steep-descent directions for a minimization process. As iterates draw closer to the solution, and the objective function decreases, the finite difference step-length is decreased until it approaches a number small enough to suggest convergence of the algorithm to the minimum value.

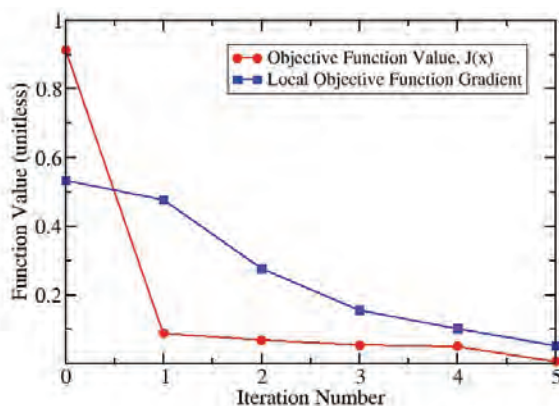


Figure 1: The objective function $J(x)$ and its local gradient value as a function of iteration step.

In Fig. 1, there is an initial steep drop in the objective function followed by gradual movement to the optimal parameter settings. The gradient of the objective function also decreases steadily as the optimum point is approached. These monotonic responses indicate that the optimization routine is stable. At the optimum value, the objective function is so small that it cannot be reduced further due to the inherent noise in the measurement. Likewise, the step size indicated for each parameter at this point is so small as to be below the precision of the instrument's settings.

In Fig. 2, the values oscillate about their final values as the optimization proceeds. The laser intensity undergoes the greatest excursions: decreasing in the first two iterations, returning to its initial value in the third iteration, and then increasing in the fourth iteration before settling into its final value. The four other parameters make an excursion in the direction of their final values in the first iteration, return to their initial value in the second iteration, and find the equilibrium values by the third iteration. This zigzag pattern is characteristic of the non-linearity of the system. This non-linearity arises from the fact that the instrument parameters are

coupled; that is, varying one requires all others to vary in response if $J(x)$ is to move closer to its optimal value. Thus, the vector x_{i+1} has a tendency to be normal to the vector x_i (in its five-dimensional space). The laser intensity varies the most, and would seem to be the dominant variable. It seeks its stable value before the other parameters can settle down to find their optimal values.

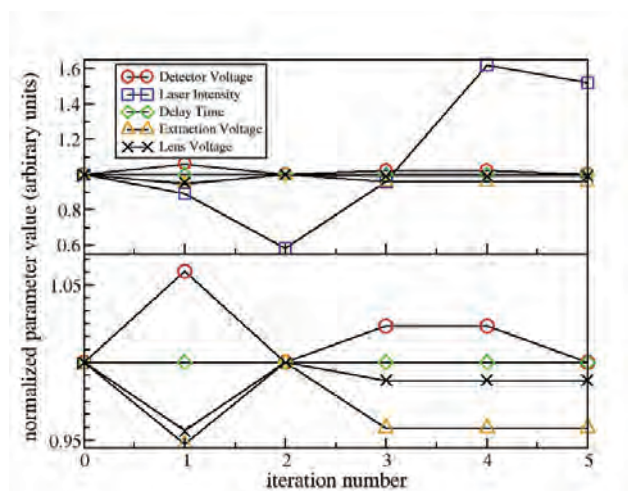


Figure 2: Individual instrument parameter values as a function of iteration number.

A specialized noise-adapted filtering method has been applied to the problem of finding the optimal instrument parameters for a MALDI-TOF mass spectrometer. Finding the optimal instrument parameters was a critical step in creating an absolute molecular mass distribution polymer Standard Reference Material[®]. The task of tuning the instrument's five main parameters could not be approached by exhaustive search methods, given the amount of effort needed to take and to reduce the data in a statistically meaningful way at each set of instrument parameters. Additionally, this method produces an estimate of the sensitivity of each optimal parameter not available to traditional exhaustive search methods. Each of the subtasks in the process could be automated to create an integrated closed-loop optimization scheme.

For More Information on This Topic

W.E. Wallace, K.M. Flynn, C.M. Guttman (Polymers Division, NIST); A.J. Kearsley (Mathematical and Computational Sciences Division, NIST)

See www.nist.gov/maldi for more information.

Platform for Characterizing Defects in Magnetic Nanoparticles

Nanoparticles are an important component of emerging technologies for medical diagnostics, targeted therapies, biomolecular detection, and next generation electronics. The efficacy of nanoparticles in these applications is challenged by the lack of methods to characterize the strength and homogeneity of nanoparticle interactions. We are developing a measurement platform to rapidly quantify nanoparticle interactions for large assemblies of nanoparticles, providing statistics on the distribution in strength of interaction, and the capability to determine the nature and concentration of defective particles.

Ronald Jones and Jason Benkoski

Nanoparticles with diameters of (1 to 100) nm are widely sought as enablers of advanced technologies for medical diagnostics and therapies, chemical and biological sensors, and microelectronics. Many of these technologies rely on the enhanced optical, magnetic, and chemical functionality inherent in particles of nanometer scale. However, properties of nanoparticles are highly sensitive to particle size, shape, and chemical composition. As a result, small variations in the manufacturing process can produce defective particles with undesirable properties, resulting in a loss of device functionality. The advancement of suitable manufacturing techniques is currently limited by a lack of measurement platforms capable of rapidly characterizing defects in nanoparticle interactions over large particle quantities.

A specific class of nanoparticles that has received significant interest is magnetic nanoparticles (MNPs). The particles typically consist of a metallic core with a polymeric flocculant coating. Recent advances in synthetic methods make the production of large numbers of MNPs with nearly monodisperse diameters and homogeneous compositions feasible. However, scaling established methods to characterize the interaction strength of a single MNP are challenged by the large numbers of particles and their small dimensions, precluding a measurement of defect concentration and homogeneity in manufacturing. As a result, indirect and often time-consuming measurements of size dispersity are used to infer homogeneity of interactions.

We are developing a methodology to rapidly characterize the homogeneity of large numbers of particles to quantify the number density of defective particles. Defective particles are particles with vanishing magnetic moment or particles with undesirable polarity. In many applications, for example, the synthesis attempts to cre-

ate large batches of dipolar particles. However, small variations in synthetic conditions can result in varying concentrations of quadrupolar particles, or even particles with higher moments of polarity.

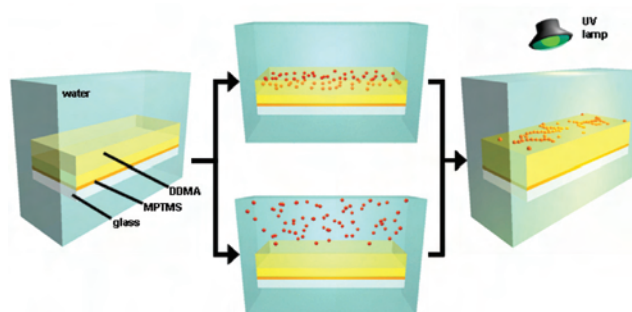


Figure 1: Schematic depicting the crosslinkable oil-water platform for characterizing nanoparticle interactions. The platform provides a rapid method to quantify the character and number of defects in magnetic interactions for a large number of particles. A wide range of particle size and chemistry are available to this methodology due to the ability to assemble oil soluble (top route) and/or water soluble (bottom route) particles.

Rather than measuring the properties of individual particles in a serial fashion, our methodology measures the shape and size of nanoparticle assemblies, where assemblies can consist of 10's or 100's of nanoparticles. Dipolar MNPs are known to assemble as long strings in solution when their magnetic moment interactions exceed other isotropic forces, including thermally induced vibrations and isotropic van der Waals interactions. In contrast, non-polar particles or multipolar particles form non-linear assemblies. Defects in MNPs are therefore characterized by the linearity within assemblies. The methodology described here uses a novel platform to freeze-in thousands of assemblies for characterization using scanning probe or electron microscopies. By measuring a large number of assemblies, where each assembly can contain 1000's of particles, high precision statistics of defect concentration are obtained.

As shown in Fig. 1, MNP assembly occurs at an oil/water interface, in which the oil phase can be flash-cured upon ultraviolet (UV) radiation exposure. The platform utilizes a photopolymerizable oil phase, 1,12-dodecanediol dimethacrylate (DDMA), to provide a portable and characterizable “snapshot” of the assembly process. The use of a low viscosity oil and water phase allows MNP assembly to proceed rapidly. With an appropriate chemistry and light source, the assemblies are frozen in less than 1 s from initial exposure, with minimal volume change of the oil phase. Freezing of the MNP assemblies precludes the alteration of as-

sembly structure by capillary forces at the air/water interface. The resulting sample is glassy, allowing storage for long-time or future measurements, and is amenable to a wide range of characterization platforms, including scanning probe and electron microscopies. Its transparency to a wide range of electromagnetic wavelengths will enable the advancement of scattering and optical imaging based characterization platforms.

While development has focused on nanoparticles, a wider range of particle interactions can be studied under identical conditions, including much larger colloidal and latex particles, particles of varying polarity, and of varying composition, including metallic and polymeric. Particles investigated to date include nonpolar $0.39\ \mu\text{m}$ poly(methyl methacrylate) latex spheres, nonpolar $10\ \mu\text{m}$ polystyrene latex spheres, highly polarizable $5\ \text{nm}$ Au nanocrystals, dipolar $10\ \text{nm}$ CdTe quantum dots, and magnetic $25\ \text{nm}$ magnetite nanoparticles. As shown in Fig. 2, the range of structures expected in these assemblies is large, making the methodology generalizable to a large range of particles.

In Fig. 3, assemblies of both micrometer scale polymer particles and nanometer scale metallic particles provide immediate qualitative and quantitative characterizations of average interaction strength, while providing data on defect concentrations. Specifically, charging on polystyrene particles as a result of the sample preparation method dramatically changes the assembled structure from dense, two-dimensional aggregates to highly branched networks. The charging appears to be uniformly applied across all particles. In contrast, gold nanoparticles follow a well defined random walk characteristic of directional forces. Similarly sized magnetite particles feature regions of dense packing, indicating the presence of particles with lower magnetic moment and/or multipolar character.

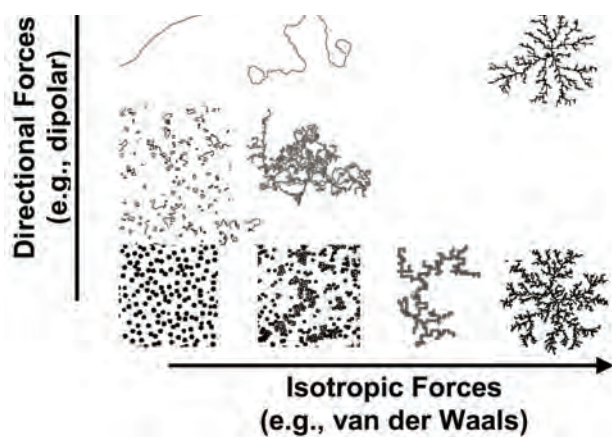


Figure 2: Representative structures from assemblies of particles with varying types and strength of interaction.

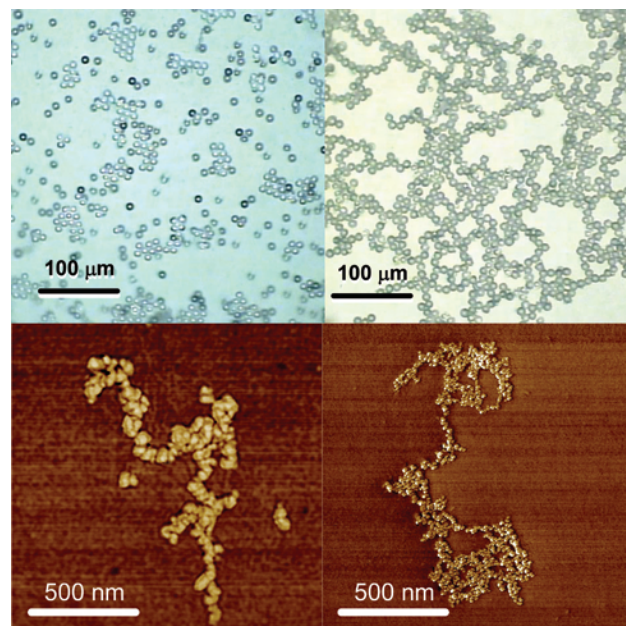


Figure 4: Top: Optical micrographs of $10\ \mu\text{m}$ PS spheres protruding from the oil/water interface after crosslinking. Shown are uncharged particles (left) with characteristic two-dimensional dense assemblies. In contrast, a small charge added to the particle creates a highly branched assembly (right). Bottom: Atomic force microscope phase image of assemblies of gold (left) and magnetite (right) nanoparticle assemblies. While the gold particles show a characteristic linear assembly, the presence of dense assembled regions in the magnetite particles may indicate the presence of particles with reduced magnetic moment.

We have demonstrated the use of a DDMA/water interface as a platform for characterizing defects in the magnetic interactions of particles with nanometer scale dimensions. The methodology characterizes the interaction strength of a large number of particles by the examining the structure of assemblies of 10's or 100's of nanoparticles at an oil/water interface. Without the ability to preserve snapshots of the aggregated structures by this process, the rapid movement of the particles would challenge microscopy characterization techniques. The high interfacial tension of the oil/water interface provides a strong driving force for the segregation of many different particle types, despite large differences in charge, polarizability, size, and surface chemistry. It therefore allows one to compare the aggregation of a wide variety of nanoparticles under remarkably similar conditions.

For More Information on This Topic

J. Douglas, A. Karim (Polymers Division, NIST); J. Pyun (University of Arizona)

Advanced Manufacturing Processes

The competitiveness of U.S. manufacturers depends substantially on their ability to create new product concepts and to quickly translate such concepts into manufactured products that meet their customers' increasing expectations of performance, cost, and reliability. This is equally true for well-established "commodity" industries, such as automotive, aerospace, and electronics; for materials suppliers of aluminum, steel, and polymers; and for rapidly growing industries based on nanotechnology and biotechnology. In support of these industries, the NIST Materials Science and Engineering Laboratory (MSEL) is developing robust measurement methods, standards, software, and process and materials data needed for design, monitoring, and control of new and existing materials and their manufacturing processes.

Our research is conducted in close collaboration with industrial partners, including industrial consortia, and with national standards organizations. These collaborations not only ensure the relevance of our research, but also promote rapid transfer and utilization of our research by our partners.

Contact: Michael J. Fasolka



Quantitative Polymer Mass Spectrometry Project Meeting



NIST Combinatorial Methods Center



NIST Combinatorial Methods Center A Pioneer and Partner in Accelerated Materials Research

Combinatorial and high-throughput (C&HT) methods hold great potential for making materials research more productive, more thorough, and less wasteful. However, significant technical barriers prevent the widespread adoption of these revolutionary approaches by industry. Through creative, cost-effective measurement solutions, and by using a customer outreach model designed for fruitful collaboration, the NIST Combinatorial Methods Center (NCCM) strives to ease the acquisition of C&HT techniques by the materials research community.

Michael J. Fasolka and Carol E. Laumeier

The NIST Combinatorial Methods Center (NCCM), now in its fifth year, continues to be an innovative resource for industrial materials researchers striving to acquire combinatorial and high-throughput (C&HT) measurement capabilities. The NCCM fosters adaptation of C&HT methodologies through two complementary efforts. First is a research program, centered in the Polymers Division's Combinatorial Methods Group, which develops and demonstrates C&HT measurement solutions for the discovery and optimization of complex materials products, including polymer coatings and films, adhesives, cosmetics, and structural plastics. Moreover, in conjunction with other Polymers Division Groups, a growing aspect of NCCM research provides C&HT methods for emerging technologies such as nanostructured materials, organic electronics, and biomaterials. All NCCM research is published in the public domain.



Figure 1: NCCM Awardees of the Department of Commerce Silver Medal for Customer Service in 2006. From left to right: C.M. Stafford, A. Karim, M.J. Fasolka, K.L. Beers, E.J. Amis.

Second, to complement its research, the NCCM conducts outreach efforts focused on disseminating new measurement methods to industry, assessing emerging industrial C&HT metrology needs, and forming a community of technology stakeholders. The NCCM leverages a unique, “non-proprietary” consortium model, the development and success of which garnered a Department of Commerce Silver Medal for Customer Service (see photo). This model promotes open discus-

sion of the metrology issues that face industrial stakeholders, and a focus on the fundamental, common needs of this community. NCCM consortium members (see table below) are served through a series of semi-annual workshops, a dedicated website, and documents that detail NCCM instrumentation. FY06 activities included two additions to the NCCM workshop series. *NCCM-8: Polymer Formulations II*, held Oct. 27-28, 2005, assessed opportunities in microscale measurement technologies for advancing formulations science, gauged related measurement needs, and reported the achievements of the Polymers Formulations project. *NCCM-9: Combinatorial Methods for Nanostructured Materials*, held Apr. 24-25, 2006, determined key metrology needs in industrial research of nanostructured polymeric materials, and set priorities for developing C&HT methods for these systems. NCCM-9's Workshop Report, NISTIR 7332, is available on the NCCM website (see below).

In addition, non-proprietary “Focus Projects” enable member companies to collaborate with NCCM researchers to produce more specific measurement solutions. Two NCCM Focus Projects were completed in 2006. The first, co-funded by Procter and Gamble and National Starch, resulted in a powerful microfluidic approach for measuring interfacial tension. The second, sponsored by Intel and National Starch, resulted in combinatorial libraries that assess the performance of epoxy adhesives for flip-chip electronics. A new Focus Project, with the goal of developing HT measurements of polymer hydrogel mechanics, was launched with Vistakon, a manufacturer of contact lenses.

NCCM Members		(*New in FY2006)
Air Products & Chem.		Insight Faraday*
Arkema Inc.		Intel
Avon*		L'Oreal
BASF		PPG Industries
Bayer Polymers		Procter & Gamble
Dow Chemical Company		Rhodia
ExxonMobil Research		Symyx Technologies*
Honeywell International		Unilever*
Hysitron International		Univ. of Southern Miss.
ICI/National Starch & Chem.		Veeco Metrology

For more information, please visit the NCCM website at www.nist.gov/combi.

Contributors and Collaborators

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



Polymer Formulations: Soft Materials Measurements on a Chip

Complex structured fluids, also known as formulations, have been an important part of modern life for many years, even though they are poorly understood. Only recently has industry begun to control and design these materials to obtain novel, valuable properties, but scientists are overwhelmed by the composition and processing variable space required. We develop and demonstrate high throughput methods to advance polymer formulations science through the fabrication of microscale instrumentation for measuring physical properties of complex mixtures.

Kathryn L. Beers

Significant progress was made this year in our efforts to build microfluidic instrumentation for the measurement of polymer solutions. New measurement capabilities were developed, several collaborators visited NIST for extended periods to learn new technologies, and high impact publications resulted from our work.

Dynamic light scattering (DLS) remains one of the most popular and powerful tools to measure size in solutions containing nanoparticles (such as latexes and suspended inorganics) and nanostructures (such as micelles and vesicles). Several prototypes were constructed that enable particle sizing in the range of 19 nm to 107 nm using less than 150 μ L of solution (Figure 1). Rapid measurements using these devices surveyed a range of solution composition and temperature to determine surfactant dissolution behavior. Simple extension of these measurements will enable phase mapping of nanostructured solutions. The instruments were designed to be integrated with existing NIST techniques for synthesis, spectroscopy, and image

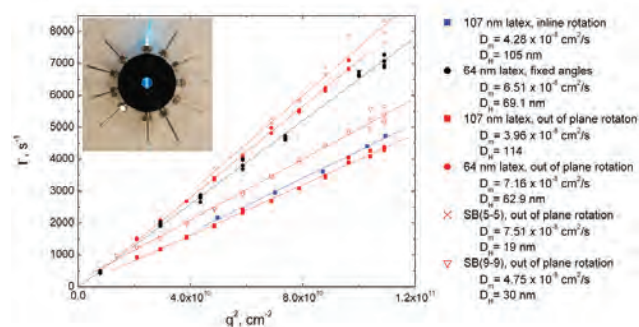


Figure 1: Diffusion measurements and particle sizing of latex spheres and block copolymer micelles conducted on a microfluidic device. Inset: Photograph of a fixed, multi-angle device.

analysis of polymer solutions in microfluidic devices. the developing industry.

Progress was also made on additional methods, including the validation and integration of droplet library fabrication, photopolymerization, and shrinkage measurements for methacrylate-based resins [*The Analyst* **131**, 1027

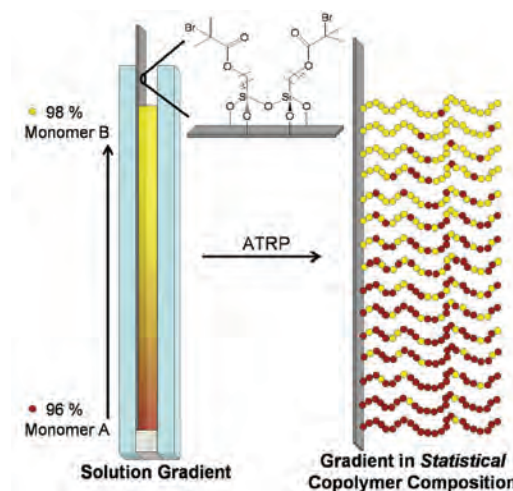


Figure 2: Illustration of a solution gradient stabilized in a confined microchannel (left) that was used to construct a polymer brush surface with a gradient in statistical copolymer composition (right).

(2006).]. Correlations between monomer composition, extent of conversion, and shrinkage were matched with off-chip measurements.

Microfluidic confinement has also enabled the stabilization of solution gradients, as validated by fiber-optic Raman spectroscopy. The power of such a solution gradient was demonstrated by fabrication of a statistical copolymer brush surface containing a gradient in composition [Fig. 2; *Adv. Mat.* **18**, 1427 (2006)], a gradient heretofore unobtainable, and thus valuable in characterizing thin film and nanoparticle behavior.

Visiting scientists from CSIRO and BASF performed research in the NIST laboratories this year. Microfluidic device design, measurement strategies for polymerization, and use of microscopy and spectroscopy tools were transferred to both organizations. A new joint project on the library design and characterization of surfactant solutions will eventually be conducted at CSIRO using NIST technology.

Contributors and Collaborators

T.Q. Chastek, C. Xu, S.E. Barnes, K.A. Page, M.J. Fasolka, E.J. Amis (Polymers Division, NIST); S. Müsigg (BASF); C. Fong (CSIRO)

Quantitative Polymer Mass Spectrometry

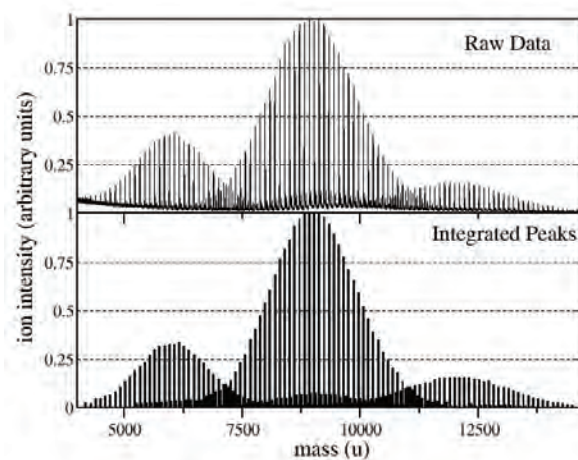
Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) has been demonstrated as a method for absolute molecular mass distribution measurement of synthetic polymers via the creation of Standard Reference Material® 2881. This means determining a comprehensive uncertainty budget for a complex measurement technique that must include both Type A and Type B uncertainties.

William E. Wallace

Currently, all absolute molecular mass polymer standards provide a single moment (e.g., M_n or M_w) of the molecular mass distribution (MMD). (By *absolute* it is meant that the standard is based on direct measurement of a physical property, and not on calibration against another polymer.) We have created a comprehensive strategy to create an absolute molecular mass distribution polymer Standard Reference Material® using matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. To create such a standard, our methods must be demonstrably free of operator bias (intentional or unintentional). Furthermore, the Type A (“random”) and Type B (“systematic”) uncertainties must be determined for each part of the experiment. The required unbiased, repeatable steps are: 1) sample preparation, 2) instrument tuning, 3) data collection, and 4) data analysis. These steps ultimately lead to a signal intensity calibration function (and, most importantly, its associated uncertainty) that relates the true MMD of the analyte to the MMD measured by mass spectrometry.

We used a narrow polydispersity polystyrene initiated with an n-octyl group, and having a peak mass (M_p) of 9 000 u. To this polymer we gravimetrically mix two n-butyl-initiated polystyrenes, one having an M_p of 6 000 u and the other an M_p of 12 000 u. The different end groups allow us to distinguish between different peaks in the mass spectrum, as shown in the top panel of the figure (right). By controlling the gravimetric mix, we created a signal-intensity calibration curve using a Taylor’s expansion around a central mass peak as our mathematical model. We used electrospray methods to create uniform MALDI targets that are free of “sweet spots” that could be reproducibly made, and whose preparation could be described precisely. Removal of the gross uncertainties inherent in typical MALDI sample preparation methods (e.g. “hand spotting”) is critical for quantitation work. With gradient-free numerical optimization methods (see Technical Highlight in this Report) we located the instrument parameter settings

in 5-dimensional space (extraction, lens, and detector voltages; laser intensity; and extraction delay time) that give the least bias in the molecular mass distribution, as well as the Type B uncertainties for the measurement. We do this by comparing the difference between the gravimetric mixture ratios with the ratios found by mass spectrometry until an optimal set of instrument settings is found. Data collection is randomized to prevent unknown changes in experiment procedure or instrument performance from creating a systematic bias in the data over periods of hours, days, and weeks. Using our time-series segmentation method, *MassSpectator* (see W.E. Wallace, A.J. Kearsley, and C.M. Guttman, “An Operator Independent Approach to Mass Spectral Peak Identification and Integration,” *Analytical Chemistry* **76**, 2446 (2004) and A.J. Kearsley, W.E. Wallace, and C.M. Guttman, “A Numerical Method for Mass Spectral Data Analysis,” *Applied Mathematics Letters* **18**, 1412 (2005), we automatically identify and integrate mass peaks to give a MMD, as shown in the bottom panel of the figure. Finally, using standard additions of the three polystyrenes (and two other polystyrenes with intermediate average masses), we created a signal intensity calibration curve as a function of molecular mass across the distribution. Variations in relative ratios of the three polymers let us determine the Type A uncertainty in the calibration curve.



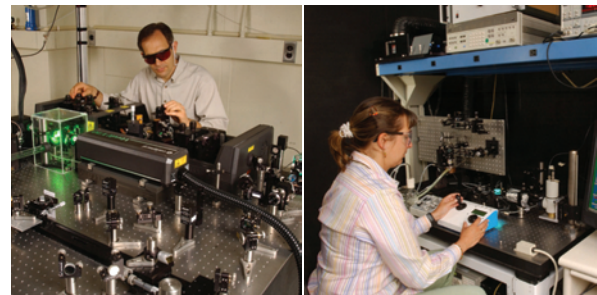
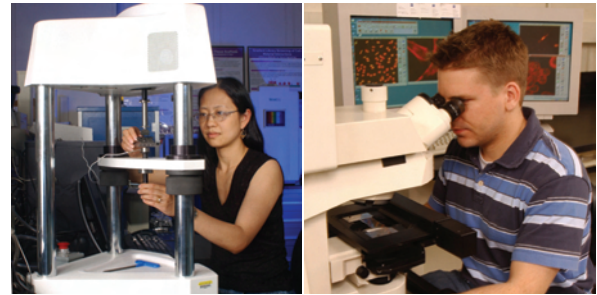
Contributors and Collaborators

M.Y.M. Chiang, S. Guo, J.H. Kim, E.A. Wilder, W. Zhang (Polymers Division, NIST); Daisuke Kawaguchi (Nagoya University); Gareth Royston (University of Sheffield)

Biomaterials

Rapid development of medical technologies depends on the availability of adequate methods to characterize, standardize, control, and mass produce them. To realize this goal, a measurement infrastructure is needed to bridge the gap between the exponentially increasing basic biomedical knowledge and clinical applications. The NIST Materials Science and Engineering Laboratory (MSEL) Biomaterials Program is a collaborative effort creating a new generation of performance standards and predictive tools targeting the metrology chain for biomedical research.

Today, all areas of materials science confront real systems and processes. In the biomaterials arena, we can no longer advance science by simply studying ideal model systems. We must comprehend complex realistic systems in terms of their structure, function, and dynamics over the size range from nanometers to millimeters. MSEL is uniquely positioned to make a major contribution to the development of measurement infrastructure through three focus areas: Systems Biology, Bioimaging, and Nanobiosensing.



Contact: Marcus Cicerone

3D Tissue Scaffolds

We are developing reference materials and noninvasive analytical methods to meet measurement needs related to 3D tissue engineering (TE). These methods and reference materials will replace destructive end-point methods currently in use, and in so doing, will facilitate more efficient and effective TE scaffold testing and design.

Marcus T. Cicerone

Result-focused rational design of 3D TE scaffolds, **R**one Holy Grail of tissue engineering, requires first that cell response can be monitored to known conditions within the bulk of the scaffold. We are developing non-invasive characterization methods that will replace some of the destructive end-point methods currently in use. The methods we are developing will result in quantifiable, reliable metrics that are relevant to success of TE constructs in properly supporting cell and tissue growth. Cells in 3D constructs respond to perfusion conditions, local surface morphology, and surface chemistry, as well as a number of other mechanical, chemical, and electrical stimuli. Work under this project focuses on characterizing the first three of these factors, as well as cell response to them.

Reference Scaffold and Structural Analysis –

There is a continuing need for reference materials and standard artifacts in this field. We are in the final stage of generating a 3D reference scaffold for porosity. These artifacts will be used as standards against which to evaluate scaffold porosity and permeability; the primary characterization data are permeability and porosity. Analysis of 3D images obtained by micro-computed tomography (μ CT) plays a major role in scaffold characterization. We expect to complete an interlaboratory comparison for determining confidence limits in specifications by December 2006. The work is a collaborative project through ASTM (Task Force F04.42.06). This work has also spurred generation of an ASTM draft guide for scaffold characterization (in preparation).

In-situ Cell and Tissue Imaging – Optical and other imaging modes have revolutionized research into many areas, including cell-material interactions. Optical imaging in 3D TE constructs poses two important problems: the rapidly dividing cells are sensitive to high light flux, and 3D scaffolds generally provide poor platforms for high-resolution imaging due to opacity. In addressing the former, we continue to develop broadband coherent anti-Stokes Raman scattering microscopy

(μ -CARS) as a powerful, noninvasive method for determining cell health and development within tissue scaffolds. Progress this year has included a new method to eliminate nonresonant background so that weak spectral features in the fingerprint region can be detected [Kee et al., *Optics Express* **14**, 3631 (2006)].

We have demonstrated a solution to another major hurdle for imaging in 3D scaffolds by developing an optically clear tissue scaffold. This scaffold is fabricated by salt-leaching from a photopolymerized glassy polymer that has been used in dental applications. Characterization of these scaffolds with respect to morphology and mechanical properties has been submitted to *Biomaterials* (S. Lin-Gibson, et al.). A report on behavior of osteoblast cells on these scaffolds has been published [F.A. Landis et al., *Biomacromolecules* **7**, 1751 (2006)].

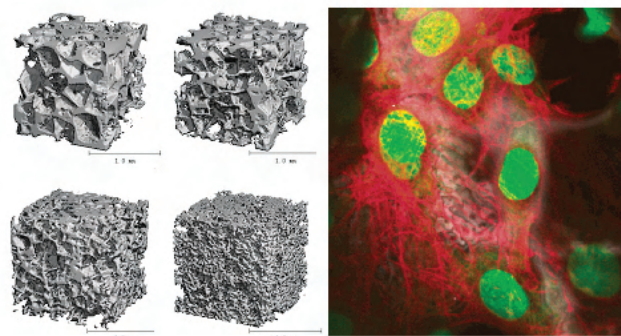


Figure 1: Optically clear salt-leached scaffolds made with varying porosity and pore size allows large range in mechanical properties as well as clear imaging of cells as far as 400 μ m into scaffold.

Applicability of 2D Results to 3D Scaffolds –

Surfaces of many 3D scaffold types present to cells as having varying degrees of curvature, however analysis of cell response to surface chemistry is most conveniently performed on flat surfaces. We have shown that in some cases the results obtained in 2D are retained in 3D scaffolds. Distinct compositions of phase-separated blends of tyrosine-derived polycarbonates have been shown to elicit marked differences in proliferation and differentiation response in 2D. We have recently demonstrated that these results carry over to 3D.

Contributors and Collaborators

Y.M. Chiang, M.T. Cicerone, J. Cooper, J.P. Dunkers, S. Lin-Gibson, F. Phelan, J.R. Smith, T. Dutta Roy, F.Wang, T.W. Kee (Polymers Division, NIST); J. Kohn (Rutgers)

Combinatorial Methods for Tissue Engineering

The goal of this project is to develop measurement methods and associated materials to characterize the interactions, at the surface, between cells and biologically active materials for use in optimizing tissue-engineered products.

Matthew L. Becker

The diversity of functional species, distinct structural features, and multiple hierarchies within classes of functional biomaterials create significant challenges to characterization. Solutions to these challenges require novel approaches to measurements, including the development of new methods and instrumentation. Our program seeks to develop combinatorial tools and methods to identify the critical physico-chemical properties influencing the biological performance of biomaterials.

Morphology Gradient Libraries - We are fabricating single and multi-variable continuous gradient libraries to generate linear variations in important physical properties, including roughness, surface energy, crystallinity, and phase separation. This approach affords opportunities to quickly identify compositions and physical properties exhibiting favorable cell-material interactions using automated characterization and data acquisition methods, and narrow the physical parameter space where higher levels of characterization are required.

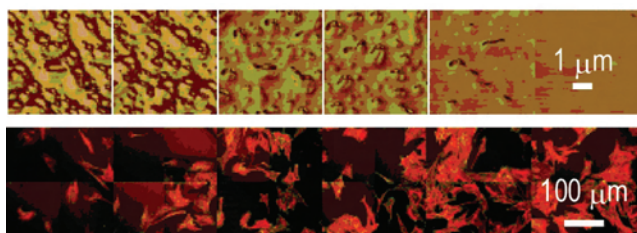


Figure 1: Diffraction patterns collected over a range of sample rotation angles. The distance between the pronounced horizontal ridges provides the sidewall angles β , while the relative intensity and placement

One of our focus areas is to develop physical and spectroscopic methods to measure the extent and associated physico-chemical changes resulting from phase separation. Phase separation is a critical component in solution processing, materials optimization, and medical device manufacturing. The various changes in properties have been shown to influence preferential protein adsorption profiles that influence the biological responses.

Bioactive Ligand Gradients - We are designing bioactive ligand density gradients to identify optimum ligand densities for directed cell adhesion, proliferation, and differentiation. We are combining traditional and automated bio-imaging techniques with emerging microanalytical techniques to obtain data that links substrate properties with morphology and biochemical signatures of protein and RNA expression in small cell populations.

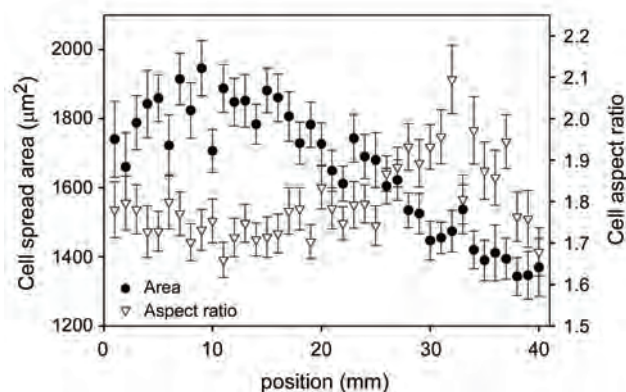


Figure 2: The plot above depicts cell area and aspect ratio as a function of position on a peptide functionalized self assembled monolayer possessing a gradient in RGD density, a peptide commonly used in cell adhesion applications.

Cell morphological, viability, and biomarker measurements are being measured on similar 2D and 3D substrates and their results compared among them and with existing data of *in vivo* samples. These well-defined substrates are being used to push the sensitivity limits of current methods and if successful, the correlations will increase the ability of *in vitro* cell-based measurements to predict cellular behavior *in vivo*.

We anticipate these efforts will provide the foundation for a framework, which would guide the early assessments of *in vitro* and *in vivo* material performance, and establish a series of metrologies for biocompatibility thresholds. These measurement solutions would provide useful guidance to materials development efforts, manufacturing process optimization, and regulatory agencies.

Contributors and Collaborators

C.G. Simon, N.D. Gallant, M.J. Kipper, K.E. Roskov, M.D. Roy, M.T. Cicerone (Polymers Division, NIST); J. Kohn, P. Holmes (New Jersey Center for Biomaterials, Rutgers University); D.L. Kaplan (Tissue Engineering Resource Center, Tufts University)

Dental Polymers and Composites: Developing a Test Suite for Total Materials Characterization

The objective of this project is to develop combinatorial platforms for characterizing salient material properties of candidate dental polymers. These platforms will aid others in the development and optimization of polymers for restorative composites with improved performance.

Sheng Lin-Gibson and Nancy J. Lin

Polymeric dental composites are widely used in the restoration of anterior lesions and small to medium sized defects in the posterior region of the mouth. While significant improvements have been made in the composites' properties, their long term performance is still less than optimal. A significant effort has been devoted to improve the composite properties by designing new dental polymers. For the matrix polymer alone, a large number of material and processing parameters influence the material properties and biological responses. High-throughput and combinatorial methods are ideal for the purpose of characterizing these materials because of their faster data acquisition and ability to span a wide parameter space, and equal processing conditions for a given specimen, resulting in a lower experimental error rate.

2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl] propane (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) are two commercially important dental monomers. 2D gradient samples of a model dental polymer consisting of a dimethacrylate mixture (BisGMA and TEGDMA) varying in composition and conversion were fabricated (Figure 1). A broad conversion range was obtained for all compositions. The conversions were measured using near infrared (IR) spectroscopy, and the mechanical properties (elastic modulus and hardness) were determined using nanoindentation with the continuous stiffness method. Our previous work demonstrated a strong correlation between vinyl conversion and mechanical properties of the cross-linked polymer.

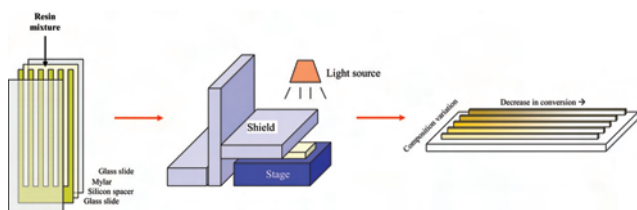


Figure 1: Fabrication of 2D gradient samples.

Cell viability on the 2D gradient samples was assessed using fluorescence microscopy (Figure 2). As the degree of conversion increased, cell attachment and viability increased. Compositions with increasing TEGDMA content had increased cell viability, but the effects were subtler.

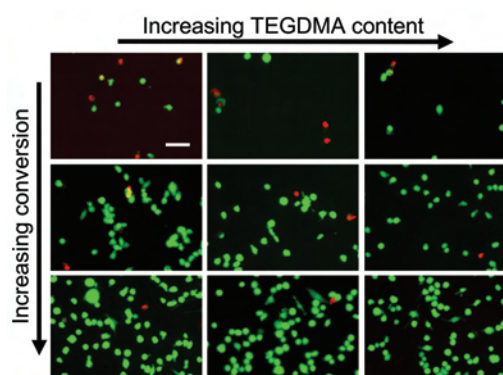


Figure 2: Fluorescent microscopy showing viability of cells cultured on 2D gradient samples. Live cells are stained green, and dead cells are stained red. Scale bar = 50 μm .

Two indicators for material biocompatibility are cell viability and cell attachment density, both of which can be quantified (Figure 3). In general, cell viability remained high until the conversion fell below 44%. A high degree of cell attachment required a higher conversion. Similar trends were seen for all compositions.

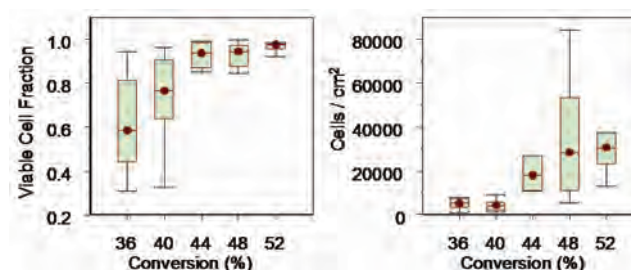


Figure 3: Cell viability (left) and cell density (right) measured as a function of methacrylate conversion for a single composition.

Continuous variable gradients are efficient for screening biological effects arising from the composition and degree of conversion. Other potential combinatorial/high-throughput techniques are also being evaluated for their ability to screen structure-properties relationships in dental materials, including relating conversion to polymerization shrinkage.

Contributors and Collaborators

J.M. Antonucci (Polymers Division, NIST)

Metrology for Biomechanical Effects on Cell/Material Interactions

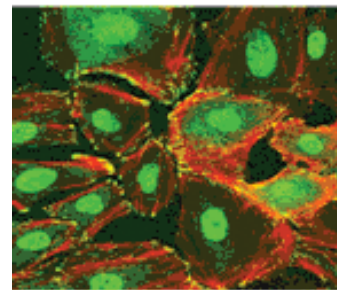
Many tissue engineered medical products are cultured under mechanical stimuli to mimic the physiological environment. This approach is currently addressed in an ad hoc way to demonstrate how cells respond under macroscopic stress conditions. However, stress at the cellular level is not well characterized. This project will develop a measurement infrastructure consisting of instrumental techniques, mathematical modeling, and characterization protocols to determine local stresses on cells from macroscopic stresses and to quantify the effect of these stresses on cell morphology, phenotype, and biochemical signaling.

Joy P. Dunkers

Metrology Development – Mechanotransduction is the process by which cells convert mechanical stimuli into biochemical signals. Most cell functions are influenced by mechanical stimuli: proliferation, migration, differentiation, apoptosis, and protein synthesis. Much work has been done to identify the specific molecular signals activated for various phenotypes, and to correlate the macroscopic stress/strain on the flexible substrate to cell response. However, there are currently no standard protocols on how these studies are conducted, or how the real time stress/strain local to the cell is determined. We believe that the existence of many apparently contradictory results in the literature is related to this lack of consistent analysis. We are creating a measurement platform to quantify the actual stress transferred to the cell and to correlate it to cellular response in 2-D and 3-D cultures. This platform will be useful to researchers, as well as to regulatory agencies, as they seek new methods to test tissue engineered medical products.

In this investigation, smooth muscle cells were selected as the model system to examine the transition from synthetic to contractile phenotypes under biaxial stress. A combination of culture techniques, bioreactor designs, and cell-based assays were used to image, quantify, and predict biological responses as a function of mechanical stimuli. Studies include dynamic culture testing, advances in optical and fluorescence *in vitro* imaging, genetic profiling, and mathematical/computational modeling. This research platform expands across the tissue engineering spectrum, starting from the simplest case of non-confluent cells to proliferation and organization into tissues.

This year we developed methods to robustly attach and thoroughly characterize extracellular matrix (ECM) proteins on the deforming substrate. Here, the ECM protein is fibronectin (FN) grafted to the deforming polydimethylsiloxane via a silane coupling agent. We characterized the FN coating in terms of surface roughness, uniformity, thickness, conformation, and rigidity. Response of smooth muscle cells (shown below, stained for focal adhesions and actin cytoskeleton) to the grafted FN was characterized by proliferation and live/dead assays. These baseline results will serve to evaluate the durability of the attached FN after the biaxial stretching.



Mathematical Modeling – Previous *in vitro* studies using cells cultured on substrates show that 1) cells sense the variation in substrate rigidity by modifying their morphology; 2) cells subjected to uniaxial stretch elongate perpendicular to the stretch direction; and 3) cells show preference to specific substrate stiffness on a stiffness gradient (durotaxis).

Guided by this, we developed a mathematical model of cell-substrate adhesion to explain the dependency of cell morphology and migration on substrate mechanics. The hypothesis is that the morphology of a cell adhering to a substrate is characterized by the competition between cell and substrate strain energies and interfacial energy (work of adhesion) at the cell periphery. The final configuration of the cell morphology is determined by the total free energy minimum of the cell/substrate system. This work is discussed further in the Highlights section of this report. [Yong Ni and Martin Y.M. Chiang, “Cell Morphology and Migration Linked to Substrate Rigidity,” *Soft Matter* **3**, 1285 (2007).]

Contributors and Collaborators

L. Pakstis, M.Y.M. Chiang, Y. Ni, N. Lin, L. Henderson, J. Cooper, M. Cicerone (Polymers Division, NIST); T. Quinn, T. Oreskovic (Materials Reliability Division, NIST); T. Vorburger, A. Zheng (Precision Engineering Division, NIST); J. Taboas, R. Tuan (NIAMS, NIH)

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 projects are conducted in collaboration with partners from industrial consortia (e.g., 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 International Packaging Consortium (IPC) Roadmap, the IPC Lead-free Solder Roadmap, the National Electronics Manufacturing Initiative (NEMI) Roadmap, the Optoelectronics Industry Development Association (OIDA) Roadmap, and the National Magnetic Data Storage Industry Consortium (NSIC) Roadmap.

Contact: Christopher L. Soles



Dimensional Metrology with Small Angle X-Ray Scattering

The feature size in microelectronic circuitry is ever decreasing, and now approaches the scale of nanometers. This trend creates a need for new measurements capable of non-destructive measurements of small features consisting of a variety of materials (polymers, nanoporous thin films, metals), with sub-nanometer precision. In this project, we are developing small angle x-ray scattering for the non-destructive measurements of the pitch, line-width, sidewall angle, average cross section, and line edge roughness in nanoscale patterns. Other applications of this technique in areas such as nano-rheology and nanofabrication are being explored.

Wen-li Wu and Ronald L. Jones

The demand for increasing computer speed and decreasing power consumption continues to shrink the dimensions of individual circuitry components toward the scale of nanometers. When the smallest, or “critical”, dimensions are < 40 nm, the acceptable tolerance will be < 1 nm. This requirement creates significant challenges for measurements based on electron microscopy and optical scatterometry. In addition, the continuing development of new materials for extreme ultraviolet photoresists, nanoporous low-k dielectrics, and metallic interconnects all require high precision dimensional measurements for process development and optimization.

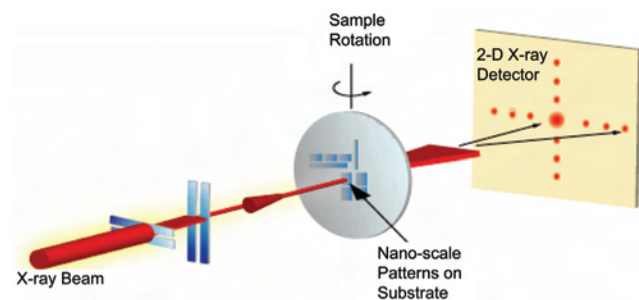


Figure 1: Schematic of the CD-SAXS geometry, showing the x-ray beam (solid line) in transmission through the patterned sample.

To address this need, we are developing a high precision x-ray based metrology, Critical Dimension Small Angle X-ray Scattering (CD-SAXS). This technique is capable of non-destructive measurements of test patterns routinely used by microelectronic industries to monitor their fabrication process. A collimated monochromatic x-ray beam of sub-Ångström wavelength is used to measure the pattern dimensions on a substrate in transmis-

sion mode. CD-SAXS has previously demonstrated a capability for sub-nm precision for periodicity, line width, sidewall angle, and height measurements.

This year, we have extended the capabilities to better quantify roughness. Structures were designed with line edges close to a sine wave with a nominal wavelength of 150 nm and amplitudes ranging from 20 nm to 60 nm. Three classes of structures were measured: (1) centerline roughness (CLR), where the center of mass of the line varies sinusoidally but the line width remains constant; (2) line width roughness (LWR), where the centerline follows a straight line and the line width varies as two opposing sine waves; and (3) line edge roughness (LER), where the line edges have some randomness in its phase angle relative to its neighbor. These controlled structures produced observable “satellite” diffraction peaks that run parallel to the main diffraction axis. The peak positions provide the wavelength of the roughness, while their intensity revealed the amplitude of the periodic component to the roughness.

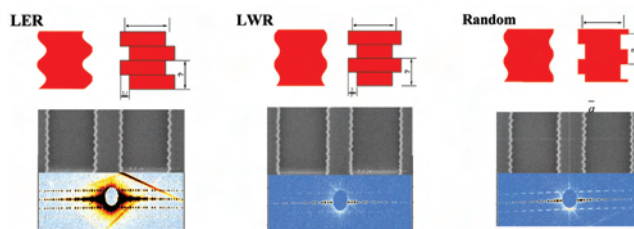


Figure 2: Schematic of model line edge roughness structures with the top-down SEM micrograph and the resulting SAXS data.

Also this year, NIST completed installation of the world’s first laboratory based CD-SAXS instrument. This instrument incorporates a rotating anode source with two different targets, advanced focusing optics, and a Bense-Hart camera. The result is a flexible system that can address both the development of CD-SAXS for the semiconductor industry and advanced structural measurements of nanostructured materials in solution or in the bulk.

Contributors and Collaborators

C. Wang, D. Ho, H. Lee, C. Soles, H. Ro, V. Tirumala, E. Lin (Polymers Division, NIST); K. Choi, B. Rice, G. Thompson (Intel); B. Bunday (ISMI); S. Knight (Office of Microelectronics Programs, NIST); J. Villarrubia, A. Vladar (MEL, NIST); P. Butler (Center for Neutron Research, NIST); Y. Liu (SEMATECH); Q. Lin, A. Grill, H. Kim (IBM); K. Char, D. Yoon (Seoul National University); J. Watkins (U. Mass-Amherst)

Organic Electronics

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 photovoltaic cells. Device performance, stability, and function critically depend upon charge transport and material interaction at the interfaces of disparate materials. We develop measurement methods to characterize the electronic and interfacial structure of organic electronics materials with respect to processing methods, processing variables, and materials characteristics.

Dean M. DeLongchamp

Organic electronic devices are projected to revolutionize new types of 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 slowed by 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 these technological challenges.

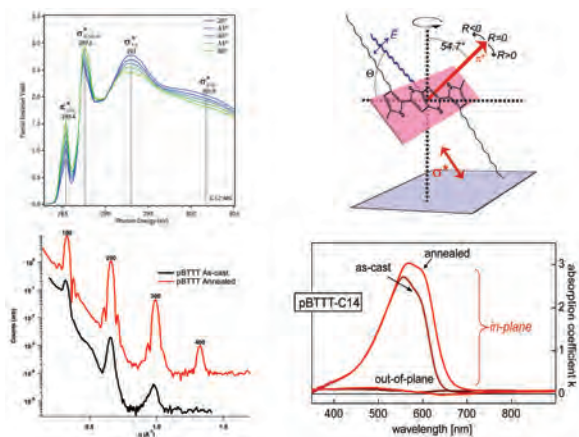


Figure 1: Several different experimental methods (NEXAFS, XRD, and ellipsometry) are brought together to determine the structure of 20 nm films to determine correlations with device performance.

Organic electronics presents different measurement challenges from those identified for inorganic devices. We are developing an integrated suite of metrologies to correlate device performance with the structure, properties, and chemistry of materials and interfaces. We apply new measurement methods to provide the data and insight needed for the rational and directed development of emerging materials and processes. Studies include

electrical measurements of organic semiconductor films, the effect of branched end-group substitutions on molecular packing, growth mechanisms of evaporated thin films, and the development of combinatorial methods to characterize materials rapidly.

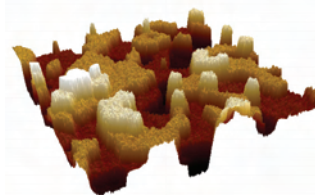


Figure 2: AFM image from terraced structure of a high carrier mobility polythiophene thin film.

This year, significant progress was made to identify the molecular characteristics of newly developed, high carrier mobility poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophenes). These polymers exhibit the highest mobility for a polymer material due to exceptional order throughout the film. Near edge x-ray absorption fine structure (NEXAFS), atomic force microscopy (AFM), ellipsometry, Fourier transform infrared (FTIR) spectroscopy, and x-ray diffraction (XRD) measurements were able to highlight the influence of substrate surface on the film morphology, to determine the tilt angle of the conjugated planes, and to highlight the importance of the side-chain packing density on the structure formation.

Several activities highlighted the increasing need for advanced measurements and materials science in organic electronics. A U.S. Measurement System Workshop was held on “Large-area Flexible Electronics and Photonics” (<http://usms.nist.gov/workshops/macroelectronics.htm>) to determine measurement needs to enable this emerging technology area. Also, NIST staff co-chaired and contributed to the development of a technology roadmap for printed and organic electronics with iNEMI.

Contributors and Collaborators

R.J. Kline, J. Obrzut, Y. Jung, T. Psurek, B. Vogel, M. Fasolka, C. Chiang, E. Lin (Polymers Division, NIST); D. Fischer (Ceramics Division, NIST); M. Gu-
rau, L. Richter (CSTL, NIST); D. Gundlach, C. Richter, O. Kirillov, (ECEL, NIST); I. McCulloch, M. Heeney (Merck Chemicals), L. Lucas, G. Jabbour (Arizona State University); M. Chabinye, J. Northrup (PARC); A. Murphy, J.M.J. Frechet, P. Chang, V. Subramanian (U. C. Berkeley); M. Ling, Z. Bao (Stanford University); Y. Wu, B. Ong (Xerox); M. Toney (Stanford Synchrotron Radiation Laboratory)

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-32 nm length scale, challenges arise because photoresists appear to be reaching their resolution limits. Unique high-spatial resolution measurements are developed to reveal limits on materials and processes that challenge the development of photoresists for next-generation sub-32 nm lithography.

Vivek M. Prabhu

Photolithography is the driving technology used by the microelectronics industry to fabricate integrated circuits with ever decreasing sizes. This fabrication technology is also rapidly being adopted in emerging areas in 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 wave lengths of light requiring photoresist films less than 100 nm thick and dimensional control to within 2 nm.

We work closely with industrial collaborators to develop 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 worked with SEMATECH to determine materials sources of line-edge roughness in 193-nm photoresists, and with Intel Corporation to investigate the effect of extreme-ultraviolet (EUV) exposure on pattern resolution of model EUV photoresist materials. We continue to provide new insight and detail into the complex physico-chemical processes used in advanced chemically amplified photoresists. Measurement methods include x-ray and neutron reflectivity (XR, NR), small angle neutron scattering (SANS), near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, solid state nuclear magnetic resonance (NMR), quartz crystal microbalance (QCM), infrared variable-angle spectroscopic ellipsometry; fluorescence correlation spectroscopy (FCS), and atomic force microscopy.

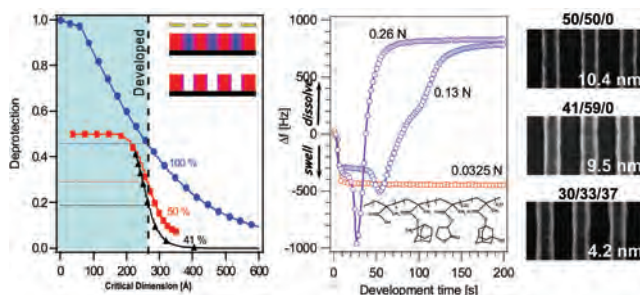


Figure 1: Copolymer composition effect on deprotection front measured by NR. Swelling and dissolution behavior of polymer thin films controlled by developer normality quantified by QCM. Evaluation of three model copolymer resists for LER for 100 nm line/space imaged with 193 nm photolithography.

Photoresists are multi-component mixtures that require dispersion of additives, controlled transport properties during the interface formation, and controlled dissolution behavior. The fidelity of pattern formation relies on the materials characteristics. Hence, we examine the influence of copolymer compositions, molar mass, and photoacid generator additive size to determine the root causes of image quality by highlighting the polymer physics and chemistry. In addition, our collaborators test our hypothesis using 193 nm and EUV lithographic tests.

Accomplishments for this past year include quantification of the copolymer composition and quencher additives effect on photoacid-reaction diffusion deprotection front for resolution and roughness fundamentals by NR, advancement of photoresist / liquid interfaces for dissolution fundamentals by QCM, effect of exposure dose on the reaction-front in model EUV materials, photoacid generator miscibility and dispersion in complex photoresist co- and ter-polymers by NMR, aqueous immersion dependence on photoacid generator leaching and depth profile by NEXAFS, and development of cross-correlation FCS with nanopositioning for labeled-polymer diffusivity in bulk and at interfaces.

Contributors and Collaborators

B. Vogt, A. Rao, S. Kang, D. VanderHart, K. Lavery, W. Wu, E. Lin (Polymers Division, NIST); D. Fischer, S. Sambasivan (Ceramics Division, NIST); S. Satija (NIST Center for Neutron Research, NIST); K. Turnquest (SEMATECH); Kwang-Woo Choi (Intel); R. Allen, W. Hinsberg, H. Ito (IBM Almaden Research Center); R. Dammel, F. Houlihan (AZ Electronics); J. Sounik, M. Sheehan (DuPont Electronic Polymers)

Nanometrology

Nanotechnology will revolutionize and possibly revitalize many industries, leading to new and improved products based on materials having at least one dimension less than 100 nm. The federal government's role in realizing the full potential of nanotechnology is coordinated through the National Nanotechnology Initiative (NNI), a multi-agency, multi-disciplinary program that supports research and development, invests in a balanced infrastructure, and promotes education, knowledge diffusion, and commercialization in all aspects of nanoscale science, engineering, and technology. NIST's unique and critical contribution to the NNI is nanometrology, defined as the science of measurement and/or a system of measures for nanoscale structures and systems. NIST nanometrology efforts focus on developing the measurement infrastructure - measurements, data, and standards - essential to advancing nanotechnology commercialization. This work provides the requisite metrology tools and techniques and transfers enabling measurement capabilities to the appropriate communities.

The NIST Materials Science and Engineering Laboratory (MSEL) plays a vital role in nanometrology work at NIST with efforts in four of the seven NNI Program Component Areas - Instrumentation Research, Metrology and Standards for Nanotechnology; Nanomaterials; Nanomanufacturing; and Fundamental Nanoscale Phenomena and Processes. Innovative projects across MSEL are defining and addressing the forefront research issues in these areas.

Contacts: Alamgir Karim; Kalman Migler



Carbon Nanotube Project Meeting



Polymers Division Small-Angle X-Ray Scattering Facility

Carbon Nanotube Materials: Achieving The Gold Standard in Quality and Characterization

The availability of high-quality, well-characterized carbon nanotube materials is essential to the development of advanced applications that exploit the nanotube's remarkable combination of properties. Our goal is to provide the methodologies that will produce Gold Standard nanotubes materials separated by length, diameter, and type. These high-quality samples will enable characterization of their electrical, optical and mechanical properties.

**Barry J. Bauer, Erik K. Hobbie
and Kalman B. Migler**

A world-wide effort to harness the extraordinary properties of carbon nanotubes and to develop revolutionary new functional applications ranging from high-speed electronics to biosensors, fuel cells, and displays is underway. However, typical nanotube materials contain dozens of different types of tubes, have a wide distribution of lengths, and frequently contain impurities. The ill-defined nature of this material prevents proper characterization, which hampers trade and application development.

Our goal is to enhance both the *quality* of nanotube materials and the *characterization methodologies* of them by the development of solution-based techniques which sort the nanotubes by type and length, and enable characterization on materials of high purity. We are currently focusing our efforts on three key areas which demonstrate the principles of our approach. First, we are developing metrics for assessing the dispersion of nanotubes in solutions and in polymers. Second, we are fractionating dispersed suspensions to produce nanotubes of well-defined length, and then characterizing the effects of length on their optical and toxicological properties. Third, we are laying the groundwork for the next phase of the project, using the length fractionated tubes to then separate by type, via combinations of flow and electric fields.

The characterization of nanotube dispersion is critical to our program, as only singly dispersed nanotubes can be separated by length and type. Further, fundamental characterizations through optical, electrical, and mechanical methods are sensitive to the degree of dispersion. We have compared a variety of optical, viscometric, and scattering techniques to measure dispersion, and found that DNA-wrapped nanotubes disperse well in aqueous suspensions, so we have chosen this material for the next phase of the project.

In the Technical Highlights section of this report, we describe our achievement of unprecedented dispersion using the DNA-wrapped nanotubes in a model polymer, and the resulting comparison of dispersion measurement techniques.

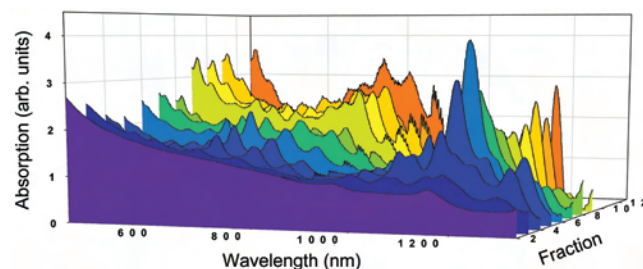


Figure 1: Absorption spectroscopy for 12 fractions that eluted from an ion-exchange column.

Next, we utilize the well-dispersed nanotubes for length fractionation through size-exclusion chromatography. We have introduced automated quality control measures into the chromatography via on-line viscometry and light scattering. We are exploring the effects of length on absorption and Raman spectroscopy, and we find a strong increase of absorbance with length as well as shifts in key Raman ratios. The well-characterized, length separated fractions are also being used in toxicology studies, and we find that the long SEC fractions show much lower toxicity.

Finally, we are laying the groundwork to take the length-separated tubes and further separate them by type (semi-conducting vs. metallic). This requires measures of the response of the DNA-wrapped nanotubes to electric fields and the complex flow fields in a field-flow-fractionation system. We have measured a wide range of electrophoretic mobilities on tubes of the same nominal length, and have measured the polarizability and impedance of the tubes in AC electrical fields. The data generated will drive the design of future separation methods.

The methods and data developed here will be utilized to develop standards for nanotube characterization, and to develop complementary reference materials.

Contributors and Collaborators

V. Bajpai, M. Becker, J. Fagan, J. Obrzut, F. Phelan (Polymers Division, NIST); A. Hight Walker, I. Mandelbaum, J. Simpson (PL, NIST); A. Allen, V. Hackley (Ceramics Division, NIST); S. Hooker, W. Johnson; T. Yildirim (NIST Center for Neutron Research); S. Arepalli (NASA); M. Pasquali (Rice U.); B. Landi, R. Raffaele (RIT)



Combinatorial Methods for Nanomaterials and Nanometrology

Industrial developers of nanomaterials strive to adapt combinatorial and high-throughput methods to accelerate product discovery and optimization. This project addresses the primary barrier to the application of these attractive measurement approaches to nanostructured polymer materials: the design of appropriate combinatorial libraries. To meet this need, we produce and demonstrate library designs that express the factors governing nanomaterials behavior, and that are amenable to high-throughput characterization by industrially relevant nanometrologies.

Michael J. Fasolka and Thomas H. Epps III

The structure and performance of nanostructured polymer materials, including self-assembling systems, nanocomposites, and lithographic resists, depend on a plethora of interdependent compositional, interfacial, and processing factors. This makes these materials prime candidates for combinatorial and high-throughput development. However, as detailed in a 2006 NIST Combinatorial Methods Center (NCCM) Industry Workshop Report, adaptation of combinatorial methods to these systems is hampered by the persistent challenge of designing appropriate combinatorial libraries (see NISTIR 7332, www.nist.gov/combi). Specifically, industry requires libraries that express the parameters relevant to nanomaterials behavior, and that can be analyzed with the measurements they currently rely upon, such as Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), and X-Ray Photoelectron Spectroscopy (XPS).

The NCCM has produced a suite of gradient combinatorial library designs that are readily employed for the high-throughput analysis of polymer nanomaterials. Gradients in temperature, composition, film thickness, and substrate surface energy (γ) provide means to rapidly and comprehensively measure the effect of these key factors on structure and performance. Moreover, these planar libraries are highly geared for characterization by automated microscopy and spectroscopy methods. In 2006, we extended gradient approaches to analyze triblock copolymer thin films. In bulk systems, these materials self-assemble into intricate nanostructures that can be harnessed for membranes and electronic devices, but it is uncertain whether these compelling motifs persist in the thin film geometries required for these applications. We demonstrated a gradient design to gauge the effect of γ on the film behavior of a triblock

copolymer that exhibits a unique gyroid morphology in the bulk. As shown in Figure 1, our library revealed that this material switched from its bulk morphology to a lamellar motif in thin films, and illuminated a critical γ (water contact angle of $\approx 70^\circ$) below which the material exhibited “autophobic dewetting.” Automated XPS and NEXAFS (Near Edge X-Ray Absorption Fine Structure) analysis along the library shows that dewetting was driven by a γ -dependent structuring of a polymer monolayer that forms at the substrate surface. This work was reported via invited lectures at meetings of the American Physical Society and the American Chemical Society in 2006.

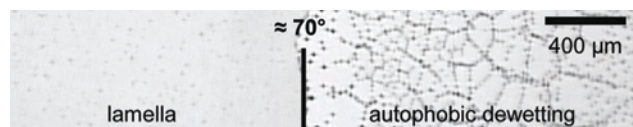


Figure 1: Optical micrograph of γ -dependent morphology and autophobic dewetting in a triblock copolymer thin film.

Also in 2006, we designed a method to prepare combinatorial libraries of film specimens for TEM analysis. The industrial need for this is paramount, since TEM is the primary tool many companies use for imaging nanostructures. As shown in Figure 2, our method employs an array of poly(acrylic acid) (PAA) droplets, which are deposited over a thin film library; in the Figure, a gradient library of block copolymer on silicon is shown. A polydimethylsiloxane (PDMS) gasket, with an array of holes, is used to sequester plugs of aqueous PAA solution while they dry atop the specimen. The system is then immersed in liquid nitrogen, which causes the PAA droplets to pull a library of 48 different film specimens from the substrate. Since they remain lodged in the gasket, the PAA plugs retain their registry. Samples are harvested by dissolving the PAA plugs to leave floating films that can be retrieved with TEM grids.

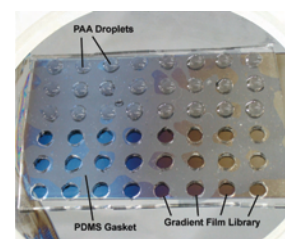


Figure 1: Combinatorial film libraries for TEM analysis.

Contributors and Collaborators

K. Roskov, D. DeLongchamp, A. Karim (Polymers Division, NIST); D. Fischer (Ceramics Division, NIST); E. Jablonski (Bucknell University); F. Bates (University of Minnesota)

Defects in Nanostructured Materials

The functionality of nanoscale materials, critical to emerging technologies in data storage, microelectronics, and medical diagnostics, is strongly dependent on the density and location of physical, chemical, and magnetic defects. Currently, a lack of tools capable of characterizing defects in these materials limits the development of these important technologies. We are developing measurement platforms capable of high precision measurements of defects in nanostructured surfaces, and materials to enable manufacturing at these scales, as well as provide insight into materials properties that control defect formation.

Ronald L. Jones and Alamgir Karim

Manufacturing reliable structures with nanometer scale dimensions is a potential route to advanced technologies for microelectronics, medical diagnostics and therapy, and data storage. However, manufacturing is challenged by the sensitivity of structural functionality to small concentrations of defects in size, shape, and chemical composition. Current methods of inspection are incapable of rapidly locating the “needle-in-a-haystack” defect until late in manufacturing stages, and are often destructive to the sample. We are developing measurement platforms capable of quantifying the type and number of defects, their location, and their resulting impact on materials properties.

In addition to advancing manufacturing methods, measurement platforms to characterize defects will advance the fundamental understanding of defect formation mechanisms, providing additional control over material properties. Controlled defect formation in bulk materials has long been an important route toward mechanical toughening in crystals, altering phase transitions in solids, and imposing the formation of amorphous glasses.

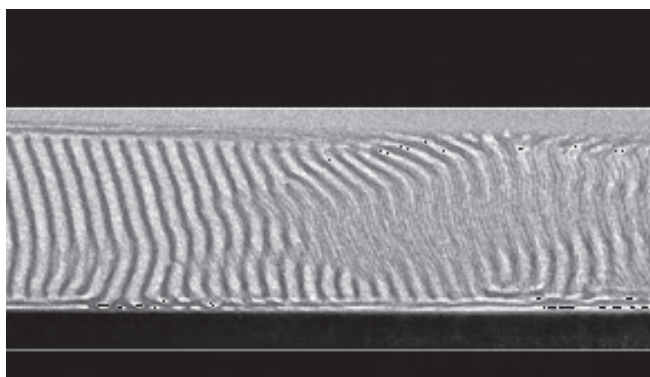


Figure 1: Transmission electron micrography of a cross sectioned porous silica film created by patterning with a block copolymer template. The image shows a wide range of structural irregularities (Image courtesy H.-C. Kim).

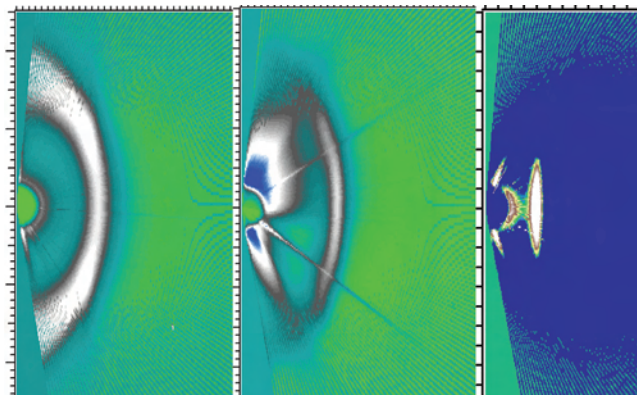


Figure 2: SAXS intensity as a function of scattering vector parallel (horizontal axis) and perpendicular to the substrate (vertical axis) for nanostructured silica films. The data shows qualitative and quantitative differences between varying degrees of orientational control, including (from left to right) randomly packed spheres, partially oriented cylinders, and highly oriented lamellae.

One platform under development uses small angle x-ray scattering (SAXS) to measure the 3D distribution of orientation within nanostructured thin films. In Fig. 1, the microphase structure of a block copolymer film has been chemically converted to a porous silica film as a potential route toward high density data storage and next generation membranes. Controlling the orientation of the morphology is critical to both applications. The data in Fig. 2 demonstrates both a qualitative and quantitative change in SAXS intensity as the orientation of the microphases is varied. Fits of the data provide high precision measures of the distribution in orientation non-destructively in a manner exportable to industry.

Other platforms being developed aim to characterize and quantify magnetic interactions in individual metallic nanoparticles, rapidly quantifying the concentration of defective particles for many applications, including medical diagnostics. Precise characterization of nanoparticle interactions is also aiding the development a “nanotagger” platform that utilizes nanoparticles to “seek, identify, and locate” chemical and topological defects on surfaces by attaching and fluorescing. Applications of these platforms focus on fundamental understanding of packing defects during self-assembly of polymer crystals and block copolymer films.

Contributors and Collaborators

J. Benkoski, B. Berry, S. Lacerda, J. F. Douglas (Polymers Division, NIST); J. Pyun (University of Arizona); S. Kim, R. Briber (University of Maryland); T. Albrecht (Hitachi); K.-W. Choi (Intel); K.-I. Nihara, H. Jinnai (Kyoto Institute of Technology); H.-C. Kim (IBM Almaden)



Mechanics of Complex Interfaces: Libraries for Probing Interfacial Adhesion

Technologies such as next-generation electronics, advanced adhesives, and functional coatings depend on robust interfaces between a variety of hard and soft materials. To ensure the reliability of new products and drive these products into new and emerging markets, industry requires means to assess the host of factors that govern the mechanical behavior of these systems. With an emphasis on combinatorial and high-throughput approaches, this project develops and demonstrates innovative tools for measuring the mechanical properties and performance of materials systems that incorporate complex interfaces.

Christopher M. Stafford

Adhesion between materials depends on a multitude of factors, including interfacial energy, interfacial roughness, chemical interactions, polymer entanglements, and a variety of energy dissipation mechanisms. Given this immense parameter space, the understanding and optimization of adhesion in a given system requires a huge number of experiments. In this capacity, combinatorial and high-throughput techniques offer a promising measurement solution for industrial researchers. As part of our effort to extend these revolutionary approaches to the mechanical analysis of systems with complex interfaces, in 2006 we designed a number of combinatorial libraries that express key factors that govern interfacial adhesion. These libraries are a foundation for gauging and optimizing the effect of these parameters. Moreover, these specimen arrays complement high-throughput measurement schemes, including our multilens contact adhesion test and our combinatorial edge lift-off test.

Polymer brushes provide a facile route for expressing diverse chemistry and functionality on a surface. As illustrated in Figure 1, by changing monomer types, surface initiator site density, and reaction times across a surface, we are producing libraries that systematically express chemical moieties, chain lengths, and molecular architectures, which dictate polymer adhesion. These types of libraries also present a unique opportunity to study the effects of molecular rearrangements at contacting interfaces.

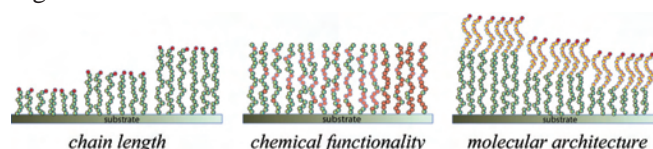


Figure 1: Illustration of different polymer brush libraries for assessing interfacial adhesion.

Roughness plays a critical role in interfacial adhesion, however systematic measurements of the effect of this factor are difficult to achieve. To meet this need, we are developing approaches to design roughness libraries that span multiple length scales. For example, a versatile method for creating roughness gradients exploits the melting and fusion of surface-adsorbed polymer microspheres. As shown in Figure 2, the scale of roughness is gradually varied by melting the spheres on a temperature gradient. In addition, we are harnessing a buckling phenomenon to design libraries that independently vary the amplitude and lateral spacing of surface roughness.

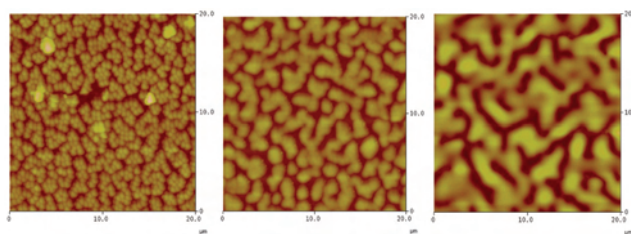


Figure 2: Atomic force micrographs of a roughness library produced by melting polymer microspheres on a temperature gradient.

Development of multi-component adhesives and coatings by industry involves testing hundreds or thousands of candidate formulations. To address this challenge, we are developing routes to prepare compositional libraries of the viscous polymer mixtures that are inherent to these systems. This work is part of a NIST Combinatorial Methods Center (NMC) Focus Project with Intel and ICI/National Starch, completed in 2006. These companies will use these libraries for the high-throughput optimization of epoxy underfill materials for flip-chip electronics. In 2007, we will develop and demonstrate the rapid measurement of the interfacial strength across these libraries using our combinatorial edge lift-off test.

In 2006, we reported our project achievements at key national conferences in the adhesion field. Invited lectures on this work were given at the two Gordon Research Conferences (Science of Adhesion, and Combinatorial and High-Throughput Material Science), the Adhesion Society, and the Materials Research Society. We also disseminated our results to industrial partners at semi-annual NMC Workshop lectures.

Contributors and Collaborators

C.M. Stafford, H. Huang, X. Hu, J.H. Kim, J.Y. Chung, M.Y.M. Chiang, C. Xu, K.L. Beers (Polymers Division, NIST); R. Huang (UT Austin); Y. Dar, S. Gibbon (ICI/National Starch); N. Patel (Intel)

Nanoimprint Lithography

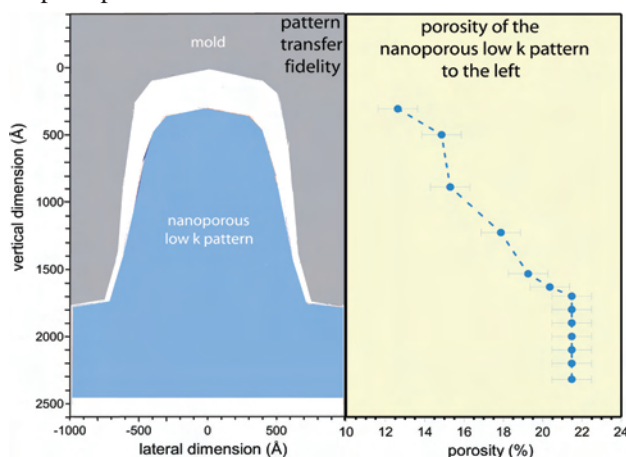
Nanoimprint lithography is a high-throughput patterning technique with the ability to directly replicate features smaller than 10 nm, not just in optimized resists, but also in functional materials. This makes the technology extremely attractive for many forms of nanotechnology, starting with CMOS applications, and extending into many emerging technologies. To fully harness the potential of nanoimprint lithography requires development of the measurement infrastructure to evaluate, quantify, and tailor the unique properties that come with patterning materials on the nanoscale.

Christopher L. Soles

There are two aspects of nanoimprint lithography introducing measurement challenges. The first aspect is resolution. Because this technique has inherently high-resolution, basic shape metrology becomes a significant challenge. Quantifying physical dimensions is critical for evaluating patterning processes, quality control, and assessing the long-term stability of nanoscale features. Currently the semiconductor industry is challenged by with shape metrology at the 65 nm technology node. The potential jump to sub-10 nm features exacerbates this challenge. The second aspect stems from directly patterning the material of interest. This differs from other lithographies where a sacrificial resist transfers the pattern into the functional material. Beyond pattern shape, it then becomes critical to quantify how the desired properties of the functional material are impacted by the imprint process. This is a new class of metrology for the nanofabrication community.

Significant progress has been made on both aspects. Critical dimension small angle x-ray scattering (CD-SAXS) and specular x-ray reflectivity (SXR) for pattern shape characterization were adapted for nanoimprint lithography. Papers were published describing how these techniques could be used to quantify, with nm precision, the fidelity of the imprint pattern transfer process. If the nanostructures are to be made of functional material, they must also be stable for long periods of time. Stability in nanostructures, especially polymeric ones, will be a major challenge for nanomanufacturing. Using CD-SAXS and SXR, we found that the imprint process can induce internal stress that can compromise the stability of the resulting nanostructures. By modifying imprint variables, such as the time, temperature, and the molecular mass of the material being imprinted, we illustrated how these stresses can be minimized.

Examples of imprinted functional materials include semicrystalline materials where the crystal morphology needs to be controlled for organic semiconductor applications, and nanoporous low-k dielectric materials for interconnect technologies. For the patterned low-k materials, the way in which the imprint process affects the porosity will be important for controlling the effective k of the pattern. The Figure below, obtained by SXR and CD-SAXS, compares the imprinted pattern cross-section to the mold, quantifying the effects of pattern shrinkage upon vitrification. A modest shrinkage occurs in the vertical direction, with almost no shrinkage in the lateral. Knowing and controlling this shrinkage will be critical for next generation devices. The panel to the right further shows how the porosity of the pattern varies as a function of height (obtained by x-ray porosimetry). The porosity is reduced in the patterned region. These types of metrologies will be critical for developing effective imprint process for low-k materials



This year our findings were published in high profile journals, including *Applied Physics Letters*, *Nano Letters*, and *Physical Review Letters*. Industrial outreach to the semiconductor industry was achieved through invited and contributed presentations at major lithography and metrology conferences. These included a Webcast for Semiconductor International that was viewed by thousands worldwide. Bilateral cooperative agreements were established and funded with Seoul National University and the Indian Institute of Technology, Kanpur.

Contributors and Collaborators

H.-J. Lee, H. Ro, Y. Ding, B. Okerberg, K. Alvine, R. Jones, E. Lin, A. Karim, W.-L. Wu (Polymers Division, NIST); D. Hines (University of Maryland); S. Pang, D. Gidley (University of Michigan)

Self-Assembly for Soft Nanomanufacturing

The self-assembly of molecules and nanoparticles is central to the formation of biological structures, and the synthetic emulation of this process offers great promise for nanometrology and nanofabrication. Accordingly, this approach to fabrication has recently been identified in U.S. chemical industry roadmaps for nanomanufacturing. We respond to this challenge by developing theoretical, computational, microfluidic, and optical methods to enable precision measurements of the thermodynamic and kinetic parameters controlling synthetic self-assembly

Jack F. Douglas and Steven D. Hudson

Self-assembly of nanoparticles into functional structures such as sensors, optical filters, and pharmaceutical agents holds great promise for inexpensive manufacturing at the nanoscale. The greatest opportunity involves self-assembly of highly directional and specific interactions that lead to structures that have a chain-like, sheet-like, or shell-like structure. The basic design rules that describe how a given set of anisotropic particles assembles into a given structure are now being developed as one component of this project. The second component addresses the critical need for methods to measure these anisotropic and specific interactions between particles; such basic information is the key to determining how the asymmetry of interacting particles encodes information about the geometry of the organized structure.

Our theoretical approach to the principles governing this process is inspired by existing models and measurements for the self-assembly of actin, tubulin, and the ubiquitous icosahedral shell structures of viral capsids. In our simulations, we introduce a family of simple, yet anisotropic, potentials that give rise to the self-assembly of linear polymeric, random surface (“membrane”), tubular (“nanotube”), and hollow icosahedral structures that are similar in many respects to their biological counterparts, yet simple enough for model experimental realization. The potentials involve equivalent particles and an interplay between directional (dipolar, multipolar) and short range (van der Waals) interactions. Specifically, we find that the dipolar potential, having a continuous rotational symmetry about the dipolar axis, gives rise to chain formation, while particles with multipolar potentials having discrete rotational symmetries (square quadrupole or triangular ring of dipoles or “hexapole”) lead to the self-assembly of sheet (see

Figure), nanotube, and hollow icosahedral geometries. These examples reveal a general design rule: the local rotational symmetries of the organizing particles tend to be preserved in the final organized structure. They also strongly motivate the need for methods to measure the anisotropic interaction strength. We also show that fluctuations in the assembly kinetics and the form of assembly and polymorphism can be controlled with appropriate seeding of the assembly process. Seeding is thus crucial to the effective control of kinetics and form of synthetic self-assembly.

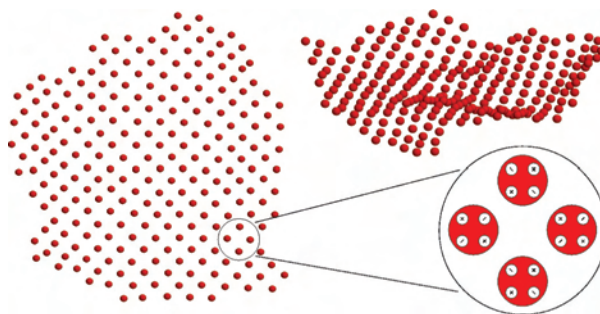


Figure 1: Self-assembled sheet preserving the local symmetry of quadrupole particles (shown in enlargement).

Extensive effort has also been made in characterizing the thermodynamic nature of self-assembly, and in the numerical and experimental procedures required in determining the thermodynamic parameters governing these transitions. A recent commentary in *Science* magazine (July 7, p.55) highlights this modeling effort.

Current method and technology development here explores the potential of particles with charged patches or magnetic moments to control assembly. Surface-sensitive and patterning techniques are being adapted to access anisotropic interactions between particles. These measurements employ the asymmetry inherent at a surface.

The geometry of these assemblies is characterized by electron microscopy, microfluidic, and optical methods. Recently, we have discovered hollow colloidal shell structures, and are working with Percec and coworkers to manipulate the interactions controlling this structure. Microfluidic traps have been used to determine interaction strength within assemblies.

Contributors and Collaborators

T. Chastek (Polymers Division, NIST); V. Hackley (Ceramics Division, NIST); Y. Xia (U. Washington); V. Percec (U. Pennsylvania); K.F. Freed and J. Dudowicz (U. Chicago); S. Kumar (Rensselaer Polytechnic Institute); W. Losert (U. Maryland); S. Velankar (U. Pittsburgh)

Safety and Reliability

We take for granted that the physical infrastructure around us will perform day in and day out with consistent reliability. Yet, failures occur when these structures degrade to where they no longer sustain their design loads, or when they experience loads outside their original design considerations. In addition, we have become increasingly aware of our vulnerability to intentional attacks. The Safety and Reliability Program within the NIST Materials Science and Engineering Laboratory (MSEL) was created to develop measurement technology to clarify the behavior of materials under extreme and unexpected loadings, to assess integrity and remaining life, and to disseminate guidance and tools to assess and reduce future vulnerabilities. Project selection is guided by identification and assessment of the particular vulnerabilities within our materials-based infrastructure, and focusing on those issues that would benefit strongly by improved measurements, standards, and materials data. Ultimately, our goal is 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:

- Develop advanced measurement methods needed by industry to address reliability problems that arise with the development of new materials;
- Develop and deliver standard measurements and data;
- Identify and address vulnerabilities and needed improvements in U.S. infrastructure; and
- Support other agency needs for materials expertise.

Contact: Chad R. Snyder



Ballistic Resistance of Polymeric Materials

This project is developing metrologies and Failure of a first responder's personal body armor prompted NIST's Office of Law Enforcement Standards (OLEES), under the auspices of the National Institute of Justice (NIJ), to initiate a program to assess the long-term durability and effectiveness of current and future soft body armor products. In response, we are developing metrologies and models to test and predict the long-term reliability of polymers used in these products.

Gale A. Holmes and Chad R. Snyder

In a recent review [1] of the potential degradation mechanisms of the ballistic fiber poly (p-phenylene benzobisoxazole, i.e., PBO), ultraviolet (UV) radiation exposure, exposure to moisture, elevated temperature exposure, and mechanical folding have been identified as mechanisms that may compromise the structural integrity of the active ballistic fiber during use. Since answers related to the long-term durability of the armor are sought, any testing methodology must allow relevant degradation mechanisms to occur under field conditions and controlled exposure conditions without compromising the structural integrity of the armor. As a result the testing methodology must be non- or minimally-invasive, precisely determine the mechanical properties of the ballistic fibers, and reflect the ballistic performance properties of the armor.

ASTM Standard D3379-75, a statistically robust testing methodology that measures the tensile strength and Young's modulus for high modulus single-filament materials that also addresses the issue of sample size, was modified to accurately measure the strain-to-failure and diameter of single filaments, with the latter providing a more accurate measure of the yield strength and Young's modulus of the filament. This test was designed to monitor changes in fiber properties without compromising the integrity of flexible body armor. In addition to showing that changes in ballistic fiber properties are readily quantified using this test, results from PBO filaments have shown that deviations of the yield strength data from the expected normal distribution can be attributed to abnormal variations in the fiber diameter of the PBO filament along its length, thus highlighting the need to profile the length of the tested fiber.

Research data from 2005 indicated that a single severe fold in a PBO fiber could result in a greater than 10 % reduction in ballistic performance, as quantified by the test method discussed above. To better quantify the

impact of fatigue on ballistic performance, a device was designed (below) for use on a servo hydraulic machine, such as those commonly used to measure the fatigue resistance of structural materials, to fold single and multiple layers of woven fabric of ballistic material. Initial data from this device indicate that repeated folding of PBO fibers can result in a greater than 20 % reduction in ballistic performance after 5 000 cycles or seven months of wear! Since this is a new testing methodology, research is being conducted to validate these preliminary test results.



Our research on the degradation pathways of PBO and PBO-like materials has focused on the role of residual phosphoric acid on the chemical degradation of these materials. A procedure was devised to extract residual acid using a soxhlet extractor, methylate any extracted phosphoric acid by diazomethane, and identify and quantify its presence by gas chromatography-mass spectrometry. This more involved procedure was devised to overcome the presence of phosphorus containing sizing material that may be added during processing. Initial results indicate that after a week-long extraction process, only 25 % of the phosphorus containing species was removed from the fiber. Research is ongoing to identify the extracted phosphorus, which is presumed to be composed primarily of the sizing additive, and to devise a more robust approach for removing the remaining phosphorus believed to be trapped in the micro and nanoscale voids of the fiber structure.

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Polymers Division FY06 Annual Report Publication List

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Polymers Division

Chief

Eric J. Amis

Phone: 301-975-6762

E-mail: eric.amis@nist.gov

Deputy Chief

Chad R. Snyder

Phone: 301-975-4526

E-mail: chad.snyder@nist.gov

NIST Fellow

Wen-li Wu

Phone: 301-975-6839

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

Group Leaders

Characterization and Measurement**Chad R. Snyder****Electronics Materials****Eric K. Lin**

Phone: 301-975-6743

E-mail: eric.lin@nist.gov

Biomaterials**Marcus T. Cicerone**

Phone: 301-975-8104

E-mail: marcus.cicerone@nist.gov

Multiphase Materials**Alamgir Karim**

Phone: 301-975-6588

E-mail: alamgir.karim@nist.gov

Processing Characterization**Kalman Migler**

Phone: 301-975-4876

E-mail: kalman.migler@nist.gov

Multivariate Measurement Methods**Michael Fasolka**

Phone: 301-975-8526

E-mail: michael.fasolka@nist.gov

Research Staff

Alvine, Kyle*

kyle.alvine@nist.gov
X-ray reflectivity & GISAXS nanostructures
Nanoparticle self-assembly
Small angle x-ray scattering
Nanoimprint lithography
Surface tension of nanostructures

Amis, Eric J.

eric.amis@nist.gov
Neutron, x-ray and light scattering
Polyelectrolytes
Viscoelastic behavior of polymers
Dendrimers and dendritic polymers
Functional biomaterials
Combinatorial methods
High-throughput experimentation

Antonucci, Joseph M.

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

Barnes, Susan E. +

susan.barnes@nist.gov
Combinatorial and high-throughput methods
Vibrational spectroscopy of polymers
Microfluidics technology
Fluorescence spectroscopy
On-line monitoring of polymer melts/extrusion

Bauer, Barry J.

barry.bauer@nist.gov
Polymer synthesis
Polymer chromatography
MALDI mass spectroscopy
Thermal characterization
Neutron, x-ray and light scattering
Dendrimers, metallic ions nanocluster
Porous low-k thin film characterization
Carbon nanotubes

Becker, Matthew L.

matt.becker@nist.gov
Polymer synthesis
Block copolymers
Peptide synthesis
Phage display
Combinatorial methods
Polymerase Chain Reaction

Beers, Kathryn L.

kathryn.beers@nist.gov
Combinatorial and high-throughput methods
Polymer formulations
Microfluidics technology
Polymer synthesis
Controlled/living polymerizations

Berry, Brian+

brian.berry@nist.gov
Inorganic nanoparticle synthesis
Thin film zone-annealing methods
Defects in nanostructured films
Block copolymer films
Combinatorial surface modification
Neutron reflectivity and small angle scattering

Blair, William R.

william.blair@nist.gov
Polymer analysis by size exclusion
chromatography
Mass spectrometry of polymers
High temperature viscometry
Rayleigh light scattering
Extrusion plastometry

Bowen, Rafael L.*

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

Bur, Anthony J.

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

Carey, Clifton M.*

clifton.carey@nist.gov
Dental plaque
Microanalytical analysis techniques
Fluoride efficacy for dental health
De- and re-mineralization
Phosphate chemistry
Ion-selective electrodes
Toothpaste abrasion & erosion

Cherng, Maria*

maria.cherng@nist.gov
Calcium phosphate biomaterials

- Chastek, Thomas Q.**
thomas.chastek@nist.gov
 Combinatorial and high-throughput methods
 Optics and fiber optics
 Optical microscopy
 Liquid chromatography
 Microfluidics
 Small angle x-ray scattering
- Chastek, Thuy T.+**
thuy.chastek@nist.gov
 Synthetic hybrid nanocomposites
 Solid state synthesis
 Electron microscopy
 Rheology of nanocomposites and gels
 Wide and small angle x-ray diffraction
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 Microfluidics
- Chiang, Chwan K.**
c.chiang@nist.gov
 Electroluminescent polymers
 Residual stress
 Impedance spectroscopy
- Chiang, Martin Y.**
martin.chiang@nist.gov
 Computational mechanics (finite element analysis)
 Strength of materials, fracture mechanics
 Engineering mechanics of polymer-based materials
 Bi-material interface
 Image quantitation
- Choi, Kwang-Woo+**
kwang-woo.choi@nist.gov
 Polymers for lithography
 Critical dimension small angle x-ray scattering (CD-SAXS)
 Extreme ultraviolet (EUV) lithography
- Chow, Laurence C.***
laurence.chow@nist.gov
 Calcium phosphate compounds and biomaterials
 Tooth demineralization and remineralization
 Dental and biomedical cements
 Solution chemistry
 Dental caries prevention
- Chung, Jun Young+**
junyoung.chung@nist.gov
 Combinatorial and high-throughput methods
 Mechanics of complex interfaces
 Stress relaxation and aging in thin polymer films
 Adhesion and fracture at soft interfaces
- Cicerone, Marcus T.**
marcus.cicerone@nist.gov
 Protein stabilization
 Glass transition theory
 Optical coherence microscopy
 Tissue engineering scaffolds
 Confocal microscopy
 Spectroscopic imaging
- Cipriano, Bani H.+**
 Polymer rheology
 Cooper, James A.
james.cooper@nist.gov
 Tissue engineering
 Polymer scaffolds
 Cell biology
 Optical microscopy
- DeLongchamp, Dean M.**
dean.delongchamp@nist.gov
 Organic electronics
 Polymer thin films
 Polyelectrolytes
 Near-edge x-ray absorption fine structure spectroscopy (NEXAFS)
 Film electrochemistry
- Dickens, Sabine***
sabine.dickens@nist.gov
 Dental composites
 Dental adhesives
 Transmission electron microscopy
 Remineralizing resin-based calcium phosphate composites and cements
- Di Marzio, Edmund A.+**
edmund.dimarzio@nist.gov
 Statistical mechanics of polymers
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 Polymers at interfaces
- Ding, Yifu+**
yifu.ding@nist.gov
 Polymer dynamics
 Glass transition and glass properties
 Inelastic light and neutron scattering
 Nanoimprint lithography
- Douglas, Jack F.**
jack.douglas@nist.gov
 Theory on polymer solutions, blends, and nanoparticle filled polymer materials
 Physics of polymers films
 Dynamics and thermodynamics of self-assembly
 Crystallization of polymers
 Defects and ordering in block copolymer films
 Nanoparticle characterization and interactions

Dunkers, Joy P.

joy.dunkers@nist.gov
Optical coherence microscopy
Image analysis
Fiber optic spectroscopy
Infrared microspectroscopy of polymers
Confocal fluorescence microscopy

Duppins, Gretchen E.*

gretchen.duppins@nist.gov
Editorial Coordinator

Dutta Roy, Tithi

tithi.duttaroy@nist.gov
Reference scaffolds for tissue engineering
Cellular response to biomaterials

Eichmiller, Frederick C.*

frederick.eichmiller@nist.gov
Clinical dentistry
Composites
Dentin adhesives
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Eidelman, Naomi B.*

naomi.eidelman@nist.gov
FTIR microspectroscopy
Characterization of dental tissues and materials
Composition of combinatorial polymer blends
Application of temperature and UV gradients to polymers

Epps, Thomas H., III

thomas.epps@nist.gov
Combinatorial and high-throughput methods
Block copolymers
Self-assembled structures
Surface energy patterning and control
Surfaces and interfaces
Scanning probe microscopy

Fagan, Jeffrey A.

jeffrey.fagan@nist.gov
Dielectrophoretic separations
Colloidal solutions
Electrooptical effects
Carbon nanotubes

Fasolka, Michael J.

michael.fasolka@nist.gov
Combinatorial and high-throughput methods
Combinatorial and high-throughput methods
NIST Combinatorial Methods Center (NCCM)
Self-assembled structures
Surface energy patterning and control
Surfaces and interfaces
Scanning probe microscopy

Flaim, Glenn M.*

glenn.flaim@nist.gov
Fabricating dental composites

Floyd, Cynthia J. E.*

cynthia.floyd@nist.gov
Dental composites
Nuclear magnetic resonance (NMR)

Flynn, Kathleen M.

kathleen.flynn@nist.gov
Melt flow rate measurements
Size exclusion chromatography
Mass spectrometry of polymers

Fowler, Bruce O.+

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

Frukhtbeyn, Stanislav*

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

Gallant, Nathan D.

nathan.gallant@nist.gov
Cell adhesion to biomaterials
Combinatorial screening of bioactive gradients

Genson, Kirsten L.

kirsten.genson@nist.gov
Highly branched polymers
Surface initiated polymerization
Surface functionalization
Atomic force microscopy
Gradient combinatorial methods

George, Laurie A.*

laurie.george@nist.gov
Network Administrator

Giuseppetti, Anthony A.*

anthony.giuseppetti@nist.gov
Casting of dental alloys
Scanning electron microscopy
Dental materials testing

Guo, Shu+

shu.guo@nist.gov
Solid mechanics
Mechanical properties of thin films
Combinatorial and high-throughput methods
Polymer thin films
Surfaces and interfaces

Guttman, Charles M.

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

Han, Charles C.+

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

Henderson, Lori A.

lori.henderson@nist.gov
 Structure-property relationships of biomaterials
 Structure-function of tissues
 Molecular engineering of DNA and proteins
 Cellular physiology and assays
 Molecular biology screening
 Polymer synthesis and characterization

Ho, Derek H+

derekho@nist.gov
 Small angle neutron scattering
 Small angle X-ray scattering
 Clay-polymer nanocomposites

Hobbie, Erik K.

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

Hodkinson, Christine S.*

christine.hodkinson@nist.gov
 Manager, Administrative Services

Holmes, Gale A.

gale.homes@nist.gov
 Composite interface science
 Chemical-structure-mechanical property
 relationships for:
 Polymer chemistry
 Mass spectroscopy
 Nanocomposites
 Ballistic resistance

Hu, Xuesong+

xuesong.hu@nist.gov
 Combinatorial Informatics
 Instrument automation
 Adhesion and mechanical properties

Huang, Heqing+

heqing.huang@nist.gov
 Combinatorial and high-throughput methods
 Adhesion and mechanical properties
 Surface initiated polymerization
 Polymer brushes

Hudson, Steven D.

steven.hudson@nist.gov
 Electron and optical microscopy
 Microfluidics
 Nanoparticle characterization and assembly
 Self-assembly
 Bio- and interfacial dynamics

Iida, Kazunori+

kazunori.iida@nist.gov
 Combinatorial and high-throughput methods
 Microfluidics and microreactors
 Controlled radical polymerization
 Living radical polymerization

Johnson, Jerainne

jerainne.johnson@nist.gov
 Spectroscopy, fluorescence upconversion and
 time resolved fluorescence
 Bench top method for evaluating materials for
 protein storage

Jones, Ronald L.

ronald.jones@nist.gov
 Neutron and x-ray scattering
 Defects in nanomaterials
 Neutron reflectivity
 3-D tomography
 Polymer surfaces and thin films
 Polymer phase transitions and computer
 simulation

Julthongpiput, Duangrut+

duangrut.julthongpiput@nist.gov
 Combinatorial and high-throughput methods
 Surface energy patterning and control
 Scanning probe microscopy

Jung, Youngsuk+

youngsuk.jung@nist.gov
 Organic electronics
 Polymer thin films and interfaces

Kang, Shuhui+

skang@nist.gov
 Fourier transform infrared spectroscopy (FTIR)
 Raman spectroscopy
 Polymers for lithography
 Polymer thin films

Karim, Alamgir

alamgir.karim@nist.gov
Combinatorial and high-throughput methods
Patterning of thin-polymer blend films on inhomogenous surfaces
Neutron & x-ray reflection and scattering
AFM and optical microscopy
Nanofilled polymer films
Nanostructured materials
Metrology for nanoscale manufacturing

Kee, Tak+

tak.kee@nist.gov
Ultrafast spectroscopy
Coherent anti-Stokes Raman scattering (CARS) microscopy
Tissue engineering scaffolds
Confocal microscopy

Khoury, Freddy A.

freddy.khoury@nist.gov
Crystallization, structure and morphology of polymers
Analytical electron microscopy of polymers
Wide-angle and small-angle x-ray diffraction
Structure and mechanical property relationships

Kim, Jae Hyun+

jaehyun@nist.gov
Fiber/matrix interface
Polymer adhesion and mechanical properties
Polymer composites
Optical coherence microscopy

Kim, Sangcheol

sangcheol.kim@nist.gov
Ordering and defects in thin nanostructured materials
Combinatorial and high-throughput methods
AFM and optical microscopy
X-ray reflectivity

Kipper, Matthew+

matthew.kipper@nist.gov
Hemotactic, chemotactic response to biomaterials
Craniofacial tissue engineering
Cell migration

Kline, R. Joseph

rjkline@nist.gov
Organic electronics
Grazing incidence x-ray diffraction
Polymer thin films morphology
AFM characterization

Lacerda, Silvia+

silvia.lacerda@nist.gov
Quantum dots synthesis and surface functionalization
Quantum dot-based biosensors
Cell-penetrating proteins and peptides for delivery of nanoparticles in living cells
Interaction of nanoparticles with animal tissues
Transmission Electron Microscopy, 3D tomography
Defects in block copolymer films
Assembling of particles in nanoporous membranes

Landis, Forrest A.+

forrest.landis@nist.gov
Crystallization and melting of miscible polymer blends
Ionomers
Optical coherence microscopy
Tissue engineered scaffolds
Static small angle laser light scattering

Laumeier, Carol E.

carol.laumeier@nist.gov
NIST Combinatorial Methods Center
Outreach Coordinator

Lavery, Kristopher A.

klavery@nist.gov
Polymer thin films and interfaces
Neutron and X-ray reflectometry
Off-specular reflectivity
Photoresist materials
Diblock copolymer thin films

Lee, Hae-Jeong+

hae-jeong.lee@nist.gov
X-ray reflectivity
Small-angle neutron scattering
Nanoimprint lithography
Structural characterization of low dielectric constant thin films
Porosimetry of porous thin films
Metrology for characterizing physical structures of nanopatterns

Lin, Eric K.

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

Lin, Nancy J.**nancy.lin@nist.gov**Combinatorial screening of scaffolds
Cellular response to materials**Lin-Gibson, Sheng****sheng.lin-gibson@nist.gov**Rheology of gels and nanocomposites
Mass spectrometry of synthetic polymers
Polymer synthesis and modification
Structure and dynamics of nanocomposite polymeric materials
Tissue engineering hydrogels**Liu, Da-Wei****da-wei.liu@nist.gov**Polymer synthesis
Thermal gravimetric analysis
Differential scanning calorimetry
Gel permeation chromatography
Infrared spectroscopy
Nuclear magnetic resonance**Lucas, Leah A.+****leah.lucas@nist.gov**Organic electronics
Combinatorial methods
Surface functionalization**Markovic, Milenko*****milenko.markovic@nist.gov**Calcium phosphate chemistry
Biom mineralization (normal and pathological)
Crystal growth and dissolution kinetics
Heterogeneous equilibria**McDonough, Walter G.****walter.mcdonough@nist.gov**Processing and cure monitoring polymer composites
Failure and fracture of polymers
Polymer composite interfaces
Dental materials**McGuiggan, Patricia****patricia.mcguiggan@nist.gov**Atomic force microscopy
Viscoelastic properties
Surface force measurements**Meillon, Mathurin+****mathurin.meillon@nist.gov**Polymer rheology
Characterization of processing aids**Migler, Kalman****kalman.migler@nist.gov**Rheology
Carbon nanotubes
Liquid crystals
Polymer blends
Polymer slippage
Sharkskin and extrusion**Obrzut, Jan****jan.obrzut@nist.gov**Dielectric relaxation spectroscopy
Electronic properties of polymers and composites
Electronic packaging
Microwave and optical waveguides
Photoelectron spectroscopy (x-ray and UV)
Reliability, stress testing**Okerberg, Brian C.****brian.okerberg@nist.gov**Polymer crystallization and morphology
Thin films and polymer blends
Hot-stage atomic force microscopy
Nanoimprint lithography
Optical and electron microscopy**Page, Kirt A.****kirt.page@nist.gov**X-ray scattering
Neutron scattering
Polymer structure and dynamics
Polymer brushes
Polymer Ionomers
Membranes
Combinatorial methods**Pakstis, Lisa****lisa.pakstis@nist.gov**Self-assembly of amphiphilic diblock copoly-peptides
Biomaterial-cell interactions
Physical characterization of polymer/biomaterial assemblies
Microscopy, scattering, rheology, spectroscopy, cell culture**Park, Jung J.+****jungjin.park@nist.gov**Microfluidics
Bioadhesion properties of nanoparticles
Biopolymer interactions**Parry, Edward E.*****edward.parry@nist.gov**Dental appliance and crown and bridges fabrication
Machine shop applications

Pathak, Jai A.+

jai.pathak@nist.gov
Rheology and linear viscoelasticity
Polymer dynamics and complex fluids
Microfluidics

Patton, Derek L.

derek.patton@nist.gov
Combinatorial and high-throughput methods
Polymer brushes
Controlled radical polymerization
Surface functionalization
Atomic force microscopy
X-ray Photoelectron Spectroscopy

Phelan, Jr., Frederick R.

frederick.phelan@nist.gov
Composites processing
Microfluidics
Viscoelastic flow modeling
Chaotic mixing
Flow in porous media
Lattice Boltzmann methods

Prabhu, Vivek M.

vivek.prabhu@nist.gov
Small-angle neutron scattering
Polyelectrolytes
Polymers for lithography
Fluorescence correlation spectroscopy
Polymer thin films
X-ray and neutron reflectivity

Psurek Tatiana+

tatiana.psurek@nist.gov
Dielectric spectroscopy
Organic Electronics
Polymer thin films

Quinn, Janet*

janet.quinn@nist.gov
Fractography
Dental materials and material properties
Composites

Richards, Nicola*

nicola.richards@nist.gov
Dental restorative materials
Polymer matrix composites

Rao, Ashwin B. +

ashwin@nist.gov
Polymer adsorption
Thin films gels
Fluorescence microscopy
Interfacial rheology

Ro, Hyun Wook+

hyun.ro@nist.gov
Nanoimprint lithography
Low-k dielectric thin films
X-ray reflectivity

Sambasivan, Sharadha+

sharadha@bnl.gov
Near-edge x-ray absorption fine structure spectroscopy (NEXAFS)
Polymers for lithography
Polymer relaxation and tribology
Self assembled monolayer orientation
Catalyst surface and bulk characterization

Schumacher, Gary E.*

gary.schumacher@nist.gov
Clinical dentistry
Composites
Dentin adhesives

Simon, Carl G., Jr.

carl.simon@nist.gov
Biocompatibility
Cytotoxicity
Signaling in human platelets
Bone marrow cell lineage/trafficking
Combinatorial methods

Skrtic, Drago*

drago.skrtic@nist.gov
Bioactive amorphous calcium phosphate-based dental materials

Smith, Jack R.

jack.smith@nist.gov
Surface science
Computational modeling
Biomaterials characterization

Snyder, Chad R.

chad.snyder@nist.gov
Dielectric relaxation spectroscopy
Thermodynamics and kinetics of polymer crystallization
Calorimetry
Thermal properties at the nanoscale
Ballistic resistance of polymers

Soles, Christopher L.

csoles@nist.gov
Polymer dynamics
Inelastic neutron scattering
Low-k dielectric thin films
X-ray and neutron reflectivity
Polymer thin films and lithography
Ion beam scattering
Nanoimprint lithography

Stafford, Christopher M.**chris.stafford@nist.gov**

Combinatorial and high-throughput methods
 Polymer thin films
 Polymer adhesion
 Mechanical properties of thin films
 Surfaces and interfaces

Sun, Limin***lsun@nist.gov**

Macroporous biomaterials
 Fiber-matrix interfacial shear strength
 CPC composites

Taboas, Juan M.+**juan.taboas@nist.gov**

Biomedical engineering
 Cell and tissue mechanics
 Mechanoactive bioreactors
 Tissue engineering

Takagi, Shozo***shozo.takagi@nist.gov**

Crystallography
 X-ray diffraction
 Calcium phosphate biomaterials
 Topical fluoridation
 De- and remineralization

Tesk, John A.+**john.tesk@nist.gov**

Characterization: biomaterials; physical and
 mechanical properties
 Reference biomaterials
 Reference data for biomaterials
 Biomaterials: orthopaedics, cardiovascular,
 dental, ophthalmic, & tissue engineered
 medical devices
 Standards for medical devices

Tirumala, Vijay.+**vijay.tirumala@nist.gov**

Small angle neutron scattering
 Block copolymer thin films
 Hydrogels
 Double network hydrogels

Tominaga, Taiki.+**taiki.tominaga@nist.gov**

Small angle neutron scattering
 Hydrogels
 Double network hydrogels

Tung, Ming S.***ming.tung@nist.gov**

Chemistry of calcium phosphate and peroxide
 compounds
 Remineralization studies
 Standard reference materials

VanderHart, David L.+**david.vanderhart@nist.gov**

Measurement of orientation in polymer fibers
 and films
 Solid-state NMR of polymers
 Measurement of polymer morphology at the
 2-50 nm scale
 Pulsed field gradient NMR

Vogel, Brandon M.**brandon.vogel@nist.gov**

Polymer synthesis
 Combinatorial methods
 Drug delivery
 Organic electronics
 Polymer thin films
 Self assembled monolayers
 X-ray scattering
 Solution NMR

Vogel, Gerald L.***gerald.vogel@nist.gov**

Dental plaque chemistry
 Chemistry of calcium phosphates
 Microanalytical techniques
 Fluoride chemistry

Vogt, Bryan D.**bryan.vogt@nist.gov**

Polymer thin film properties
 X-ray and neutron reflectivity
 Polymers for lithography
 Quartz crystal microbalance
 Ordered mesoporous materials
 Organic electronics

Wallace, William E.**william.wallace@nist.gov**

Mass spectrometry
 Geometric data analysis methods

Wang, Francis W.**francis.wang@nist.gov**

Photophysics and photochemistry of polymers
 Fluorescence spectroscopy
 Cure monitoring of polymerization
 Tissue engineering

Wang, Chengqing+**chengw@nist.gov**

Small angle x-ray scattering
 Critical Dimension metrology
 Light scattering
 Polymer and colloidal solutions

Weir, Michael*

michael.weir@nist.gov

Biomaterials

Tissue engineering

Degradable hydrogels

Growth factor dynamics and cellular response in biomaterials

Wu, Wen-li

wen-li.wu@nist.gov

Neutron and x-ray scattering and reflectivity

Electron microscopy

Mechanical behavior of polymers and composites

Polymer surfaces and interfaces

Polymer networks

Wu, Tao+

tao.wu@nist.gov

Combinatorial and high-throughput methods

Polymer formulations

Polymer synthesis

Interfacial tension measurements

Xu, Chang+

chang.xu@nist.gov

Combinatorial and high-throughput methods

Polymer formulations

Surface polymerization

Xu, Hockin*

hockin.xu@nist.gov

Bone tissue engineering

Scaffold and cell interactions

Fiber and whisker composites

Zhao, Hongxia (Jessica)+

jessica.zhao@nist.gov

Computed fluid dynamics

Data acquisition

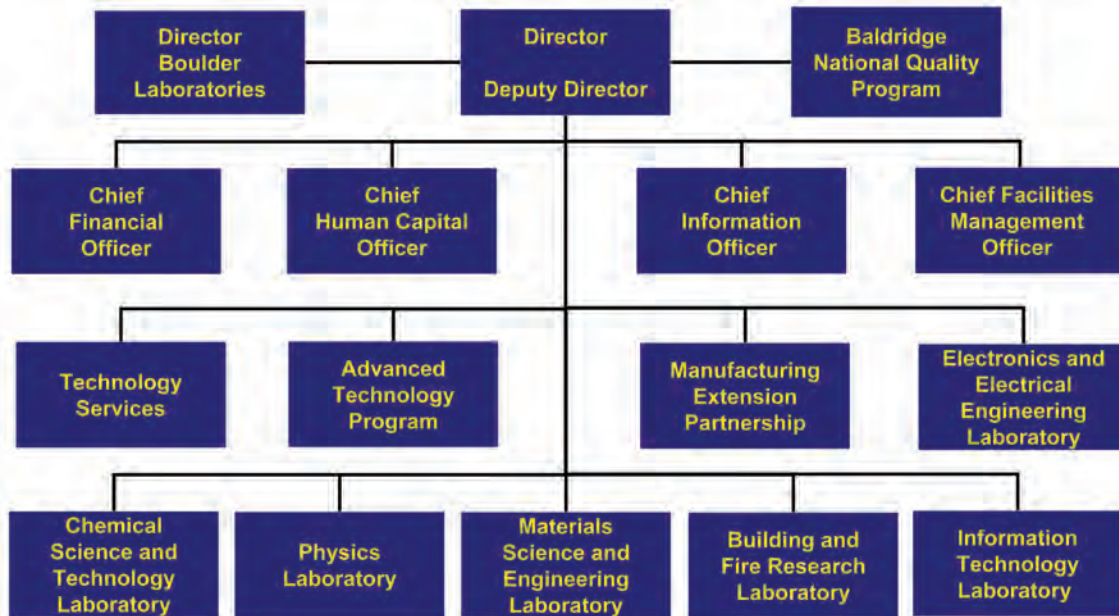
Multivariate analysis

Signal processing

* Research Associate

+ Guest Scientist

National Institute of Standards and Technology



Materials Science and Engineering Laboratory



Polymers Division (854.00)

Eric J. Amis, *Chief*
 Chad R. Snyder, *Deputy Chief*
 Wen-li Wu, *NIST Fellow*
 Dawn Bradley, *Administrative Officer*
 Lisa Hazel, *Division Office Assistant*
 Lisa Fedders, *Administrative Assistant*

Characterization and Measurement (854.01)
 Chad R. Snyder, *Leader*
 Bronny Webb, *Office Assistant*

M. Chiang
 K. Flynn
 C. Guttman
 G. Holmes
 F. Khoury
 D. Liu
 W. McDonough
 W. Wallace

W. Blair
 E. DiMarzio
 J. Kim
 F. Landis
 E. Park
 J. Tesk

Electronics Materials (854.02)
 Eric K. Lin, *Leader*
 Bronny Webb, *Office Assistant*

C. Chiang
 D. DeLongchamp
 J. Kline
 K. Lavery
 J. Obrzut
 V. Prabhu
 S. Stanley
 B. Vogel

K. Choi
 D. Ho
 Y. Jung
 S. Kang
 H. Lee
 T. Psurek
 A. Rao
 V. Tirumala
 D. Vanderhart
 C. Wang

Biomaterials (854.03)
 Marcus T. Cicerone, *Leader*

J. Antonucci
 M. Becker
 J. Dunkers
 N. Gallant
 L. Henderson
 N. Lin
 S. Lin-Gibson
 M. Matos
 L. Pakstis
 M. Roy
 C. Simon
 F. Wang

J. Johnson
 M. Kipper
 Y. Lee
 Y. Liu
 W. Regnault
 J. Sun
 Y. Yang
 J. Zhao

Multiphase Materials (854.04)
 Alamgir Karim, *Leader*
 Bronny Webb, *Office Assistant*

K. Alvine
 J. Benkoski
 J. Douglas
 R. Jones
 B. Okerberg
 C. Soles

B. Berry
 Y. Ding
 J. Han
 S. Kim
 S. Lacerda
 J. Park
 H. Ro
 X. Zhang

Processing Characterization (854.05)
 Kalman Migler, *Leader*

B. Bauer
 J. Fagan
 E. Hobbie
 S. Hudson
 F. Phelan

T. Chastek
 H. Hu
 J. Taboas

Multivariant Measurement Methods (854.06)
 Michael J. Fasolka, *Leader*

K. Beers
 T. Chastek
 K. Gensen
 C. Laumeier
 P. McGuiggan
 K. Page
 D. Patton
 C. Stafford

A. Bur
 J. Chung
 H. Huang
 K. Iida
 L. Lucas

* Organization as of 9/29/06

