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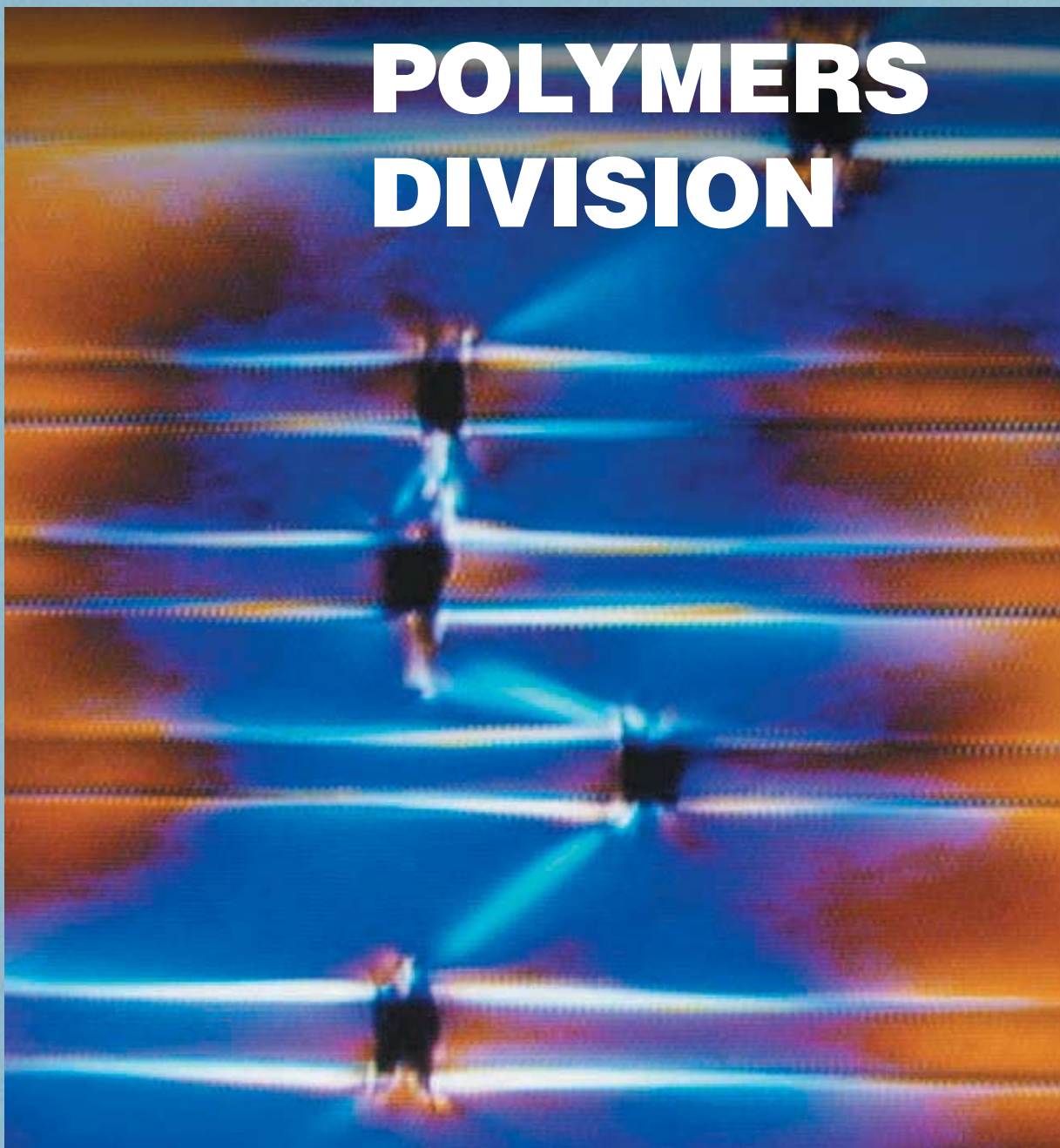
NISTIR 6796

September 2001

# MSEL

**FY 2001 PROGRAMS  
AND ACCOMPLISHMENTS**

## **POLYMERS DIVISION**



**Advance measurement methods to characterize microstructure failure in composites**

This optical image is a planar array of glass fibers embedded in epoxy resin matrix deformed under tension. The arrays are used to investigate the failure initiation in fibrous composites. In the optical image, the fibers are spaced (30 to 45) mm apart and the dark regions along each fiber are cracks that extend into the surrounding polymer matrix. The light blue regions that connect the fiber breaks show high deformation shear bands that emanate from the tips of the matrix cracks.

**National Institute of  
Standards and Technology**  
Karen H. Brown,  
Acting Director

**Technology  
Administration**

**U.S. Department of  
Commerce**  
Donald L. Evans,  
Secretary



# **MATERIALS SCIENCE AND ENGINEERING LABORATORY**

**FY 2001 PROGRAMS  
AND  
ACCOMPLISHMENTS**

# **POLYMERS DIVISION**

Eric J. Amis, Chief

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NISTIR 6796

September 2001

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Certain commercial materials and equipment are identified in this report in order to specify adequately the experimental procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply necessarily the best available for the purpose.

## Executive Summary

The Polymers Division provides measurement methods, standards, and concepts to facilitate technology development, manufacture of products, commerce, and use of synthetic polymers. Projects are selected based on assessments of current needs and in anticipation of future needs as determined from topical workshops, industry roadmaps, as well as visits to companies and other research organizations. Much of our work is performed collaboratively with customers. Over 35 companies, in addition to trade associations and other federal agencies participated in the work of the Division. The close interactions with customers assure that the work remains focused.

The work of the Division is organized into three groups that focus on areas where synthetic polymers are exploited for their unique properties—electronics materials, lightweight structural materials, and biomedical materials. Two other groups are concerned with needs that crosscut the applications areas—better control of polymer processing and more rapid test methodology.

- The Division is building on the success of its effort to characterize properties of porous thin films under development as low-k dielectrics for use as interlevel dielectric films in the next generation IC chips. The new metrology we have developed received strong endorsements by both International SEMATECH and the National Research Council panel performing a crosscutting assessment of NIST programs in microelectronics. In anticipation of the needs of the microelectronics industry for measurement methods to identify characteristics of photoresist polymers that limit further reductions in feature size, the Division successfully used neutron scattering to elucidate the shape of features produced by photolithography. Other measurement strategies are under development to determine how macromolecular dynamics and other molecular characteristics are affected by the thickness of polymer thin films of the sort used in today's photoresists.
- For structural applications polymeric materials are combined in manufacture with other materials, particulates, fibers or other polymers to achieve property enhancement, cost reduction and/or improved processibility. Although many successful products have been developed it is recognized that future progress rests on improving predictions of resultant properties from constituent properties, particularly at the molecular level. Our work in this area builds the connections between computer simulations of molecular behavior and macroscopic properties. This year we developed a new instrumental method that characterizes how fracture of a single glass fiber affects failure processes of neighboring fibers and the matrix resin in a fiber-reinforced composite.
- Increasing use is made of synthetic polymers in human implants to restore body function and improve quality of life. New therapies are under development through tissue engineered products approaches. This year we demonstrated the utility of a new approach to produce a polymeric scaffold of controlled morphology by coextrusion of incompatible polymers followed by leaching of one polymer to provide three-dimensional connected pores. Workshops this year with providers of medical products and services identified a prioritized list of needed reference biomaterials and data. The Division has responded by issuing the first NIST reference biomaterial for orthopedic applications, a medical grade polyethylene that will be used for comparative studies and for developing improved materials.
- The Polymers Division is pioneering the development of combinatorial methods to measure rapidly properties of materials. The approach is similar to that used with a great deal of success in the pharmaceutical industry in discovery of new drugs. The key components of a combinatorial method are a sample in which composition, film thickness or other characteristics are controlled, a technique to image the entire specimen for properties of interest, optical microscopy, for example, and analysis techniques capable of treating exceedingly large amounts of data. We have reported successes in each aspect of the combinatorial process, most notably development of a method of imaging polymer adhesion for a polymeric library. Not only has it been demonstrated that the combinatorial approach can greatly reduce measurement time, but we have also observed new phenomena in several experimental systems including the structure of thin films of block copolymers.
- The Polymers Division has a sustained effort in developing methods to measure polymer properties during their processing. The initial application was in measurement of temperature in the resin, rather than in the processing equipment as is traditionally done. This work showed that the resin temperature was frequently much higher than that given by the traditional temperature method. This sensor work has been extended to measurement of polymer orientation that is of particular interest in film blowing. Other optical methods have been developed to elucidate the origins of "sharkskin" surface imperfections in extrusion of polyolefins. With these tools better control of polymer processing and strategies to improve end products are made possible.

• The Division's work to establish matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS) as a quantitative tool for synthetic polymers advanced this year with the successful completion of an inter-laboratory comparison with 23 institutions. For the first time, NIST has provided the MALDI MS of polystyrene Standard Reference Material 2888. Of particular significance, we have overcome the ineffectiveness of conventional methods of cationization of polyolefins and demonstrated the mass spectroscopy of polyethylene by a covalent cationization method. Although this polymer type dominates the synthetic polymer market, determination of their molecular mass and molecular mass distribution has been difficult and not quantitative.

In looking forward to next year, several significant advances can be anticipated. Our pioneering work demonstrating high throughput experimental methods will be given a new home in an extensively remodeled laboratory and with the initiation of an industrial consortium, the NIST Combinatorial Methods Center. Another laboratory remodel will provide facilities to initiate a new program in metrology for tissue engineering that includes collaborations with the NIST Biotechnology Division and two institutes at the National Institutes of Health. Both of these projects have received support from the NIST competence building program after success in the 2000 and



2001 competitions. In polymer processing we will focus on new measurement technology that will provide the ability to control extrusion instabilities of sharkskin and gross melt fracture. In the microelectronics area we are working to develop an extension of our porous thin films measurement method that can be implemented in the industrial laboratory without the need for access to our specialized neutron and x-ray facilities.

Among the principal outputs of the Division are technical publications; the number of papers published is the highest among all NIST Divisions. Every year in our annual report we provide a list of publications for the past year. The Division also is-

sues a CDROM of its publications for each calendar year. To provide more timely access to our technical publications, the publications are also being organized for distribution on the Division web site. The collection is organized by research group, keywords from the papers, and a set of subject terms that correspond to current thrusts in polymer science and technology. The most recent version of the Polymers Division web site is available at <http://www.nist.gov/polymers>.

The first year of the 21st century has been an excellent one for the Polymers Division as we have also enjoyed the celebration of the NIST Centennial. I hope this annual report provides a useful overview of our activities. We are always pleased to provide more details. Feel free to contact us for more information.

Eric J. Amis  
Chief

# Technical Highlights

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The following Technical Highlights section includes expanded descriptions of research projects that have broad applicability and impact. These projects generally continue for several years. The results are the product of the efforts of several individuals. The Technical Highlights include:

- Mass Spectrometry of Polyethylene by the “Covalent Cationization Method”
- Combinatorial Study of Surface Pattern Formation in Thin Block Copolymer Films
- Measurement Methods Aid Development of Photoresists for Next-Generation Photolithography
- Polymer Mass Distribution by Mass Spectrometry
- Multi-Fiber Failure Propagation
- Biocompatibility of a Moldable, Resorbable, Composite Bone Graft
- The Mechanism of Sharkskin



## Mass Spectrometry of Polyethylene by the "Covalent Cationization Method"

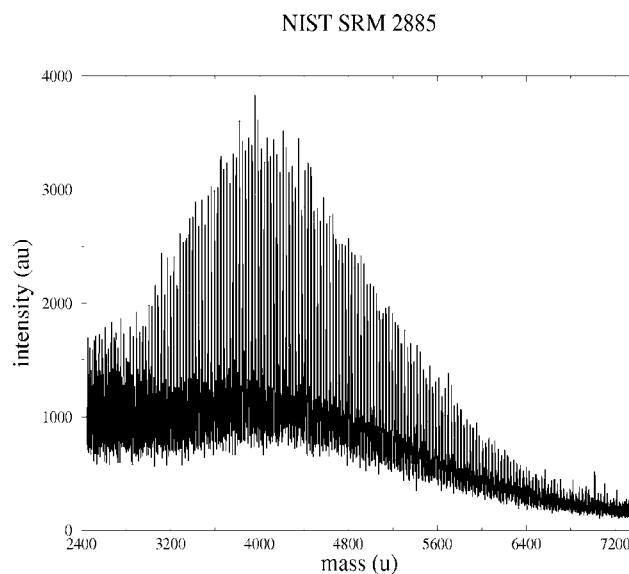
Saturated hydrocarbon polymers, polyethylene and polypropylene, are the most widely used of all synthetic polymers. Their molecular mass and molecular-mass distribution (MMD) are critical in determining processing and performance properties. Mass spectrometry is currently the most promising method for obtaining accurate absolute MMDs; however, polyethylene and other polyolefins have not been amenable to mass spectrometric characterization due to the ineffectiveness of conventional methods of cationization. A new method has been developed in which an organic cation is covalently bonded to the polymer to produce the necessary ionization for successful matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry (MS).

Polyolefins dominate the synthetic polymer market. While they have a very long production history, new developments in metallocene catalysts have caused a great resurgence of activity resulting in a wide variety of new applications and increased material production. The new catalysts can provide unprecedented control of polymer molecular mass and molecular mass distribution, copolymerization control, stereochemistry, etc. Molecular mass distributions of polyolefins currently are determined by gel permeation chromatography, a method that requires calibrations by mass standards. Such standards do not exist for these new types of polyolefins, thus crude approximations are used that introduce large uncertainties. MALDI has provided valuable information on the nature of the polymerization process and the resultant structure for many other polymer types, but not for polyolefins. If polyolefins could be routinely analyzed by MALDI, development time for new catalysts and polymers could be greatly reduced.

Synthetic polymer cationization by metals such as sodium, potassium, silver, copper, etc., involves association of cations with functional groups on the polymer. Examples of functional groups include the carbonyl groups of methacrylate polymers, the double bonds of diene polymers, and the phenyl groups of styrenics. Polymers that lack polar, unsaturated, or aromatic groups cannot be analyzed by MALDI. Thus, polyolefins (polyethylene, polypropylene, polyisobutylene, poly(methyl pentene), etc.) are excluded.

A chemical modification method has been developed in the Polymers Division that allows mass spectrometry to be performed on these materials for the first time. Two synthetic steps are involved: bromination of the polymer, followed by conversion of the brominated site to a charged ammonium or phosphonium group. Here we give results for a low mass fraction of a commercial polyethylene: NIST Standard Reference Material, SRM 2885. The bromination reaction employed brominates sites of carbon-carbon double bonds, present in low concentration in many commercial polyethylenes. The content of carbon-carbon double bonds of structure  $RCH=CH_2$  (vinyl) of SRM 2885 is determined from Fourier-transform infrared spectroscopy. The determined value,  $(0.125 \pm 0.01)$

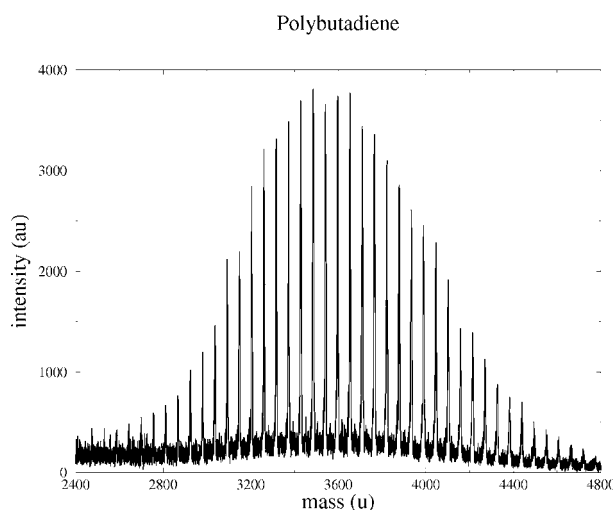
$C=C$  per 100 C, corresponds to approximately one vinyl group for every 2 molecules as estimated from the certified mass average molecular mass of  $6280 \text{ g mol}^{-1}$  and a polydispersity of 1.13. The vinyl content is reduced by bromination to  $0.32 \pm .03$  of its original value. Next, the brominated polymer is treated with tri-phenyl phosphonium (TPP). Using integrated intensities from alkyl benzenes the phenyl content in TPP-treated polyethylene is estimated to be 0.27 phenyl/100 C, or 2 per original vinyl group, approxi-



mately. Since each phosphonium group contains 3 phenyls and the reaction yields one phosphonium group per reacted vinyl the qualitative results are in agreement with the observation that approximately one-third of the original vinyl groups remain unreacted by the treatment employed here. Hence, an estimated one-third of the original polyethylene molecules are labeled with TPP by the chemistry employed.

The figure above shows the MALDI-TOF-MS results from SRM 2885 that has been modified by the covalent cationization method. No smoothing or baseline subtraction was used in the data presented. A strong MALDI signal was produced from the modified polymer while the

unmodified and the brominated polymer produced no signal at all. Oligomers are clearly present up to 7000  $\text{g mol}^{-1}$ , higher than ever observed before for intact, saturated-hydrocarbon oligomers by mass spectrometry. Current work centers on extending the mass range to higher values more representative of commercial polymers. The mass spectrum of SRM 2885 shows a strong repeating pattern of 28  $\text{g mol}^{-1}$ ; however, a pronounced repeat of 14  $\text{g mol}^{-1}$  is also apparent. This may be due to fragmentation of the polymer in the mass spectrometer or may be a consequence of the polymerization chemistry of olefins. The abundance of tightly spaced peaks with 14  $\text{g mol}^{-1}$  spacing below 3000  $\text{g mol}^{-1}$  suggests the existence of fragmentation. However, these peaks also exist at the very high mass end of the spectrum above 6000  $\text{g mol}^{-1}$ . It is known that premature chain termination can produce molecules with an odd number of carbon atoms and thus



can give a repeat spacing of 14  $\text{g mol}^{-1}$ . It is possible that both of these two effects may be occurring in this mass spectrum.

While simple modification of as-polymerized polyolefins with bromine and TPP represents a model case, the covalent cationization method applies to other chemistries and polymer types as well. Many other types of chemistry other than functionalizing vinyl groups are possible. For example, hydroxy-terminated polystyrene, polybutadiene, and hydrogenated polybutadiene (*fa* polyolefin) have been modified by converting the hydroxy to bromide by treatment with  $\text{PBr}_3$  and then converting to  $-\text{N}^+(\text{CH}_3)_3$  or  $-\text{P}^+(\text{C}_6\text{H}_5)_3$  by treatment with trimethyl amine and TPP respectively. The figure on the left shows a hydroxy-terminated hydrogenated polybutadiene covalently cationized with tri-methyl ammonium. The spectrum shows excellent resolution and low background making it ideal to determine molecular-mass distribution. Conventional metal cationization methods fail for this material even though oxygen is present in the end group because the oxygen is in such low abundance that metal cationization becomes a very unlikely event. Covalent cationization overcomes this by chemically adding a charge to each chain.

### Industry Interaction:

*Efforts to expand the MALDI technique to nonpolar polyolefins are in progress. Major product monitoring cost- and time-savings should accrue to industrial polyolefin suppliers and users with this technique when perfected.*

Board on Assessment of NIST Programs, National Research Council

### For More Information On This Topic:

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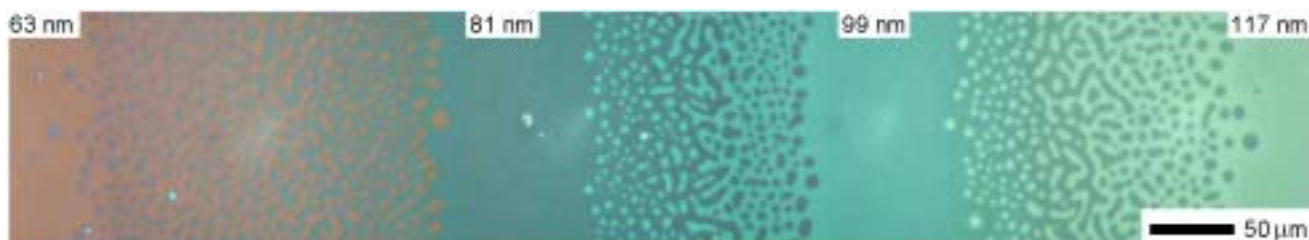
Bauer, B.J., Wallace, W.E., Fanconi, B.M., Guttman, C.M. "Covalent Cationization Method" for the Analysis of Polyethylene by Mass Spectrometry. *Polymer* 42, 9949–9953 (2001).

## Combinatorial Study of Surface Pattern Formation in Thin Block Copolymer Films

*Unique properties of block copolymers in melts, blends and solutions lead to their use as adhesives, emulsifying agents, thermoplastic elastomers, compatibilizers, etc. Many applications exploit the ability of these materials to self-organize into ordered structures in bulk and in thin films. The nature of interactions in block copolymer systems is determined by exploiting the ability of block copolymers to form quantized periodic structures in thin films that directly reflect molecular parameters such as block lengths, chemical interactions between block constituents, and interactions with inorganic substrates. Combinatorial gradient methods are used to validate a vast body of existing literature and simultaneously discover new knowledge reflecting the influence of different molecular parameters on entropic, enthalpic and kinetic relationships in block copolymers.*

Block copolymers are amphiphilic polymer materials composed of two different polymers joined by a covalent bond. This linkage of chemical functionality inhibits phase separation of the polymers beyond a molecular scale and makes these materials useful as stable elastomers, adhesives, and as surfactants stabilizing polymer blends against phase-separation. The tendency of block copolymers to self-organize into ordered nanoscale patterns in bulk and in thin films has also led to recent intense interest in using these materials as templates for nanoscale arrays in thin films and photonic devices. Block copolymer films exhibit seemingly stable surface patterns over large-length scales (tens of

eters. Among questions about basic phenomenology, factors governing the size of the island and hole patterns (e.g., molecular mass  $M$  and temperature  $T$ ) in these films are not well understood. Notably, the size of these patterns is often large in comparison to the lamellar spacing  $L_0$  (or even film thickness  $h$ ) so that the molecular interpretation of these patterns is subtler than ordering in bulk block copolymer materials. The precise thickness range in which the films remain smooth is another basic film property that requires further investigation. Since these film properties are crucial for the development of a theoretical description relating the self-organizing process to fundamental mo-



**Figure 1. True color optical micrographs of a PS-*b*-PMMA film having a gradient in thickness from 63 nm to 117 nm. The addition of three successive lamellae to the surface is shown.**

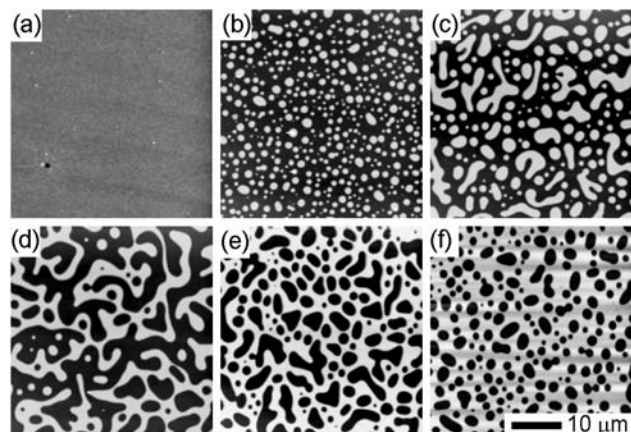
micrometers) whose origins are not understood, but which provide an attractive methodology for forming surface patterns of tunable dimension. We determine, by combinatorial high-throughput approach, the range of morphology types that arise through self-organization in these films and the factors that influence their size and stability. The high information content generated by the combinatorial (“combi”) method revealed surface pattern types overlooked in the past and the phenomenology governing the size of these patterns. The combi results on self-organization in such systems should be helpful to understand the physical origin in terms of competition between micro phase-separation and surface elasticity, and the fundamental nature of molecular interactions between the components of the block copolymer and with surfaces.

Previous studies of surface pattern formation in block copolymer films have not yielded a predictive theory that quantitatively relates the phenomena to molecular param-

lecular interactions in the system, we have investigated pattern formation in block copolymer films using combinatorial methods on films produced by a flow-gradient technique to have a range of  $h$  and  $M$ .

Near symmetric poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) diblock copolymers with different  $M$  were used to prepare thickness gradients on Si wafers. The wafer was attached to a robotic stage and a small amount of solution spread under a suspended knife-edge at constant acceleration to form a thickness gradient. Film thickness was measured using an automated UV-visible interferometer. For the current experiments, up to four PS-*b*-PMMA gradient films were placed on the same wafer and annealed at 170 °C under vacuum to allow ordering of the block copolymers. Optical microscopy and atomic force microscopy (AFM) were used to characterize the surface patterns. Previous studies showed that when PS-*b*-PMMA is cast and annealed on a Si substrate the PMMA preferentially segregates to the substrate while the PS segregates to the air interface. The limited data in literature from individual (single-thickness, single molecular mass) film studies suggests that this behavior produces smooth films for thick-

ness ranges near the characteristic values that are half-integer multiples of lamellar spacing,  $L_o$ , while hole and island patterns form when the film thickness deviates substantially from the characteristic values.



**Figure 2.** AFM micrographs (white corresponds to higher topography) of a PS-*b*-PMMA gradient film at different thicknesses showing: (a) the smooth morphology; (b) and (c) islands; (d) labyrinthine pattern; and (e) and (f) holes on the surface of the films.

An example of the morphological change in the block copolymer films as a function of  $h$  is shown in Figure 1. This image shows optical micrographs of a 26k PS-*b*-PMMA ( $L_o = 17$  nm) continuous gradient film with a thickness range of  $\gg 54$  nm corresponding to the addition of three lamellae layers. The morphology evolves from smooth to islands to labyrinthine to holes to smooth as the film thickness increases. The regions of hole and island pattern formation are consistent with previous observations on films of fixed thickness, but the observation of the *broad smooth regions* and the *labyrinthine* morphology are novel. Figure 2 shows AFM micrographs of the surface patterns at higher magnification. The film is smooth for the thinnest film, with islands forming as  $h$  increases that coalesce into a labyrinthine pattern. For even greater  $h$  a continuous lamella with hole forms. These morphological trends are observed for all  $M$  and thickness range up to  $6.5 L_o$ . The importance and implications of the novel observations are discussed below.

The observation of the broad smooth regions implies a change in film thickness across this area where the block chains of styrene and methyl methacrylate can stretch up to

a maximum of 14 percent with increase of film thickness, or contract down to a minimum of 14 percent with decrease of film thickness, without forming additional layers. These maximum and minimum limits of extensibility are novel results that will be useful in developing a theoretical understanding of the relative importance of entropic (chain stretching) versus enthalpic (chemical interaction parameter) factors in block copolymers. The results on limits of extensibility are also found to be nearly invariant with molecular mass thus generalizing the phenomena. No statistically significant variation in this value was found with increasing  $h$  up to the maximum of  $\gg 6.5 L_o$  tested, indicating that height variation is confined to the *outermost lamella* that is another novel observation. We attribute the height variation resulting from chain deformation in the outermost surface lamella to the kinetics of the ordering process.

The kinetics of the self-organization process can be measured by the continuous gradient approach as well, as demonstrated for the structural evolution of the novel labyrinthine regime. This was obtained by measuring the dependence of the pattern size on  $M$  at different times. The scale (1) of the patterns decreases with an increase in  $M$  (a non-intuitive result), yielding the relationship  $\lambda$  (nm)  $\sim M^{-1.65}$ . This behavior is attributed to the increasing surface elasticity of the block copolymers with increasing  $M$  that serves to inhibit formation of large surface features.

In summary, combinatorial methods have been successfully applied to observe novel morphologies and to establish fundamental kinetic relationships in the ordering properties of block copolymer films. These results agree well with existing non-combinatorial literature data on the same systems, validating the combinatorial approach and the continuous gradient method. The results will enable developing a theoretical understanding of key questions in block copolymers such as the nature of interactions between blocks, as well as block interactions with different materials. The investigative combinatorial tools and methodologies developed will accelerate research in practical application areas of block copolymers such as compatibilization, adhesives, etc., in the future through the development of a NIST Combinatorial Methods Center.

*“This...is an excellent example of using a clever (combinatorial) trick to extract new and important insights from what even the authors admit is a well-studied system. Well done!”—Physical Review Letters Manuscript Review*

### For More Information On This Topic:

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Smith A.P., Douglas, J.F., Meredith, J.C., Amis, E.J., Karim A. Combinatorial Study of Surface Pattern Formation in Thin Block Copolymer Films, *Phys. Rev. Lett.*, 87, 015503, (2001).

Smith A.P., Douglas, J.F., Meredith, J.C., Amis, E.J., Karim A. High-Throughput Characterization of Pattern Formation in Symmetric Diblock Copolymer Films. *J. Poly. Sci. Polym. Phys.* 39, 2141 (2001).

## Measurement Methods Aid Development of Photoresists for Next-Generation Photolithography

*Photolithography, the process used to fabricate integrated circuits, is the key enabler and driver for the semiconductor industry. As lithographic feature sizes decrease to the sub-100-nm length scale, significant challenges arise because the feature size is reaching the limits of current structural characterization methods. In addition, both the image resolution and the thicknesses of the imaging layer approach the inherent macromolecular dimensions characteristic of the polymers used in the photoresist film. Unique high-spatial resolution measurements are developed to understand the materials and processes challenges facing the development of photoresists for next-generation sub-100-nm lithography.*

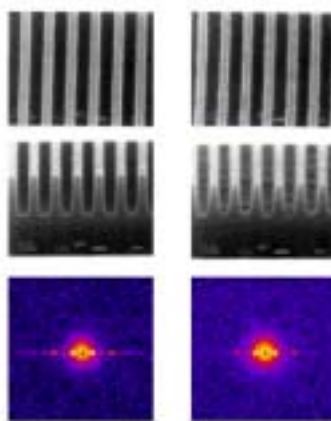
### Photolithography

Photolithography remains the driving technology in the semiconductor industry to fabricate integrated circuits with ever decreasing feature sizes. There are significant challenges in extending this technology to fabricate the smaller feature sizes (sub-100 nm) needed to continue performance increases in integrated circuits. To succeed, the critical dimensions (CD) of the lithographic structures must be controlled to within 10 nm. An increasingly difficult challenge lies in measuring structural parameters (feature size, shape and quality) over these length scales. Further, new radiation sources with shorter wavelengths (193 nm and 157 nm) require photoresist films less than 100-nm thick to ensure optical transparency and uniform illumination. In these ultrathin films, confinement can induce deviations in several key materials parameters such as the macromolecular conformation, glass transition temperature, viscosity or transport properties. It is not yet clear how deviations due to confinement will affect the ultimate resolution in these ultra-thin photoresist films.

To advance this key technology, we work closely with industrial partners including IBM, Shipley and Brewer Science to develop unique high-spatial resolution measurements to better understand the lithographic process, to guide the development of materials, and to provide high-quality data for key model photoresist systems needed in advanced simulation packages. We have made significant advances in two areas, a new method for the structural characterization of lithographically prepared structures and the first measurements of the atomic-level dynamics of polymers in ultrathin films.

### Structural Metrology with SANS

As feature sizes continue to decrease with dimensions approaching 100 nm, the allowable resolution limits of the lithographic process become more stringent and difficult to measure. The precise measurement of the size and quality of lithographically prepared features as they decrease in size is critical for evaluating and improving new lithographic processes and materials. Current microscopy-



**Figure 1. Top-down and edge-on SEM images and two-dimensional SANS data from several periodic grating patterns with 150-nm linewidths.**

based techniques such as scanning electron microscopy (SEM) and atomic force microscopy often require specialized modifications to enable the measurement of either the critical dimension or feature resolution parameters. More importantly these techniques become extremely challenging as feature sizes continue to decrease.

We have demonstrated the powerful use of small-angle neutron scattering (SANS) to quickly, non-destructively, and quantitatively characterize both the size and profile of lithographically prepared structures as prepared on a silicon wafer substrate. Until recently, SANS instruments were unable to measure lithographic feature sizes (sizes greater than 300 nm) and neutron beam fluxes were insufficient to measure scattering from thin-film structures. Today, the high-intensity NIST Center for Neutron Research (NCNR) neutron source, new focusing optics, and smaller lithographic features allow for the SANS measurements. Other important advantages include: a) the measurement of structures on silicon because single crystal silicon wafers are transparent to neutrons; b) a measurement metric averaged over an area of several  $\text{cm}^2$ ; c) less stringent SANS instrument requirements as lithographic structures decrease in size; and d) no need for a calibration standard.

We have demonstrated the SANS metrology through an analysis of the scattered intensity from a periodic grating structure (figure above) with a nominal linewidth of 150 nm. In the SANS data, up to six orders of diffraction peaks are observed. The position and intensity of these peaks provide measures of CD and the cross-sectional shape with nanometer resolution. SANS measurements may serve as a powerful tool to validate calibration standards and is one of very few methods able to provide high-resolution metrology for the evaluation of new materials and processes for structural features expected to be smaller than 100 nm in size.

Local Polymer Dynamics

Current photoresists use a photogenerated acid catalyzed deprotection reaction on the polymer to produce a solubility change in exposed areas. The local, atomic-level, dynamics of the photoresist polymer directly affect transport processes essential to modern photoresists, such as the diffusion of photogenerated acids and other small molecules within the polymer matrix. To date, changes in the local dynamics of polymer thin films have been inferred from changes in macroscopic quantities such as the apparent glass transition temperature,  $T_g$ , as a function of film thickness and substrate interaction energies. Direct measurements of the segmental motions of polymer chains confined to ultrathin films will provide a molecular picture of observed changes in these macroscopic quantities and insight into differences in photoresist transport processes in ultrathin films. By using different polymers and polymer/substrate combinations, we obtain crucial insight into the dynamical effects of polymer thin-film confinement.

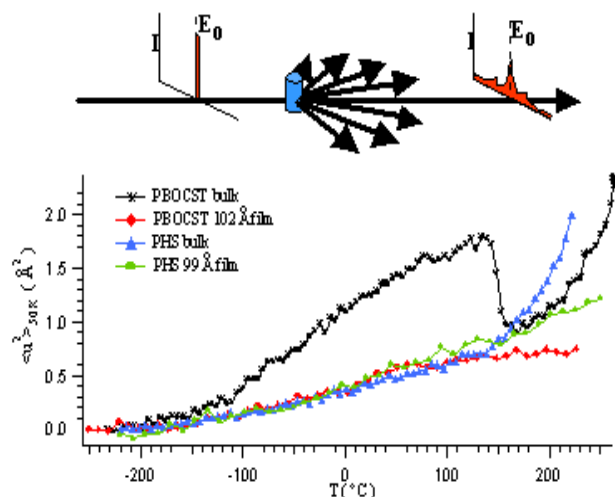


Figure 2. Mean-square displacement,  $\langle u^2 \rangle$ , as a function of temperature for a protected polymer (PBOCSt) and a deprotected polymer (PHS) for both the bulk material and 10-nm films.

Incoherent neutron scattering at the NCNR High Flux Backscattering Spectrometer was used to directly probe the atomic and segmental motions of polymer films as thin as 75  $\text{\AA}$  on silicon substrates for the first time. This technique characterizes motions on a frequency scale of 200 MHz or faster in terms of a mean-square-displacement  $\langle u^2 \rangle$ . We find that thin-film confinement generally diminishes  $\langle u^2 \rangle$ , irrespective of the polymer/substrate interactions. The degree to which  $\langle u^2 \rangle$  is suppressed appears to depend on the level of vibrational anharmonicity in the polymer. Strongly anharmonic polymers show larger decreases in  $\langle u^2 \rangle$ , particularly below the bulk  $T_g$ . For example, the protected (before exposure) photoresist polymer shows a high level of mobility (large  $\langle u^2 \rangle$ ) below the glass transition that is suppressed strongly by confinement. However, the deprotected version of this polymer shows a much lower level of sub- $T_g$  mobility (primarily harmonic motions) with very little effect from confinement (Figure 2). The markedly different behavior between related polymers provides important insight into the dependence of photoresist properties on the chemical structure of the polymer, information important to photoresist designers.

*“The continuous miniaturization of semiconductor devices poses many challenges to lithography...One of these challenges is to measure precisely the size, shape and quality of the circuit patterns. The SANS method is a new technique to measure lithographic patterns [and] capitalizes on the unique capabilities at NIST...”*

Q. H. Lin—IBM T. J. Watson Research Center

*“The gate CD [critical dimension] control requirements for the 130-nm node and below are also among the most difficult challenges [for lithography]. Advances in process control, resist materials, line edge roughness and metrology will be necessary to achieve less than 10-nm CD control.”*

1999 International Technology Roadmap for Semiconductors.

For More Information On This Topic:

E.K. Lin, C.L. Soles, W.L. Wu (Polymers Division, NIST)

Wu, W.L., Lin, E.K., Lin, Q.H., Angelopoulos, M. “Small Angle Neutron Scattering Measurements of Nanoscale Lithographic Features,” *J. Appl. Phys.*, 88, 7298 (2000).

Soles, C.L., Lin, E.K., Lenhart, J.L., Jones, R.L., Wu, W.L., Goldfarb, D.L., Lin, Q., Angelopoulos, M. “The Effects of Thin-Film Confinement on the Thermal Properties of Typical Deep-UV Photoresist Resins,” submitted to *J. Vac. Sci. Tech. B.* (2001).

## Polymer Mass Distribution by Mass Spectrometry

*Molecular mass distribution is the characteristic that most affects processing and properties of polymers. However, in absence of absolute methods for measuring mass distribution, methods that require calibration must be used. Owing to the lack of suitable calibration standards for most polymers, alternative methods of determining mass distribution are sought. Mass spectrometry is an absolute method for determining mass of molecules of essentially single mass. With recent advances the method may work for synthetic polymers, as well, provided that the signal strength depends on mass in a predictable manner. An inter-laboratory comparison of analysis of polystyrene by mass spectrometry has been completed with the objective of assessing the current status of the method and evaluation of how moments of the measured mass distribution compare to those determined with classical methods.*

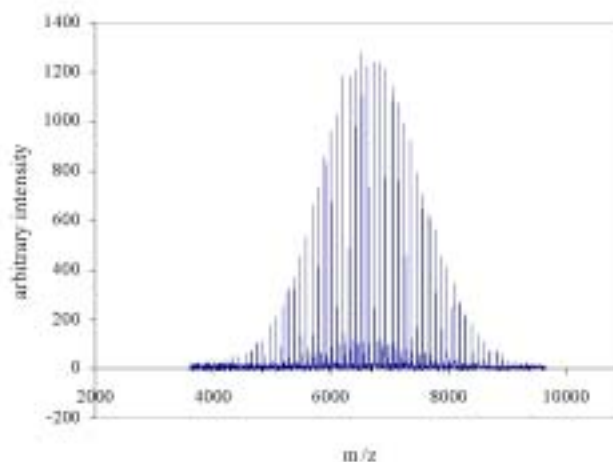
Matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS) is a new method of polymer analysis that works well for biopolymers, proteins and nucleic acids, that are essentially of single mass (excluding isotopic effects). The situation is quite different with synthetic polymers owing to the presence of a distribution of masses that not only spreads the signal over a range of masses corresponding to the polymer's mass distribution, but also invokes questions of how the signal at the detector is affected by having a distribution of masses. As preliminary to developing a research program that addresses issues of how sample preparation, laser intensity, instrument parameters and detector response may be affected by mass distribution, NIST organized and led an inter-laboratory comparison to determine the current status of measurements and began a dialog on quantitative mass spectrometry of synthetic polymers.

The inter-laboratory comparison was designed in consultation with the American Society of Mass Spectrometry Working Group on Synthetic Polymers. Membership in this special interest group represents many industrial laboratories, including those of major producers of synthetic polymers. Samples of well-characterized low-molecular mass polystyrene were sent to any institution requesting it.

The polystyrene was custom synthesized to specifications provided by NIST to insure that the number average molecular mass could be determined by high-resolution nuclear magnetic resonance (NMR) and the mass average molecular mass by light scattering. These values by classical methods were used to compare moments calculated from the MALDI mass spectrum. One end of each polystyrene molecule contained a t-butyl group that was not only detectible by NMR but also was useful in assessing the quality of end group determinations by MALDI MS.

A total of 23 institutions participated in the inter-laboratory comparison (10 industrial, 9 academic and 4 government laboratories). NIST Polymers Division also characterized the polymer by NMR for  $M_n$  and by light scattering for  $M_w$ .

Fourier transform infrared spectroscopy confirmed the presence of the t-butyl end group, as anticipated by the synthesis method. Size exclusion chromatography was used to insure vial-to-vial homogeneity in the samples distributed to participants. Each participating laboratory was asked to perform MALDI mass spectrometry using two distinct protocols, one prescribed and the other left to the discretion of the participants.



**Figure 1. Mass spectrum of polystyrene used in interlaboratory comparison by MALDI MS.**

Participants were instructed to report their mass spectra as well as moments of the mass distribution. The latter request was used to assess the status of analysis software, which is largely provided by MALDI MS instrument manufacturers.

Analysis of the moments reported by the participants revealed inconsistencies among laboratories in calibrating instruments. These inconsistencies also affected determinations of end group mass. By compiling all the reported spectral data (as opposed to reported moments) using both protocols into one analysis it was found that MALDI ToF MS returned an  $M_n$  of  $(6610 \pm 100)$  g/mole and an  $M_w$  of  $(6740 \pm 90)$  g/mole, uncertainties are standard uncertainties. These numbers were below those of the classical methods, but still within the overlapping uncertainty ranges. Detailed results of this study have been recently published in *Analytical Chemistry*.

The polystyrene used in the inter-laboratory comparison will be available as Standard Reference Material (SRM) 2888, certified for mass average molecular mass by light scattering. The NMR determined number average mass and the MALDI MS data, including the full mass spectrum, will also be available as supplemental data. This is the first polymer molecular mass standard to have its mass distribution presented. Although polystyrene calibrants for gel permeation chromatographs are readily available, this new polystyrene SRM demonstrates the potential of MALDI MS for mass distribution measurements in synthetic polymers.

The establishment of a standard method for determination of mass distribution by MALDI MS will facilitate its acceptance as a new method. Owing to the importance of mass measurements within the polymer industry, analytical laboratories that serve the industry and research laboratories in general, an effort was initiated to develop a standard measurement protocol for mass measurements by MALDI MS. A new technical working activity, TWA 28, was formed under the auspices of VAMAS, the Versailles Project on Advanced Materials and Standards. Laboratories in five countries, Canada, Italy, Germany, Japan and the United States are engaged in developing a measurement protocol for analysis of the mass distribution of polystyrene by mass spectrometry. The framework of the proposed measurement method will be the sample preparation and measurement outline used in the inter-laboratory comparison augmented to reflect knowledge gained in the analysis of the inter-laboratory comparison. Although the measurement uncertainty of the inter-laboratory comparison was much less than common with classical methods no estimate could be made of systematic uncertainties, type B.

An assessment will be made of possible sources of systematic uncertainty. Collaborative research will be undertaken to reduce sources of uncertainty, where possible.

*“NIST develops standards for MS of polymers...important because mass distribution of synthetic polymers affects processing and properties.”*

*C & E News 6/11/2001*

### For More Information On This Topic:

C.M. Guttman, B.M. Fanconi (Polymers Division)

Guttman, C.M., Wetzel, S.J., Blair, W.R., Fanconi, B.M., Girard, J.E., Goldschmidt, R.J., Wallace, W.E., VanderHart, D.L. NIST-Sponsored Interlaboratory Comparison of Polystyrene Molecular Mass Distribution Obtained by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry: Statistical Analysis. *Analytical Chemistry*, 2001, 73, 1252-1262.



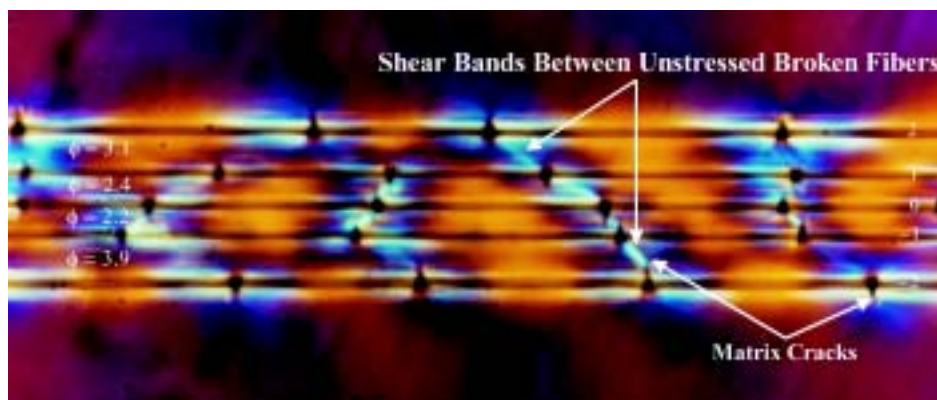
## Multi-Fiber Failure Propagation

*With the increasing use of advanced composites in structural applications, understanding how to predict and manage failure in composite structures has become a critical problem. As noted by the Automotive Composite Consortium, there is a major need to generate relevant materials property data that can be used in a computational program by design engineers to predict composite performance. In response to this need, test methodologies and a tow-based modeling program are being developed to facilitate the seamless integration of critical materials data into composite analyses.*

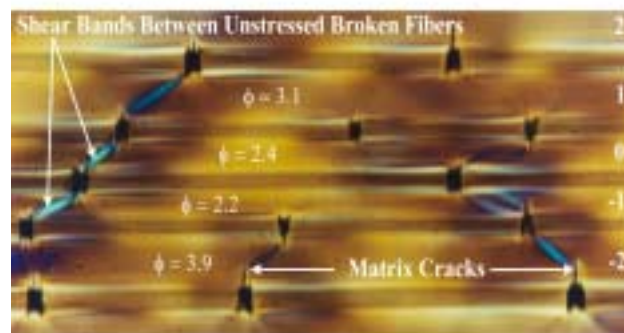
The implementation of advanced materials in structural applications is often hampered by the inability of the design engineer to predict reliably failure behavior, failure strength, fatigue behavior, energy absorption characteristics, and mechanical response of the composite part to multi-axial loading conditions. Because of their complex architecture, composites are analyzed on many different scales, with micro-mechanics and macro-mechanics being two broad classes. Micro-mechanics provides information about non-averaged localized properties (e.g., constituent deformation and stresses and localized failure behavior—fiber, matrix and interphase). Qualitatively these localized properties have been shown to strongly influence the performance properties of the composite. In contrast, macro-mechanics analyses, which are used at the lamina level and higher, use average strength and stiffness properties and failure criteria defined by average stresses and overall lamina strengths. Although the latter approach is computationally expedient, it fails to predict the effect of microstructure changes on composite failure behavior.

The goal of our work is to provide the necessary links between macro-mechanics approaches and micro-mechanics properties. For reliable prediction of composite performance properties, non-averaged micro-mechanics properties that account for the composite environment must be included, while keeping the computational process tractable. The microstructure of the composite lamina is being used to guide the selection of appropriate micro-mechanics experiments and analysis techniques to obtain micro-mechanics parameters. Initially, we use 2-D multi-fiber arrays in experiments to quantify the interaction between fibers during fiber fracture, constituent deformation behavior in the composite environment, and the localized failure behavior of the fiber, matrix and interphase region.

Results are shown in Figures 1 and 2, where fiber fractures with debonding and associated matrix crack formation are illustrated for a 2-D multi-fiber array composed of E-glass fibers embedded in diglycidyl ether of bisphenol-A (DGEBA) epoxy resin cured with meta-phenylene diamine (m-PDA). Although the interfiber spacing,  $\phi$ , is less than

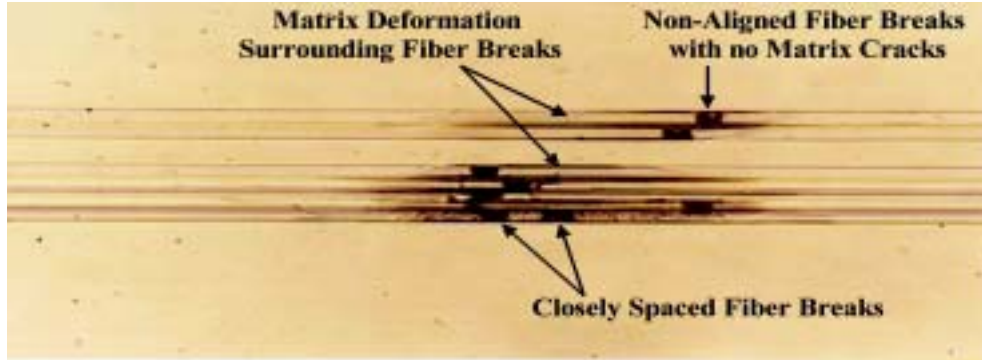


**Figure 1.** Fiber break patterns from E-glass/DGEBA/m-PDA 2-D multi-fiber array immediately after removing stress. The interfiber spacing is denoted by  $\phi$ .



**Figure 2.** Fiber break patterns from E-glass/DGEBA/m-PDA 2-D multi-fiber array 24 h after removing stress. The interfiber spacing is denoted by  $\phi$ .

four fiber diameters in the array, the fiber breaks in adjacent fibers are not aligned vertically as predicted by theory. Computational predictions indicate that the stress overload in adjacent fibers is smaller for non-aligned breaks. Hence, the composite toughness is predicted to be higher. The mechanism(s) that generates the non-alignment of fiber breaks, however, is not well understood. The change in contrast between Figure 1 and Figure 2 visually represents the stress relaxation in the viscoelastic matrix after a period of 24 h. The persistent hue after 24 h between fiber breaks in adjacent fibers is permanent defor-



**Figure 3. Fiber break patterns and matrix deformation in E-glass/DGEBA/m-PDA 2-D multi-fiber array (unstressed and fibers touching).**

mation. Although the origin of these deformation regions are not clearly understood, 45-degree deformation bands emanating from the matrix cracks during the test under tensile conditions have been observed.

Using the same constituent composition, fiber fracture in a multi-fiber specimen with the fibers touching is shown in Figure 3. In this specimen, matrix crack formation has been suppressed, and clustering of the non-aligned fiber breaks is observed. The extensive matrix damage around the fiber breaks occurred when the applied stress on the specimen was removed. However, the absence of this type of deformation in the non-touching 2-D array (Figure 3), suggests that the matrix deformation is higher surrounding the fiber breaks in the touching fiber specimen. In addition, this matrix damage along with the location of each fiber break has been observed by optical coherence tomography (OCT).

Capitalizing on the ability of OCT to see changes in the deformation state in the resin, residual stresses have been observed in 2-D multi-fiber specimens. These stresses may influence the observed failure behavior.

In previous research on single-fiber specimens we have noted that the matrix is non-linear viscoelastic. However, reconciling this effect with the occurrence of brittle fracture in composite specimens has been problematic. A 2-D multi-fiber array specimen was taken in several steps to a strain level that induces fiber fracture. During a period of

5 min, numerous non-aligned fiber breaks occur in the observation region, reflecting the role that the matrix has on the stress redistribution process in adjacent fibers after fiber fracture (See video at website: <http://polymers.msel.nist.gov/researcharea/multiphase/project-detail.cfm?P2D=56>). At the end of this period the specimen fails in a brittle manner away from the

observation region. This video indicates that the nucleation of the critical flaw that induces brittle composite failure may be time dependent and controlled by the viscoelastic matrix and the mode of interphase failure that accompanies fiber fracture.

*“...understanding how to manage the dissipation of energy in composite structures during crash conditions has become critical problem. The goal is to meet or exceed the standard that has been set by steel.”*

Nancy L. Johnson  
Director for Focal Project 3–ACC  
Vehicle Analysis and Dynamics Lab–GM

*“Although DOE and others are doing crash energy management modeling, computational models that accurately predict energy dissipation during crash scenarios are still lacking.”*

Raymond G. Boeman, Ph.D.  
Automotive Composites Specialists  
Oak Ridge National Laboratory

**For More Information  
On This Topic:**

G.A. Holmes, W.G. McDonough, C.C. Han (Polymers Division, NIST)

See website: <http://polymers.msel.nist.gov/researcharea/multiphase/project-detail.cfm?PID=56>

## Biocompatibility of a Moldable, Resorbable, Composite Bone Graft

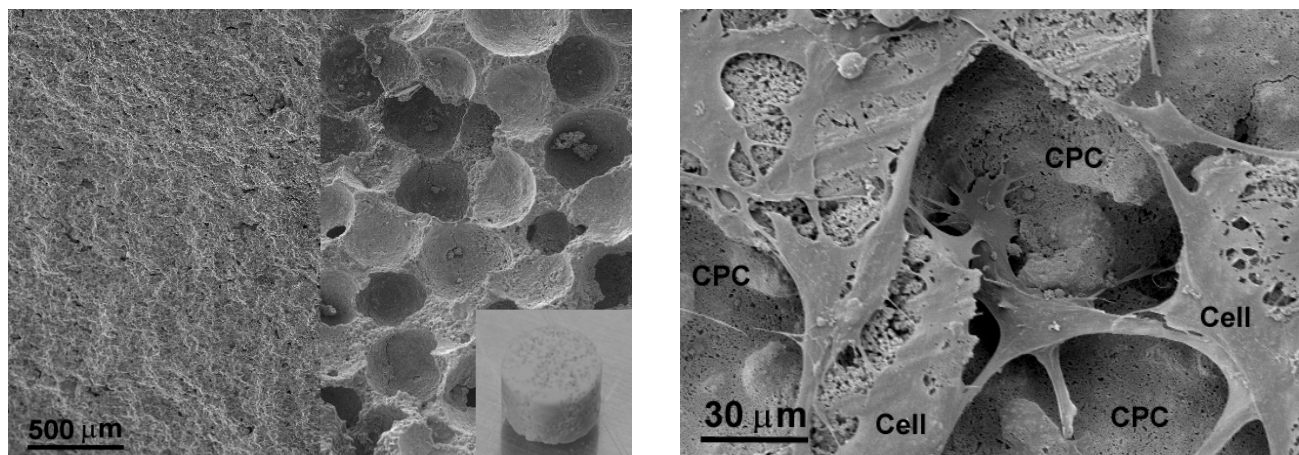
*The blessing of living longer is accompanied by the burden of aging. There is an overall risk of fractures of the hip, spine and distal forearm that will afflict 40 percent of women and 13 percent of men 50 years of age and older. Restoring form and function to bone defects in an elderly, osteoporotic population of more than 52 million Americans, over the age of 65 by the year 2020, will be a daunting challenge. To meet this challenge, scientists from the Polymers Division and the American Dental Association Health Foundation have used polymers, calcium phosphates and growth factors to develop a biodegradable composite bone graft for bone regeneration. The composite bone graft was found to be biocompatible and to release at a controlled rate a growth factor that stimulates bone regeneration.*

Over 100,000 bone grafts are performed each year in the United States, but the amount of available autologous bone is limited and available material is difficult to shape. Thus, the development of a synthetic, moldable bone graft material is a primary goal of the tissue engineering industry. A self-setting calcium phosphate cement (CPC) that can be sculpted to fit the contours of a wound and consists of dicalcium phosphate and tetracalcium phosphate was designed by co-workers from the American Dental Association Health Foundation at NIST. We sought to improve this cement by making it macroporous and osteoinductive through inclusion of polymer microspheres and a bone growth factor, respectively.

We have assessed the biocompatibility of the macroporous composite bone graft (CPC polymer) consisting of self-setting calcium phosphate cement and biodegradable polymer microspheres (175  $\mu\text{m}$ –355  $\mu\text{m}$  diameter) using cell culture techniques. CPC powder was mixed with polymer microspheres and water to yield a workable paste. The cement then hardens into a matrix of hydroxyapatite microcrystals containing polymer microspheres. The rationale for this design is that the microspheres will stabilize

initially the graft, but then can gradually degrade, functioning as a ‘polymer porogen’ to leave behind macropores for colonization by osteoblasts. The CPC matrix then potentially could be resorbed and replaced with new bone.

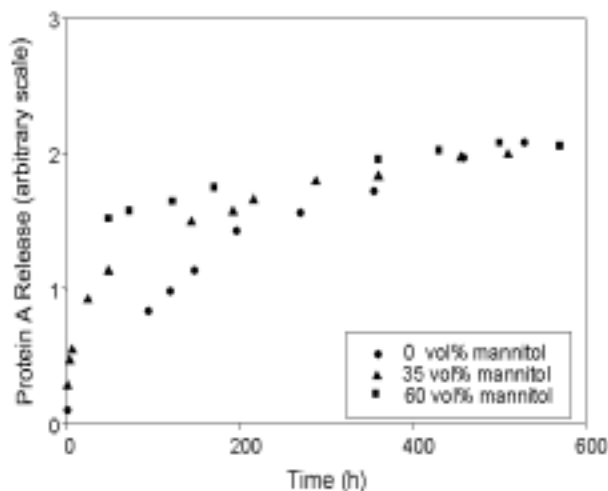
In the present work, osteoblast-like cells (MC3T3-E1 cells) were seeded onto control CPC (CPC cement only, without polymer microspheres) or CPC-polymer specimens and evaluated with fluorescence microscopy (live-dead stain), scanning electron microscopy (SEM), environmental scanning electron microscopy (ESEM) and the Wst-1 assay (a colorimetric, enzymatic assay for mitochondrial dehydrogenase activity). Examples of data are shown in Figures 1–3. Cells were able to adhere, attain a normal morphology, proliferate, and remain viable when cultured on the new composite graft (CPC-polymer) or on the control graft (CPC alone). These results suggest that our new cement consisting of CPC and polymer microspheres is biocompatible. This is first time that a ‘polymer-in-mineral’ (polymer microspheres dispersed in a CPC matrix) cement has been formulated that is moldable, resorbable and that can form macropores after the cement has set.



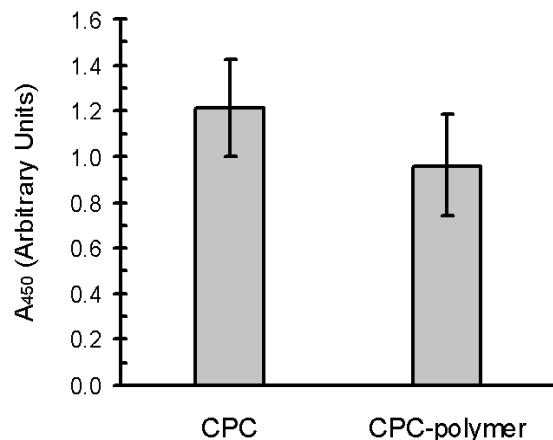
**Figure 1 (left):** SEM of the interior of CPC without polymer microspheres (left half) or with polymer microspheres (right half). The specimens were aged for 3 months in cell media to allow complete degradation of the polymer microspheres. Macropores (175  $\mu\text{m}$ –355  $\mu\text{m}$  in diameter) formed by the degradation of the polymer microspheres are visible in the right half panel. The inset is a larger view of the entire CPC-polymer specimen (6 mm in diameter by 4.5 mm in height). **Figure 2 (right):** SEM of cells cultured overnight on a CPC specimen which shows that cells can adhere and maintain a normal morphology when cultured on the cement. “Cell” indicates the cells and “CPC” indicates the cement.

Additionally, we have improved the CPC by providing controlled release of an osteoinductive protein, transforming growth factor- $\beta$ 1 (TGF- $\beta$ 1). Initial release studies using a model protein (fluorescein-labeled Protein A) showed that protein release kinetics could be modulated by adjusting the amount of a porogen (mannitol) included in the CPC (Figure 4). More recent studies have used TGF- $\beta$ 1 (Figure 5) in a composite of CPC with salicylic acid as the porogen. In addition, release kinetics have been studied in CPC-containing biodegradable polymers as porogens, similar to the CPC-polymer described above. These studies have shown that release kinetics can be governed not only by the volume fraction of the porogen, but also by the composition of the porogen included in the cement (mannitol, salicylic acid or degradable polymer). These data have garnered interest from several biotechnology companies that focus on the development of bone grafts.

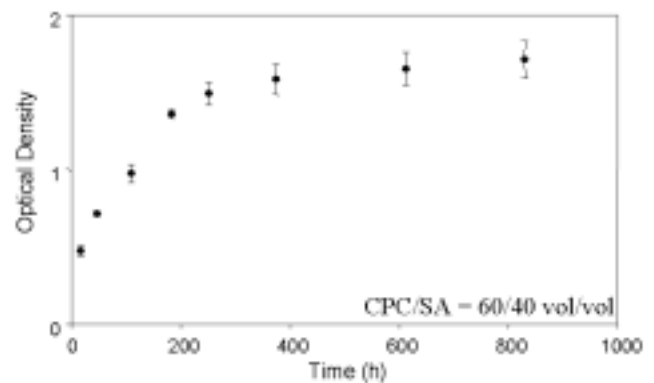
*The “polymer-in-mineral formulation is what separates” this cement “from the prior mineral-in-polymer formulations”—Reviewer for Journal of Orthopaedic Research*



**Figure 4:** Release of fluorescein-labeled Protein A into phosphate-buffered saline at 37 °C from CPC/mannitol composite containing varying volume % of mannitol.



**Figure 3:** Wst-1 assay for cells cultured 2 weeks on CPC and CPC-polymer specimens. The enzyme reaction was quantitated by measuring the absorbance (450 nm) of the reaction wells and shows that the amount of dehydrogenase activity (which is proportional to cell number) present on CPC specimens is statistically the same as that found on specimens of CPC and polymer microspheres (CPC-polymer).



**Figure 5:** Release of TGF- $\beta$ 1 into phosphate-buffered saline at 37 °C from CPC/salicylic acid composite.

**For More Information  
On This Topic:**

F.W. Wang, C.G. Simon, Jr., C.A. Khatri (Polymers Division, NIST)

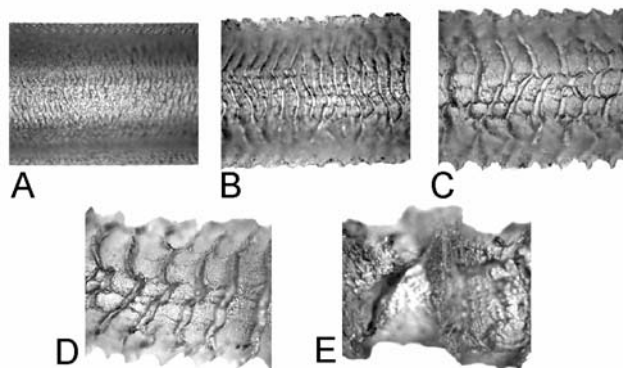
Wang F.W., Khatri C.A., Hsui J.F., Hirayama S., Takagi S. (2001) Polymer-filled calcium phosphate cement: mechanical properties and protein release. *J. Dent. Res.* 80:591.

Simon, Jr., C.G., Khatri C.A., Wight S.A., Wang F.W. (2001) Preliminary Report on the Biocompatibility of a Moldable, Resorbable, Composite Bone Graft Consisting of Calcium Phosphate Cement and Poly(lactide-co-glycolide) Microspheres. *J. Orthoped. Res.*, submitted.

## The Mechanism of Sharkskin

*The rate limiting step in the manufacture of several important classes of polymeric materials is an extrusion instability known as “sharkskin” in which the manufactured plastic has a rough surface containing a repeated pattern of ridges. This roughness causes a loss of clarity and a loss of ability to control final part size. Studied since the second world war, the cause of sharkskin remains an unsolved problem. Here we use the NIST Extrusion Visualization Facility to capture the step-by-step kinetics of this extrusion instability. We are thus able to determine which of the proposed causes of sharkskin is actually responsible.*

Over the past 50 years, there has been sustained interest in the understanding and control of instabilities that occur upon pressure driven extrusion of molten polymers. These instabilities limit the manufacturing rate and the materials selection in continuous forming operations, such as sheet extrusion. Processors are forced to sacrifice final mechanical properties to achieve greater processability. From the scientific point of view, the understanding of these instabilities is challenging; despite much progress, fundamental issues remain unresolved. An understanding of the cause of sharkskin would enable a more rational design of materials in order to eliminate it.



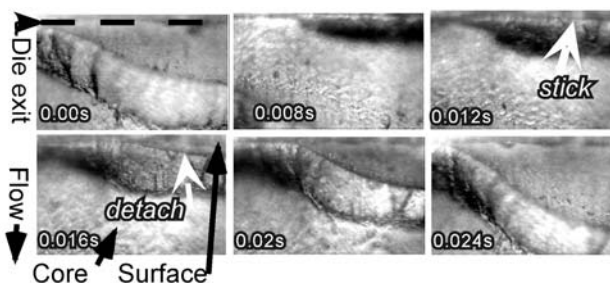
**Figure 1:** As the extrusion rate increases, the final product becomes progressively distorted. (A) through (D) are known as sharkskin and (E) is known as gross melt fracture.

In the case of extrusion through a capillary die, at sufficiently low extrusion rates, the polymer’s surface is smooth as it exits from the die. At progressively higher extrusion rates, a series of flow instabilities occurs. The first instability that may occur is known as sharkskin or sharkskin melt fracture and is characterized by surface roughness. At higher extrusion rates, one observes an oscillating stick-slip transition, followed at higher rates by gross melt fracture in which the polymer is extruded in an extremely irregular fashion. The occurrence of the instabilities is dependent on many factors, including polymer chemistry, molecular architecture, molecular mass and distribution and polymer/wall surface interactions.

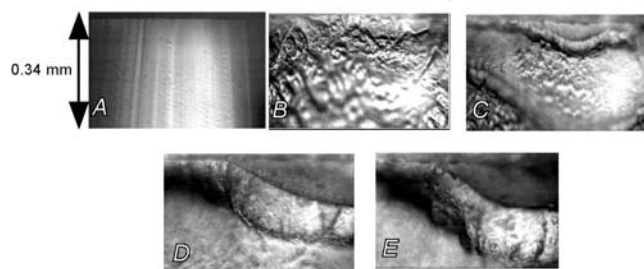
In this work we focus on the sharkskin instability. The driving force behind the attempts to understand sharkskin is that linear polyethylene of narrow molecular mass distribution particularly is susceptible to this instability. As this instability occurs at relatively low-extrusion rates, it is troublesome. The subject has received renewed attention because newer metallocene-based polyethylene offer advantages in mechanical properties, but often suffer from this extrusion instability. There have been numerous suggestions for the mechanism of sharkskin and for an elucidation of the conditions that produce it.

In 1977 it was suggested that sharkskin is caused by a tearing of the polymer at the exit lip due to the high extensional flow forces generated at this point. Under these conditions, the extensional stress exceeds the cohesive strength of the molten polymer. In an alternative picture, the material undergoes cavitation just inside the tube, causing sharkskin. Others have suggested that sharkskin is due to an unstable flow boundary condition that oscillates between stick and slip. These models (and several others not mentioned for reasons of space) all make specific predictions about the nature of the polymer flow field. Of particular relevance is the question of whether or not the polymer sticks to the wall during sharkskin, or if it slips.

The aim of these experiments is to distinguish among the various possibilities described above. Many of these models can be tested through a combination of micro-velocimetry, optical imaging, and surface modification through fluoropolymer additives. We further conduct experiments under conditions of maximum industrial



**Figure 2:** High-speed video microscopy reveals that the polyethylene splits into a core region and a surface region as it exits the capillary tube.



**Figure 3: High-speed images of the exit region as the extrusion rate increases. Figures (B–E) correspond to (A–D) in the first image sequence (Figure 1).**

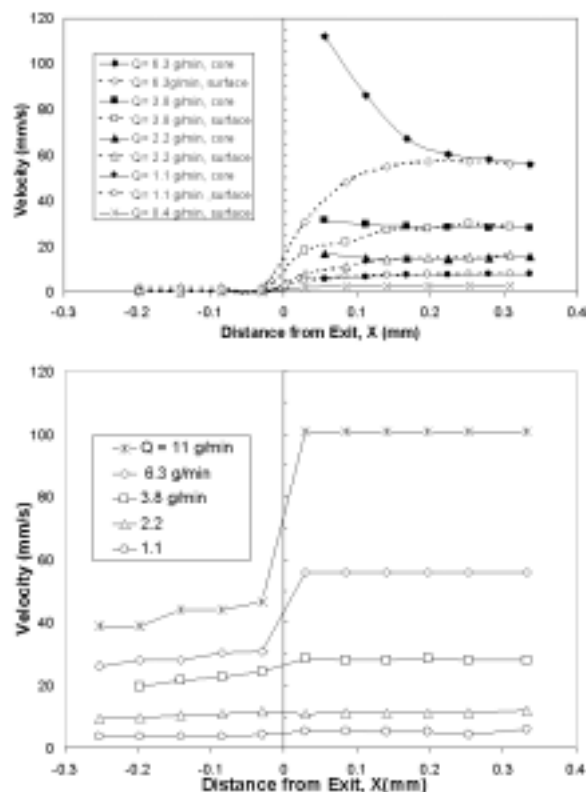
relevance by use of polyethylene processed by twin-screw extrusion.

In one set of experiments, we use high-speed video microscopy to monitor the kinetics of the flow discontinuity outside the die (Figure 2). We found that the polyethylene material splits cohesively into a slow moving surface region and a fast moving core region, the latter contains the majority of the material. The surface region bulges upwards and then breaks off from the exit lip.

When we monitor the flow kinetics inside the capillary tube, we find that the flow kinetics is smooth, even well above the onset of the sharkskin instability. Unsteady flow conditions are observed only under shear stresses close to that of gross melt fracture. Significantly, we find that sharkskin can occur under conditions of both stick and slip. This observation helps to reconcile many years of debate on the question of whether stick or slip boundary conditions prevail during sharkskin. We find that either one is possible, as long as the critical stress at the exit is exceeded!

A crucial test of exit stretching as a cause of sharkskin was done by comparing the onset of sharkskin in resins with and without a fluoropolymer additive. We found that the extensional deformation rate was comparable at the onset; the first parameter that has shown to correlate with the onset of sharkskin.

Now that we understand the mechanistic aspects of the instability, we can concentrate on material related questions. For example, why does long-chain branching and molecular mass distribution affect this instability, and why related materials (such as polypropylene) suffer much less from this instability?



**Figure 4: Flow velocimetry inside the tube ( $x < 0$ ) and outside it ( $x > 0$ ) is shown for the case of the bare surface (upper plot) and in the case of a fluoropolymer additive (lower).**

*“Our experiments with NIST using their Extrusion Visualization Facility have resulted in breakthroughs in our abilities to conceptualize and understand how fluoropolymers reduce sharkskin. These measurement tools strongly impact our efforts in new product development.”*

Claude Lavallée  
3M Canada Company

**For More Information  
On This Topic:**

K.B. Migler

Migler, K.B., Lavallée, C., Dillon, M.P., Woods, S.S., Gettinger, C.L., Visualizing the elimination of sharkskin through fluoropolymer additives: Coating and polymer-polymer slippage, *Journal of Rheology* 45, 565-581 (2001).



# Combinatorial Methods

The Combinatorial Methods Program develops new measurement techniques and experimental strategies needed for rapid acquisition and analysis of physical and chemical data of materials by industrial and research communities. A multi-disciplinary team from the NIST laboratories participates to address key mission driven objectives in this new field, including needed measurement infrastructure, expanded capability, standards and evaluated data.

Measurement tools and techniques are developed to prepare and characterize materials over a controlled range of physical and chemical properties on a miniaturized scale with high degree of automation and parallelization. Combinatorial approaches are used to validate measurement methods and predictive models when applied to small sample sizes. All aspects of the combinatorial process from sample “library” design and library preparation to high-throughput assay and analysis are integrated through the combinatorial informatics cycle for iterative refinement of measurements. The applicability of combinatorial methods to new materials and research problems is demonstrated to provide scientific credibility for this new R&D paradigm. One anticipated measure of the success of the program would be more efficient output of traditional NIST products of Standard Reference Materials and evaluated data.

Through a set of cross-NIST collaborations in current research areas, we are working to establish the infrastructure that will serve as a basis for a broader effort in combi-

natorial research. A Combinatorial Methods Working Group (CMWG) actively discusses technical progress within NIST on combinatorial methods through regular meetings. The technical areas and activities of the CMWG are available in a brochure “Combinatorial Methods at NIST” (NISTIR 6730). Within MSEL, novel methods for combinatorial library preparation of polymer coatings have been designed to encompass variations of diverse physical and chemical properties, such as composition, coating thickness, processing temperature, surface texture and patterning. Vast amounts of data are generated in a few hours that promote our understanding of how these variables affect material properties, such as coatings wettability or phase miscibility. Additional focus areas for both organic and inorganic materials include multiphase materials, electronic materials, magnetic materials, biomaterials assay, and materials structure and properties characterization. State-of-the-art on-line data analysis tools, process control methodology, and data archival methods are being developed as part of the program.

In order to promote communication and technology transfer with a wide range of industrial partners, an industry-national laboratories-university combinatorial consortium, the NIST Combinatorial Methods Center (NCCM) is being organized by MSEL. The NCCM will facilitate direct interactions on combinatorial measurement problems of broad industrial interest and efficient transfer of the methods developed to U.S. industry.

**Contact Information: Alamgir Karim**



## High-Throughput Measurements of Crystallization and Nucleation in Polyolefins

Kathryn L. Beers, Alamgir Karim

The ability to direct or suppress order in polymeric thin films has many practical implications for industrial materials. In particular, the degree of crystallinity in semi-crystalline polymer films can be affected dramatically by a host of processing conditions such as solvents, thermal history, additives, etc. Developing a high-throughput method of screening these effects has the potential to quickly optimize the processing of materials, as well as probe many of the outstanding theoretical issues regarding the nature of polymer crystallization.

The gradient film technology developed at NIST presented itself as a promising solution. Concerns regarding the continuity of the films, however, prompted a general “proof of principle” test application. Hence, isotactic polystyrene, *i*PS, extensively a slowly crystallizing polymer, was investigated. In one continuous film, the crystal growth rates,  $G$ ,

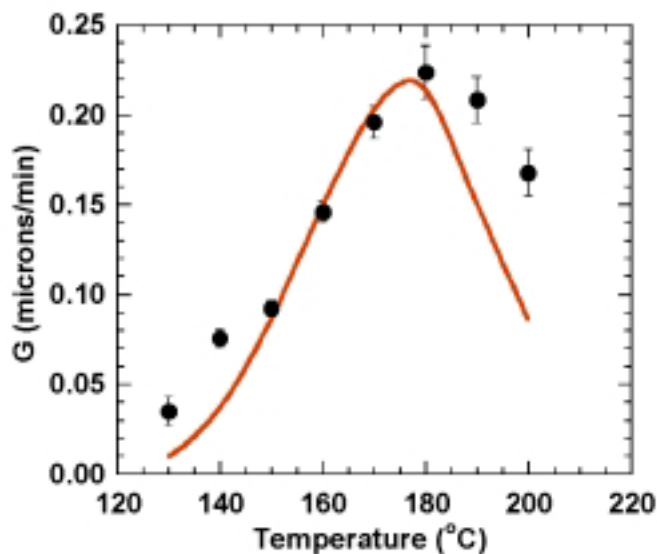


Figure 1. The measured rates,  $G$ , as a function of crystallization temperature,  $T$ . (Curve is data from J. Boon, *et al.*, *J. Polym. Sci., Pt. A-2*, 1968, 6, 1971.)

*The morphology and degree of crystallinity in semi-crystalline thin films has a dramatic impact on their performance factors such as stability, optical properties and conductivity. Since the parameter space governing this problem is large and the theoretical understanding of thin-film crystallization is limited, we study a model polymer (isotactic polystyrene) as well as isotactic polypropylene using combinatorial, high-throughput methods. The effects of film thickness, under-cooling temperature and nucleating agents are currently under investigation. The morphology and kinetics of spherulitic structure growth is investigated combinatorially.*

were measured as a function of temperature and film thickness, yielding data from one experiment, which previously would have required the preparation of dozens of discrete films.

The films were prepared using the gradient flow coating technique. Crystal growth was observed using a Nikon Optiphot optical microscope and crystal structure analysis was carried out using a Nanoscope Dimension Series atomic force microscope.

Because *i*PS crystallizes comparatively slowly, it is possible to study the kinetics over a wide range of temperatures, from just below  $T_m$  to close to the glass transition temperature,  $T_g$ . In this case, a span of 70 °C was typically covered (from 130 °C to 200 °C), a range in which it has been shown that the rate passes through a maximum between 175 °C and 180 °C. Good agreement was found in the high-throughput experiment on continuous films for these rates as a function of temperature (Figure 1). More recently, the effects of film thickness,  $h$ , on the rate of crystallization in *i*PS thin films were studied;  $G$  decreased with  $h$  below 50 nm. We observed a similar trend in the continuous films.

Under similar experimental conditions, isotactic polypropylene yields faster, more difficult to measure rates of crystallization; however, the dependence of morphology and degree of crystallization on common nucleating agents can be observed in conjunction with other parameters such as  $h$  and  $T$ . Films containing small amounts of nucleating agents, such as 4-biphenyl carboxylic acid, and ranging in thickness from 50 nm to 150 nm are currently under investigation in the temperature range from 100 °C to 150 °C.

These results validate the high throughput/combinatorial approach to investigating polymer crystallization in thin films, accelerating the pace of experimentation by increasing the parameter space available for sampling. Furthermore, the dependence of  $G$  on  $h$  and  $T$  was explored in two dimensions to a degree previously considered unfeasible.

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## Combinatorial Mapping of Polymer Film Wettability

Karen M. Ashley, Amit Sehgal,  
D. Raghavan, Alamgir Karim

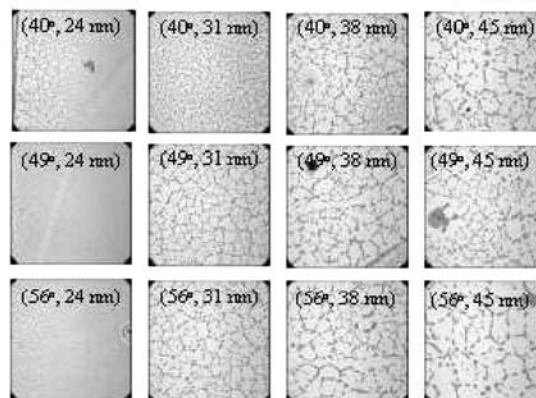
The ubiquitous use of polymer films in protective coatings, paints, inks, and adhesive layers relies on the ability of the polymer to spread effectively on or “wet” the underlying substrate. The advent of conducting polymers, molecular electronics, and polymers in the photonics and electronics industry, and the concurrent drive to smaller devices have further extended use of ultrathin films, where film stability is critical to the performance of the device. Conversely, a fundamental understanding of stochastic processes such as dewetting generates nano- to micro-scale surface structures that may be utilized for optical and biological applications.

Interfacial interaction of the polymer with the underlying substrate is one of the key parameters that influence the stability of thin polymer films. An approach to preparing gradient energy surfaces is developed, by immersing an Si-H passivated silicon wafer in Piranha solution ( $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ ) at a controlled rate, producing a monotonic variation of solvent (water and di-iodomethane) contact angles across the surface. As expected, regions of the substrate that had longer exposure to the Piranha solution and higher concentrations of  $\text{H}_2\text{SO}_4$  in the Piranha solution were more hydrophilic (lower water contact angles).

Thickness gradients of low molecular mass polystyrene were prepared on the chemical gradient wafers orthogonal to the surface energy dispersion using a velocity-gradient knife-edge coating apparatus. Film thickness ( $h$ ) of the coating was measured by automated spectroscopic spot interferometry producing contour maps of film thickness. Thus, a typical combinatorial library sample film is prepared to map efficaciously thin-film wettability.

Combinatorial sample libraries were screened by reflection optical microscopy for dewetting behavior. Composite images were obtained as shown in the figure, characterized by substrate water contact angle and initial film thickness of polystyrene given in parenthesis. Dewetting occurred by the growth of small circular holes whose rims impinge to form small polygons within 2 h of annealing time at 100 °C. We performed a quantitative analysis of the dewet structures by dividing the combinatorial library into a virtual

*The stability of thin polymer films is of primary significance not only in their extensive application as photoresists, paints and adhesives, but increasingly in electronic and photonic devices and in the biomedical industry. Knowledge of failure mechanisms of thin polymer film breakup, in the context of variables such as substrate surface energy, thickness and temperature, is crucial for their applicability. We use combinatorial methods to explore rapidly parameter space to map regions of film wettability and simultaneously further fundamental understanding of thin-film rupture.*



array of individual cells with varying contact angles and film thickness values. By using an automated batch program, the images were thresholded and the number of polygons determined.

The local polygon density ( $N_p$  per unit area in an image box) of dewetted polymer was found to obey a power-law relationship with film thickness ( $N_p \sim h^{-4.3}$ ) that is in agreement with reported literature value for ultra-thin films on strongly hydrophilic surfaces (spinodal-dewetting regime). After validating the high-throughput screening method by comparison to previous studies of thickness effect on dewetting, a novel power-law relationship between the water contact angle of the substrate ( $\theta_{\text{water}}$ ) and the number of polygons of dewetted polystyrene film at constant thickness was also established to be ( $N_p \sim \theta_{\text{water}}^{-3.6}$ ). These studies suggest that the late-stage dewet polymer pattern dimensions are critically sensitive to surface hydrophilicity and film thickness.

A more versatile and critical approach to preparing gradient energy surfaces is being developed by depositing chlorosilane self-assembled monolayers on silicon surface followed by exposure to UV radiation. Combinatorial libraries of a biocompatible polymer poly(DL-lactic acid), and phase separated blends with poly( $\epsilon$ -caprolactone) for use as patterned templates for cell proliferation studies are being investigated on these surfaces.

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# Anisotropic Adhesion Between Polymers, Metals, Ceramics and Biomaterials

Alfred Crosby, Alamgir Karim, Eric J. Amis

We have developed a combinatorial technique to investigate adhesive interactions between a polymer and another polymer, ceramic or metal. The primary goal in the development of this technique was to design a high-throughput, parallel processing adhesion test that allows the adhesive strength dependence on multivariable parameters and environmental conditions to be determined.

This combinatorial methodology for measuring polymer adhesion is largely built upon the theory of Johnson, Kendall, and Roberts (JKR), which facilitates the measurement of adhesive forces between two contacting surfaces. In the classical use of this theory, a hemispherical lens of one material is brought into contact with a complementary substrate, and subsequently separated. In our work, rather than using a single hemispherical lens, we use an array of microlenses. During this process, the contact area and displacement of each microlens is recorded through the use of an image acquisition system integrated with an optical microscope. With these parameters, the JKR theory can then be used to quantify the adhesion energy between the two contacting materials. Along each axis of the array, a gradient in different environmental parameters or material properties can be placed. Examples of such gradient properties are: surface energy, temperature, thickness, crosslink density, blend composition and strain. If two orthogonal

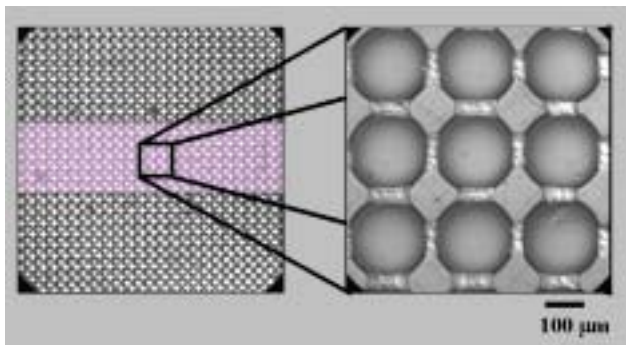


Figure 1: PDMS microlens used for combinatorial adhesion test.

*Polymer adhesion is important to numerous technologies including electronic packaging, coatings and paints, biomedical implants, and pressure-sensitive adhesives. Current methods for characterizing adhesion are either inefficient or ineffective. Here we develop and implement a combinatorial method to qualitatively and quantitatively map polymer interfaces to assess the dependence of anisotropic polymer adhesion on multivariable parameters. This technique allows us to not only identify optimal environments for the adhesion of given polymer interfaces, but also facilitates the fundamental investigation of how molecular structure and chemistry define adhesion.*

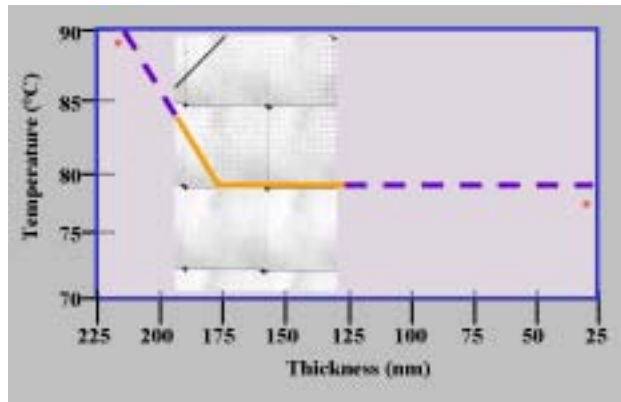


Figure 2. Temperature and thickness dependence on critical PS welding temperature.

gradients are placed on the array, then each microlens contact point will yield a measurement of adhesion for a unique combination of parameters. With our current microlens libraries, we are capable of measuring 1,600 different points of adhesion within a single test.

To demonstrate this methodology, we investigated the effect of thickness and temperature on the self-adhesion of polystyrene (PS). In this test, a microlens array was made from poly(dimethylsiloxane) (PDMS). Onto this PDMS array, we floated a thin layer of PS containing a thickness gradient. The complementary substrate for this test was a PS-coated silicon wafer with an applied temperature gradient. During contact, the PS molecules diffuse across the interface, entangle, and strengthen the interface, thus causing the PS coating of the PDMS microlenses to delaminate within the contact regions. This “welding” of the contact areas occurs above a critical temperature and below a critical thickness over the time scale of our test. This measurement is useful for the microelectronics industry where adhesion of thin polymer layers determine the integrity of electronic packaging, but the general technique will have impact on the numerous industries where adhesion plays a dominant role.

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## Patterned Polymeric Substrates for Directed Cell Growth

Amit Sehgal, Alamgir Karim, Eric J. Amis

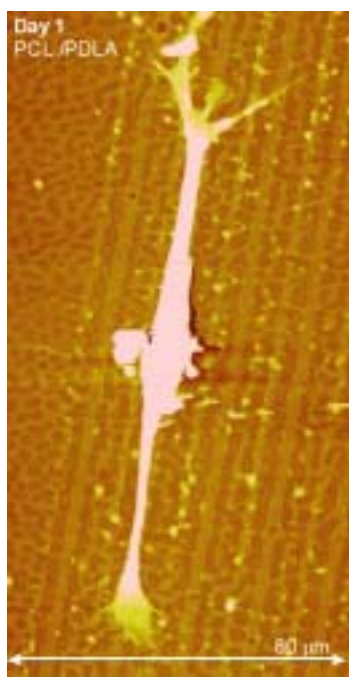
Cellular organization in tissue is guided by or even altered by the extra-cellular matrix, a heterogeneous complex environment, comprising of spatially distributed structural and functional components. We utilize blend phase separation to create novel multi-component biomimetic materials, where the intrinsic heterogeneity is exploited to build in structure and function. We are also motivated by the awareness that the biomedical industry is constrained to the use of relatively few materials approved by regulatory bodies, often compromising on the mechanical or the functional demands of the medical device. The use of blends of approved materials, where one component provides bioreceptive functionality while the other provides the structural reinforcement, greatly enhances the range of biocompatible materials available to the industry to improve ultimately the performance of medical devices. Further, we harness the physics of blend phase separation in confining geometries of thin films and chemically patterned substrates to create highly structured polymeric templates to guide and test cellular response.

Pattern-directed phase separation of polymer blends was used to create libraries of spatial distribution of bioreceptivity. The substrates are patterned chemically by soft

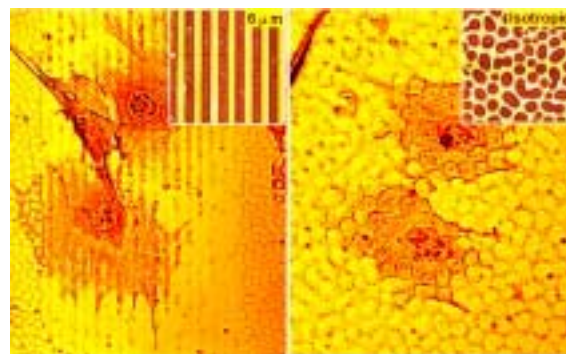
*The new paradigm for clinically relevant biomaterials is inspired by nature itself. The level of complexity inherent in the organization of tissue is extended to the design of biomaterials with a high level of control of surface functionality and topography. We combine the rich microstructure of polymer blends with tools such as surface patterning to create unique highly structured test-substrates for cell response. These surfaces have a systematic variation of spatial scales and properties across a single test-substrate to assay optimal structure for cellular reception in a high-throughput fashion.*

lithography to have a range of stripe pattern sizes on single test substrates. The self-organization of a biodegradable blend of poly( $\epsilon$ -caprolactone) [PCL] and poly(D-L lactic acid) [PDLA] on the chemical stripe patterns then generates a model blend substrate to correlate cell response to the scales of spatial distribution and size of the blend components. Here, the PCL comprises the semi-crystalline structural component while the PDLA is the more bioreceptive hydrophilic component.

Evaluation of response of osteoblast-like mouse calvarial (MC3T3) cells on the phase separated patterns shows anisotropic cell focal adhesion specifically to the PDLA rich phase where the underlying material anisotropy guides the preferential cell orientation (Day 1). This is followed by anisotropic liquid like cell spreading (Day 3) where the cell pseudopodia develop preferentially along the PDLA rich ridges. This behavior is also found in the non-patterned isotropic regions but the cell spreading is isotropic. It was also found that the periodicity of the focal adhesion is regulated by the underlying pattern frequency. The systematic variation of surface structure enables us to interrogate the effect on possible cytoskeletal rearrangement and regulation of specific pathways and ultimately guide cell function.



**Figure 1. Anisotropic cell adhesion on PCL/PDLA patterns.**



**Figure 2. Pattern directed cell spreading. (Day 3)**

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# Microwell Arrays for Laser Capture Microdissection (LCM)

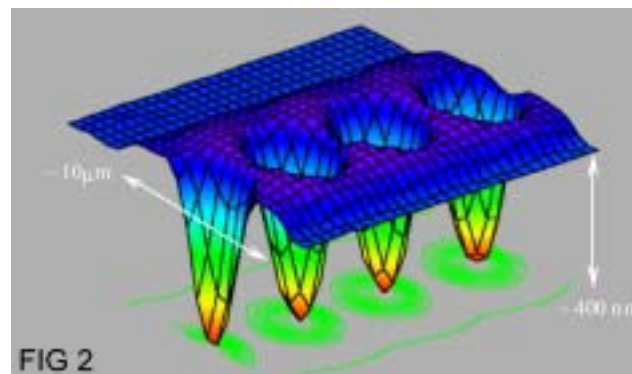
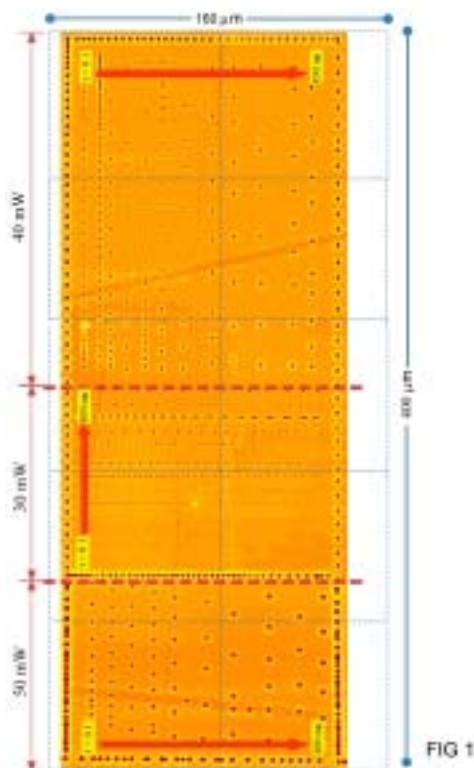
Giovanna Cantoni, Amit Sehgal,  
Robert F. Bonner, Alamgir Karim

*LCM was developed as a prototype research tool at the National Institute of Child Health and Development (NICHD) and the National Cancer Institute (NCI) of NIH. It refers to a microscope equipped with a laser to target and capture single cancerous cells from frozen tissue sections on a fusible polymer film. We have developed methods to augment the LCM by enabling encapsulation of the captured cells in microwells of femtoliter ( $10^{-15}$  L) volumes with minimal dilution enabling in-situ single cell analysis. We demonstrate the use of combinatorial methods for mapping parameter space for laser-induced microfabrication of microwell arrays.*

LCM was designed to target specific cell populations (cancerous cells) from tissue sections to study genetic mutations without “contamination” from surrounding (healthy) tissue. Resuspension in aqueous media however limits analysis of the extracted DNA, RNA and proteins from the captured cells due to high levels of dilution. This motivates encapsulation of captured cells in tailor-made microwells with femtoliter volumes preserving high macromolecular concentrations with increased sensitivity enabling new detection and in-situ analysis methods.

Our method of laser-induced fabrication simply employs the use of an absorbing dye in a thin polymer films creating thermally induced microchannels and microwells. Given the

range of variables (laser power, pulse duration, spot size, film thickness, dye concentration, thermal conductivity of the film, substrate, etc.) we resort to combinatorial methods for high-throughput mapping of microfabrication parameters. An example of high-throughput characterization (Figure 1) of a grid of programmed contiguous atomic force microscopy scans of a microwell array maps the effect of laser power and pulse duration on critical microwell dimensions while other parameters (dye concentration, thickness) on a single surface are held constant. The wells form ideal receptacles for captured dried tissue (Figure 2).



The thermally induced fabrication process is extremely sensitive to the thickness of the insulating polymer film or proximity to the thermally conductive glass substrates. Section profiles confirm the expected increase in depth with pulse duration that becomes constant as the well nears the polymer glass interface. This suggests an ablative process that ceases as thermal conduction to the glass lowers the peak surface temperature of the depleting polymer layer. An opposing effect was discovered at lower laser powers, suggesting a non-ablative mechanism whereby a locally fused film (lower peak temperatures) buckles to form a meniscus due to the differential in surface tension of the fluid and the surroundings. This process allows for a novel method for structuring thin films without chemical modification (oxidation or etching).

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## Tissue Development in Co-extruded Polymer Scaffolds

Newell R. Washburn and Alamgir Karim

A method for preparing polymeric scaffolds for tissue engineering without the use of organic solvents has been developed. Borrowing techniques from polymer processing, a biocompatible polymer such as poly( $\epsilon$ -caprolactone) or poly(ethyl methacrylate) is blended with a biocompatible, water-soluble polymer such as poly(ethylene oxide). After annealing the blend, the water-soluble component is dissolved yielding a porous material. The pore connectivity and characteristic length scale may be controlled by tuning the blend composition and annealing time and temperature. In this work we have focused on blends that have a continuous network of pores and length scales ranging from 10  $\mu\text{m}$  to 100  $\mu\text{m}$ .

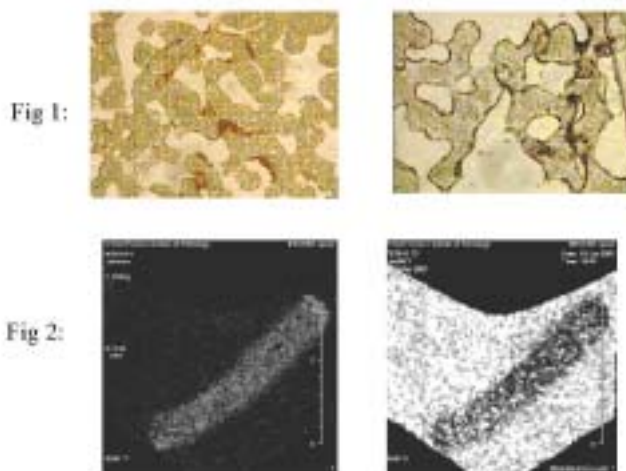
We are using these scaffolds to investigate several fundamental issues in tissue engineering such as the influence of scaffold composition, dimensions, and structural anisotropy on cell proliferation and matrix deposition. Concomitantly, we are also developing new techniques for characterizing both the materials and the tissue development in them.

Figure 1 shows images of poly(ethyl methacrylate) scaffolds that were prepared with a continuous network of pores having a characteristic dimension in excess of 100 micrometers. The scaffold was seeded with primary chick osteoblasts and cultured in a perfusion bioreactor for 6 weeks. Afterwards, the cell-scaffold constructs were fixed and stained for collagen using Sirius Red and mineral using von Kossa then sectioned using standard histological techniques. The stained areas in the porous structure are areas where significant matrix deposition has occurred.

In collaboration with researchers at the Armed Forces Institute of Pathology and National Institutes of Health, we have been developing the use of magnetic resonance imaging for studying tissue development in situ. In Figure 2 are shown the T1 and magnetization transfer (MT) scans for these scaffolds after 5 weeks of culture. The

*A method for preparing tissue engineering scaffolds using techniques borrowed from polymer processing has been developed. Characterization of tissue development in these scaffolds is under way in collaboration with researchers at the Armed Forces Institute of Pathology (AFIP) and the National Institutes of Health (NIH). Primary chick osteoblasts were cultured on the scaffolds in a perfusion bioreactor and matrix deposition was monitored using magnetic resonance imaging and histology.*

image shown is a cross-section of a 2-mm-thick disk and the spatial resolution of the scans is 100  $\mu\text{m}$ . The T1 scan has black regions where water has been excluded from regions of mineral deposition and the MT scan has bright regions where collagen deposition has occurred. The contrast in the scans is consistent with the observation that the cell coverage is likely inhomogeneous, leading to inhomogeneous matrix deposition.



**Figure 1. Histology sections of scaffolds that were stained for mineral (left) and collagen (right). The field of view is 100  $\mu\text{m}$ .**

**Figure 2. Magnetic resonance imaging scans for mineral (left) and collagen (right). The image is a cut through the scaffold, which is 2 cm in diameter.**

Current work is focused on calibrating the magnetic resonance signal for performing quantitative assessment of tissue development and addressing the fundamental issues related to tissue engineering discussed above. We also are attempting to develop functional imaging techniques that yield more information about metabolic activity of the cells.

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# Interface of Materials with Biology

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

Four major activities constitute this program:

- The dental industry is composed largely of small manufacturers with very little R&D capability. The dental materials projects, carried out in close collaboration with the American Dental Association fill that need by developing improved materials and techniques, patenting these inventions, licensing to these small companies, and most importantly, providing technical assistance to these licensees for producing and improving their products. This has provided U.S. companies with products that successfully compete on a worldwide market. Our research focuses on improved understanding of the synergistic interaction of the phases of polymer-based composites and the mechanisms of adhesion to dentin and enamel. This approach will ultimately lead to materials with improved durability, toughness and adhesion to contiguous tooth structure.
- The tissue engineering industry shows the potential for explosive growth in the coming years as biomedical research is moving from academic science to industrial application at an increasing rate. Our work seeks to bridge the gap between knowledge generation by cell biologists and product development in industry. In collaboration with the NIST Biotechnology Division we are developing a set of measurement methodologies and reference materials to use in assessing interactions in complex systems of living cells with synthetic materials. The expected outcomes of this work include reference substrates that induce gene expression associated with specific stages in cellular activity, and engineered DNA vectors that signal fluorescently these responses in adherent cells.
- Regenerating form and function to bone defects in an elderly, osteoporotic population of Americans will be a daunting challenge. To meet this challenge, we are developing metrology methods to characterize the biocompatibility of bone grafts for bone regeneration. Quantitative methods being developed include bioassays for the adhesion, viability, proliferation, and alkaline phosphatase activity of bone cells, as well as confocal microscopy and optical coherence tomography for measuring the growth of bone cells into bone grafts. A combinatorial approach is being used to rapidly identify compositions and surface features of bone grafts that provide desirable properties such as biocompatibility and mechanical durability.
- The NIST Center for Neutron Research and the NIST Biotechnology Division are engaged in the study of biomimetic films that serve as models of cell membranes and which are of fundamental importance in understanding such key biological processes as phospholipid self-assembly, molecular recognition and cell-protein interactions. Recent improvements in neutron reflectometry at the NCNR, coupled with advances in biomimetic film fabrication at metallic interfaces pioneered in the Biotechnology Division, afford enhanced sensitivity for probing membranes and membrane-protein complexes. New phase sensitive measurement techniques and model-independent data analysis methods have demonstrated the feasibility of obtaining reliable depth profiles of membrane structures in contact with biologically relevant aqueous environments, achieving subnanometer spatial resolutions.

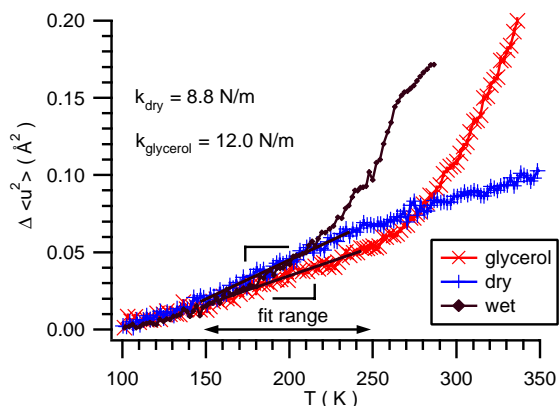
Fundamental to all the work in this program is the recognition that surfaces and interfaces play a critical role in biological systems and, in particular, in the interactions of synthetic or designed materials with biological systems and function. By providing the unique expertise in the NIST Materials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

**Contact Information: Eric J. Amis**

## The Dynamic Effects of Protein Stabilization in Glass Forming Liquids

Christopher L. Soles, Amos M. Tsai

It is well known that the primary (amino acid sequence), secondary (beta sheet, alpha helix, etc.) and tertiary (folded) structures of a protein are crucial for enzymatic activity. However, dynamics ranging from the picosecond thermal fluctuations to the millisecond (and slower) conformational changes are also requisite for biological function. At the high frequency end, neutron scattering quantifies the local thermal fluctuations in terms of a mean square atomic displacement  $\langle u^2 \rangle$ . Several studies have shown that in hydrated proteins there is a dynamic transition,  $T_d$ , near 180 K to 220 K (reportedly the  $T_g$  of super-cooled water) where a sudden change of  $\langle u^2 \rangle$  occurs and above which the thermal fluctuations become strongly anharmonic. It is also known that  $T_d$  coincides with the onset of enzymatic activity. These fluctuations are thought to enable the large-scale conformational changes that accompany biological function.



In proteins stabilized with a viscous alcohol/sugar co-solvent,  $T_d$  typically shifts to higher temperatures. This is seen in the above figure where the dynamics of dehydrated, hydrated, and glycerol-preserved chicken egg white lysozyme are compared. Glycerol shifts  $T_d$  to tem-

*The stability of protein and enzyme molecules is of great interest to the pharmaceutical industry. However, the main attributes constituting a stable environment are not yet fully identified. Excesses in temperature and/or dehydration irreversibly damage most enzymes, proteins, and cellular structures. While a few viscous alcohol or sugar co-solvents are known to provide this stability, the responsible mechanisms are poorly understood. Inelastic neutron and low-frequency Raman scattering are used to probe the dynamic effects of these viscous sugars/alcohols to help resolve the mechanisms of protein stabilization.*

peratures commensurate with its own glass transition. It is believed generally that the reduced mobility imparted by the viscous glycerol, a widely used cryo-protectant in biological freeze-drying processes, is vital for stability.

This leads to the notion that a high  $T_d$  is desirable in a protein stabilization scheme. However, there is more to protein stabilization than glass formation alone. Below  $T_d$  glycerol suppresses  $\langle u^2 \rangle$  the harmonic motions of lysozyme. This is quantified as a stiffening of the elastic force constant defined by the thermal evolution (i.e., slope) of  $\langle u^2 \rangle$ ; stiffer vibrations increase less dramatically in amplitude with  $T$ . From the previous figure, glycerol stiffens the force constants of lysozyme by 40 percent.

The effects of this vibrational stiffening are also seen in the full inelastic neutron scattering spectra. The positions of the Boson peak of the dry and glycerol-preserved lysozyme are analyzed in terms of their force constant. In glycerol the low-frequency mode is shifted to higher energies compared to dry state at the same temperature. This shift occurs at the same temperatures where the suppression of  $\langle u^2 \rangle$  is observed. If this low-frequency vibration is modeled as a harmonic oscillator ( $\omega^2 = k/m$ ), the square of the peak frequency also stiffens by 40 percent, mirroring the  $\langle u^2 \rangle$  data.

The similarities in  $\langle u^2 \rangle$  and the low-frequency vibrational spectra suggest that a stabilized protein also has a higher frequency Boson peak. Recently we corroborated this in mesophilic and thermophilic (thermally stable)  $\alpha$ -amylase; both a suppressed  $\langle u^2 \rangle$  and higher frequency Boson peak are seen in the naturally thermophilic protein. This provides a powerful tool to assess new preservation schemes, a process currently done by trial and error. While  $\langle u^2 \rangle$  measurements are limited by the availability of neutrons, Boson peak measurements are accessible with conventional low-frequency Raman scattering. This may provide the pharmaceutical industry a readily available tool to help evaluate protein stabilization schemes.

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# Structure-Property Relationships in Dental Polymers

Joseph M. Antonucci

This project is directed toward enhancing our basic understanding of how monomer structure and variations in comonomer compositions influence the photopolymerization process and the polymeric network structure, both critical factors that determine the potential properties that can be achieved with dental polymers and their derived materials, e.g., composite restoratives. Dental matrix polymers are described often simply as highly cross-linked networks with little or no characterization done beyond a measurement of overall vinyl conversion. Although the results of physical and mechanical property testing also have been reported widely for dental polymers, these data would be more useful with knowledge of how monomer structure and resin composition variations affect the development of cross-linked polymers. Generally this information is difficult to interpret and use as a guide for the development of improved materials.

In addition, the project is intended to define the currently unknown co-reactivity of structurally different co-monomers that are typically used in dental polymers. For lack of this information, the reactivity and cross-linking potential of dental resins are generally assumed to be equal. The use of selected model monomers is designed to demonstrate the influence of specific structural features on polymer properties and should have significant impact on the development of improved materials. An examination of non-methacrylate co-monomers, such as vinyl esters and vinyl ethers, offers a means to modify network formation and also appears to allow for higher conversion and improved mechanical properties.

It is known that widely used dental monomers such as the hydroxylated dimethacrylate Bis-GMA and the urethane dimethacrylate UDMA form strong hydrogen bonds that are of different types. The effect of hydrogen bonding on monomer viscosity is well known, but its influence on the polymerization process and its potential to influence network structure has been overlooked. These aspects are being examined along with studies of some model hydrogen bonding monomers that directly may provide poly-

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

mers with improved properties. An interesting example of the profound effects of hydrogen bonding involved the comparison of 2-hydroxyethyl methacrylate (HEMA) with its isomer, ethyl- $\alpha$ -hydroxymethylacrylate (EHMA). The stronger intramolecular hydrogen bonding of EHMA vs. HEMA has a significant effect on both monomer and polymer properties. Also, subtle changes in monomer structure, for example the substitution of ether linkages into a predominantly hydrocarbon dimethacrylate, can produce dramatic differences in polymerization rate and polymer properties. The systematic introduction of heteroatoms into dimethacrylate monomers currently is being examined to explain why these differences exist and how they can be employed to obtain polymers with improved properties. The use of multi-modal distributions of comonomers with varied chain lengths offers a simple means to achieve an increased level of vinyl conversion, network structure variations in the polymer and corresponding improvements in the physical, chemical and mechanical properties of dental polymers and derived materials.

A major part of this project is directed at implementing strategies of maximizing vinyl conversion while minimizing polymerization shrinkage. Currently we are investigating high molecular mass urethane and silyl ether derivatives of Bis-GMA, as well as new types of high molecular mass diluent monomers, for their efficacy in reducing residual vinyl unsaturation, polymerization shrinkage and the water uptake of their polymers. In addition, the use of alternative initiator systems are under investigation in an effort to enhance photopolymerization efficiency and alter polymer network formation. This project is expected to lead to a better understanding of structure-property relationships of monomer/resin systems that should translate into polymeric dental materials with improved clinical performance. The results of these studies should extend well beyond the dental materials venue to include a significant number of other applications that rely on the rapid formation of cross-linked polymeric network having optimal properties from photopolymerizable monomer systems.

### Contributors and Collaborators:

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## A Moldable, Resorbable, Macroporous, Composite Bone Graft Containing Growth Factor

Carl G. Simon, Jr., Chetan Khatri,  
Francis W. Wang

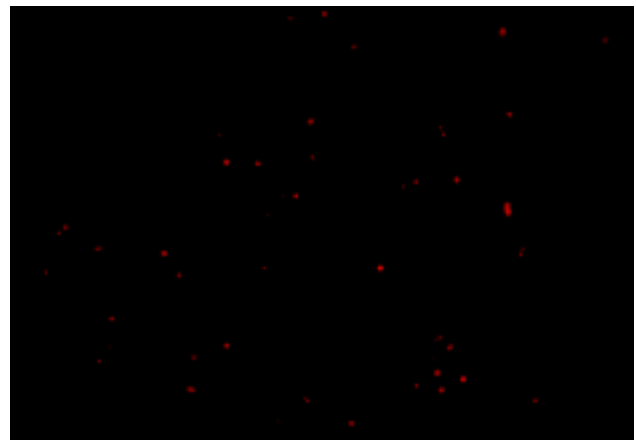
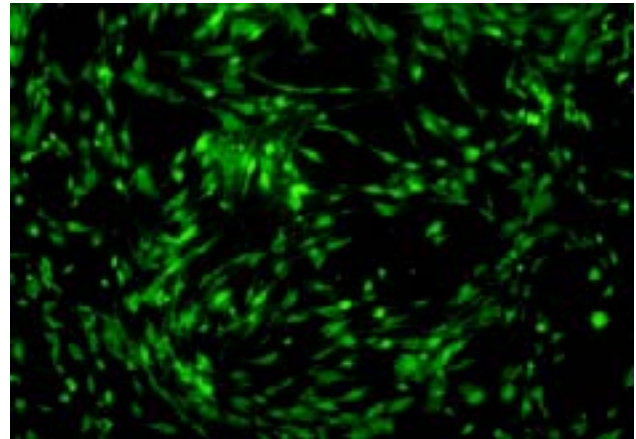
*The rapidly expanding tissue engineering industry is in need of improved measurement technology to aid in the development of new biomaterials. We are developing this technology through the design and testing of a novel composite bone graft. Techniques for assessing cell morphology, adhesion and proliferation on opaque specimens are being evaluated with the aim of proposing the best assays as new standards to appropriate agencies (ANSI, ASTM, FDA, ISO). Thus, this project can yield a new synthetic bone graft as well as new standards for use by the tissue engineering industry.*

Over 100,000 operations requiring bone grafts are performed each year in the United States to repair osseous defects resulting from trauma or disease. Autografts are widely used by surgeons, but the amount of bone available for autografts is limited and available material is difficult to shape. Thus, the development of synthetic materials for use as bone grafts is a primary objective of the tissue engineering community. We are using this opportunity to develop metrology to serve this burgeoning industry and to develop a novel composite bone graft.

Our graft consists of a calcium phosphate powder and small spheres made from a biodegradable polymer that are mixed with water to form a paste. The paste can be molded and then sets like cement within 30 min to form a solid matrix of microcrystalline hydroxyapatite that contains the polymer spheres. In vivo, the spheres should degrade to leave behind macropores for colonization by bone tissue. We are assessing the biocompatibility of the composite graft and are making the graft osteoinductive by adding bone growth factors.

By facing challenges that are common to the entire tissue engineering industry in the context of this real problem, we can evaluate and improve the existing biocompatibility metrology. Specifically, we have implemented new techniques for assessing cell morphology, adhesion and proliferation during culture on opaque substrates such as our bone graft. We are characterizing new fluorescent indicators of cell viability (see figures) and are improving upon cell preparation techniques for environmental scanning electron microscopy which allows high-resolution imaging of hydrated samples. In addition, we are evaluating a new colorimetric assay for quantifying cell number that is easier to use and faster than standard assays.

After characterizing our composite bone graft with these new techniques, we will move to make the best techniques into standardized assays with the appropriate agencies (ANSI, ASTM, FDA, ISO). Thus, this project may yield a new synthetic bone graft material as well as new standards for use by the tissue engineering industry.



**Cells growing on a bone graft specimen which has been fluorescently double-stained for live (green, top) and dead cells (red, bottom). Both panels are the same field of view seen through different filters.**

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# Bioactive Polymeric Composites for Mineralized Tissue Regeneration

Joseph M. Antonucci

Over the broad range of solution conditions when precipitation occurs spontaneously, amorphous calcium phosphate (ACP) precedes the formation of HAP. ACP has been shown to have high solubility in aqueous media and to undergo rapid conversion to HAP, especially at low pHs. Both of these properties suggest its use as a bioactive filler in polymeric materials for the preservation or repair of enamel, dentin, cartilage and bone.

Utilizing conventional dental matrix resins (e.g. 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)phenyl] propane (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA) and 2-hydroxyethyl methacrylate (HEMA)) and ACP or modified versions of ACP as a filler phase, we have prepared photopolymerizable bioactive composites that had adequate physicochemical and mechanical properties and their bioactivity resides in the remineralization potential of ACP as a consequence of the sustained release of calcium and phosphate ions into simulated saliva media.

However, compared to conventional glass-filled composites, ACP composites are still relatively weak in mechanical strength. In an effort to improve their reinforcing capabilities, we have modified ACP during its synthesis with glass-forming agents such as tetraethoxysilane (TEOS) and zirconyl chloride. This has resulted in modest improvement of mechanical properties, such as biaxial flexure strength. Further improvements may be feasible by the use of coupling agents with these modified ACP fillers and alternative matrix resins. Another strategy for enhancing mechanical properties is to employ hybrid filler phases consisting of ACP filler admixed with silanized glass fillers and/or polymer fibers, such as oriented polyethylene fibers. Preliminary studies have yielded encouraging results for all these strategies.

These studies also have shown that certain variations in methacrylate resin chemical structure and composition

*Crystalline hydroxyapatite (HAP) is considered to be the final stable product in the precipitation of calcium and phosphate ions from neutral or basic solutions and it is also the structural prototype of the major mineral component of bones and teeth. Recently, there has been increasing interest by biomaterials community in utilizing polymers of various types as matrices and as reinforcements (especially in fiber forms) for calcium phosphate-based composites. Customers for this technology include dental and biomedical manufacturers and practitioners.*

may affect the rate and extent of the ion release from ACP-filled composites, the internal conversion of ACP into HAP, the conversion of methacrylate groups, as well as the mechanical properties of the composites.

Recent studies have involved assessing the effect of substituting ethyl- $\alpha$ -hydroxymethylacrylate (EHMA) for HEMA. EHMA, a unique isomer of HEMA, is much more hydrophobic than the completely water miscible HEMA. Preliminary results indicate that ACP composites utilizing EHMA are significantly stronger than similar composites based on HEMA. In related research, a facile synthesis has been developed for new types of low-shrinking, crosslinking monomers of controlled biodegradability and hydrophilicity that also enable high loadings of ACP in composites.

These various types of polymeric calcium phosphate materials are designed to be bioactive, biocompatible and highly conformable to mineralized tissue. Injectable, photopolymerizable ACP composites appear feasible as well. All these ACP composites are expected to have significant remineralization potential and should find use in remineralizing white spots and caries lesions in tooth structure, especially interproximally and gingivally. If successful, ACP composites would have significant advantages over other remineralizing therapies. Currently, a strong need exists for protective liners, bases, prophylactic sealants and adhesive restoratives that are manipulated easily and that can provide efficacious long-term protection against demineralization and even have remineralization capabilities. In addition, bioactive ACP composites with biodegradable polymer matrices may find wider applications as therapeutic materials with the ability to provide osteoconductive environments conducive to promoting bone healing, such as is needed in dental (endodontic, periodontal etc.) and other biomedical applications.

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# Materials for Microelectronics

Today's U.S. microelectronics and supporting infrastructure industries are in fierce international competition to design and produce new smaller, lighter, faster, more functional, and more reliable electronics products more quickly and economically than ever before.

Recognizing this trend, in 1994 the NIST Materials Science and Engineering Laboratory (MSEL) began working very closely with the U.S. semiconductor, component and packaging, and assembly industries. These early efforts led to the development of an interdivisional MSEL program committed to addressing industry's most pressing materials measurement and standards issues central to the development and utilization of advanced materials and material processes within new product technologies, as outlined within leading industry roadmaps. The vision that accompanies this program—to be the key resource within the federal government for materials metrology development for commercial microelectronics manufacturing—may be realized through the following objectives:

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

With these objectives in mind, the program presently consists of 20 separate projects that examine and inform industry on key materials-related issues, such as: electrical, thermal, microstructural, and mechanical characteristics of polymer, ceramic, and metal thin films; solders, solderability and solder joint design; photoresists, interfaces, adhesion and structural behavior; electrodeposition, electromigration and stress voiding; and the characterization of next generation interlevel and gate dielectrics. These projects are conducted in concert with partners from industrial consortia, individual companies, academia, and other government agencies. The program is coupled

strongly with other microelectronics programs within government and industry, including the National Semiconductor Metrology Program at NIST.

## **FY2001 Projects (and division leading project)**

### **Lithography/Front End Processing**

Characterization of Ultrathin Dielectric Films (Ceramics)  
Lithographic Polymers (Polymers)

### **On-chip Interconnects**

Interconnect Materials and Reliability Metrology (Materials Reliability)  
Measurements and Modeling of Electrodeposited Interconnects (Metallurgy)  
Thin Film Metrology for Low-k Dielectrics (Polymers)

### **Packaging and Assembly**

Packaging Reliability (Materials Reliability)  
Solder Interconnect Design (Metallurgy)  
Solders and Solderability Measurements for Microelectronics (Metallurgy)  
Tin Whisker Mechanisms (Metallurgy)  
Wafer Level Underfill Experiment and Modeling (Metallurgy)  
Wire Bonding to Cu/Low-k Semiconductor Devices (Metallurgy)  
X-ray Studies of Electronic Materials (Materials Reliability)

### **Crosscutting Measurements**

Dielectric Constant and Loss in Thin Films and Composites (Polymers)  
Electron Beam Moiré (Materials Reliability)  
Ferroelectric Domain Stability Measurements (Ceramics)  
Measurement of In-Plane CTE and Modulus of Polymer Thin Films (Polymers)  
Mechanical Properties of Thin Films (Ceramics)  
Permittivity of Polymer Films in the Microwave Range (Polymers)  
Polymer Thin Films and Interfaces (Polymers)  
Texture Measurements in Thin-Film Electronic Materials (Ceramics)  
Thermal Conductivity of Microelectronic Structures (Materials Reliability)

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

Barry J. Bauer, Eric K. Lin, Wen-li Wu

As integrated circuit feature sizes continue to shrink, new low-k-interlevel dielectric materials are needed to address problems with power consumption, signal propagation delays, and crosstalk between interconnects. One avenue to low-k dielectric materials is the introduction of nanometer-scale pores into a solid film to lower its effective dielectric constant. Specifics of the pore architecture may affect other properties, hence characterization of the pore structure of thin nanoporous low-k dielectric films is critical and beyond the capabilities of conventional methods.

The small sample volume of 1- $\mu\text{m}$  films and the desire to characterize the film structure on silicon wafers narrow the number of available measurement methods. We have developed a novel combination of small-angle neutron scattering (SANS), high-resolution x-ray reflectivity (HRXR), and ion scattering techniques to determine important structural and physical property information about thin porous films less than 1  $\mu\text{m}$  thick. These measurements are performed directly on films supported on silicon substrates so that effects of processing on structure can be investigated.

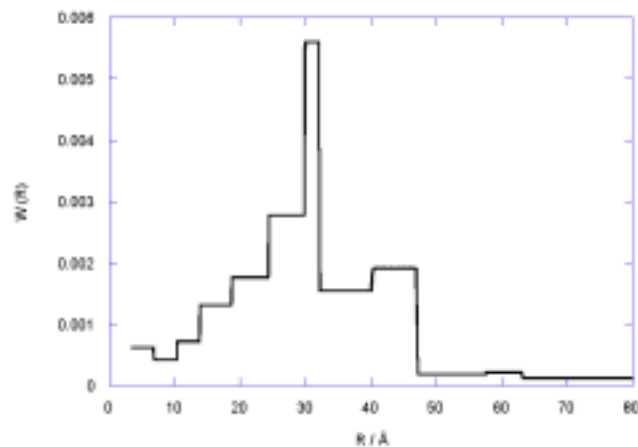
During the past year, we focused efforts in three areas: continuing characterization of current industrially relevant materials through International SEMATECH, establishing new collaborations with Rohm and Haas and Dow Chemical, and developing advanced measurement methods for more thorough and accurate film characterization. International SEMATECH, a consortium of microelectronics companies, provided more than 20 separate samples for characterization by NIST, including spin-on glass materials, films from chemical vapor deposition, and organic thin films. The structural information provided by NIST is placed into a master database that includes data from a variety of sources, detailing both the structural and material properties needed to evaluate candidate materials.

New measurement methods have been developed to more thoroughly and accurately characterize pore and matrix morphology. HRXR measures the average film thickness and average density of the wall and voids. By infusing

*NIST is providing the semiconductor industry with unique on-wafer measurements of physical and structural properties of porous thin films important as low-k interlevel dielectric materials. The methodology uses several complementary experimental techniques to measure the average pore and matrix morphology, including pore size distributions. New methods have been developed to measure pore and matrix morphology in films having complex structures.*

toluene into the voids, the volume fraction of connected voids can be measured by HRXR along with the average density of the wall material and closed pores. When the toluene vapor is lower than the saturated vapor pressure (partial pressure), the small pores fill first, and measurement of the overall density by HRXR allows calculation of the complete pore size distribution.

Other new techniques being developed include SANS measurements on films that have been infused with mixtures of normal toluene and deuterated toluene. The match point measures where the neutron contrast of the toluene matches that of the wall material. This measures porosity and wall density in a way that is independent from the HRXR measurements and applies to all morphology types. When the match point has been determined, the films can be infused with the match mixture at various partial pressures in a way analogous to the HRXR. Pore size distributions can be estimated from the partial pressure SANS, and at the saturation point, any residual scattering present gives information on sample heterogeneity.



**Figure 1. Representative pore size distribution calculated from HRXR partial pressure measurements.**

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## Polymer Fundamentals of Photolithography

Eric K. Lin, Wen-li Wu

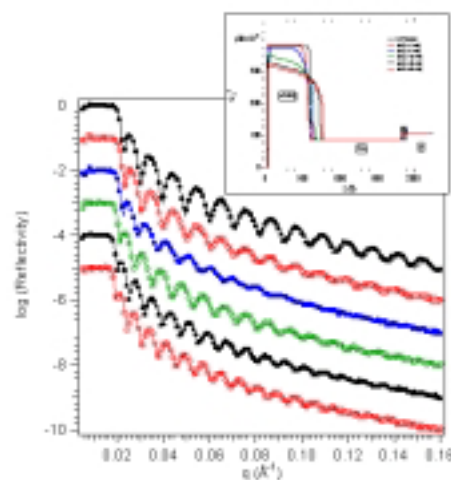
In photolithography a pattern is transferred to the silicon substrate by altering the solubility of areas of a polymeric photoresist thin film exposed to light through a mask via an acid catalyzed deprotection reaction. To fabricate smaller features, next-generation photolithography will be processed with wavelengths of light requiring photoresist films less than 100-nm thick and dimensional control to within 2 nm. Many new material and transport issues arise when fabricating structures over these length scales.

To advance this key technology, we work closely with industrial collaborators to apply high-spatial resolution and chemically specific measurements to understand varying material properties and process kinetics at nanometer scales. The unique measurement methods we apply include x-ray (XR) and neutron reflectivity (NR), small-angle neutron scattering (SANS), incoherent neutron scattering (INS), near-edge x-ray absorption fine structure (NEXAFS), and combinatorial methods. Our efforts focused on the fundamentals of polymer materials and processes that control the resolution of photolithography including: (1) the physical properties and polymer chain conformation within sub-100-nm structures; (2) the spatial segregation and distribution of photoresist components; (3) the transport and kinetics of photoresist components and the deprotection reaction interface; and (4) the structural characterization of lithographically prepared structures.

This past year, we made significant progress in elucidating molecular behavior of important lithographic processes. We performed the first measurements of the three-dimensional conformation of polymer chains (SANS) and the local dynamics of model photoresist polymers (INS) confined in sub-100-nm thin films. These results provide important insight into observed deviations in material properties and transport processes within sub-100-nm imaging layers needed in the future (see Accomplishment Report "Measurement Methods Aid Development of Photoresists for Next-generation Photolithography").

Using NR and XR, we have shown that moisture uptake in photoresist films (a critical component in some resists) is

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



**Figure 1. Neutron reflectivity data and real space profiles from bilayers of deuterated poly(methyl methacrylate) and poly(hydroxystyrene). The data show the interfacial evolution over nanometer-length scales.**

uniform, not segregated to a hydrophilic or hydrophobic substrate. Additional NR measurements (Figure 1) show the interfacial development of partially miscible polymer layers (similar to soluble and insoluble areas of an exposed resist) with nanometer resolution. We have applied NEXAFS to measure the distribution of photoacid generator molecules within the top (2–3) nm of the resist film relative to the bulk concentration. The surface segregation of important resist components and the resulting chemistry strongly affect the quality of the fabrication process. SANS measurements of lithographically prepared structures have been extended and applied to new photoresist formulations and structural sizes. Finally, we are applying combinatorial methods to quantify quickly important temperature boundaries in the compositional dependence of the thermal deprotection of photoresist polymers mixtures.

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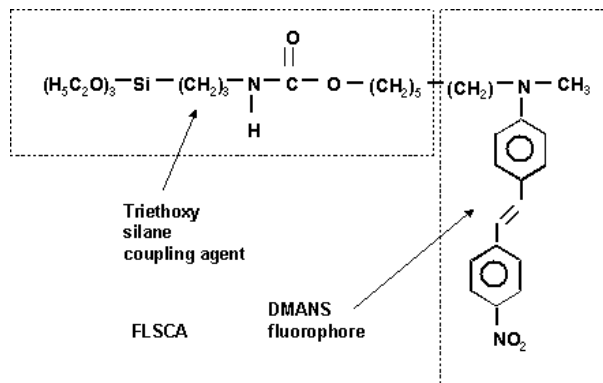
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# Characterizing Buried Polymer/Substrate Interfaces

Joseph L. Lenhart

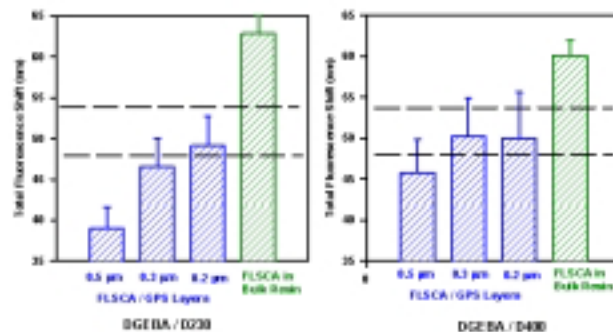
The measurement system consists of chemically attaching a fluorophore, dimethyl-amino-nitro-stilbene (DMANS) to a triethoxy silane-coupling agent, generating a fluorescently labeled silane-coupling agent (FLSCA) that bonds with hydroxyl groups on glass or metal surfaces. FLSCA-coated glass surfaces were immersed in epoxy resin. A blue shift in the emission maximum from the fluorophore and an increase in fluorescence intensity could be measured during resin cure. Since the DMANS probe is grafted into the silane layer, the fluorescence response is completely from the interfacial region. FLSCA was diluted on glass surfaces



with glycidoxypropyltriethoxysilane (GPS), a coupling agent used as a surface primer in glass fiber-reinforced composites. Experiments were conducted as a function of the FLSCA/GPS layer thickness. The thickest silane layer exhibited a smaller fluorescence shift during cure, suggesting incomplete resin penetration into these layers (see right). The resin was composed of a stoichiometric mixture of diglycidyl-ether-bisphenol A (DGEBA) cured with a diamine hardener polypropylene-glycol-bis-2-aminopropyl ether (Jeffamine D400 or D230). Two molecular mass Jeffamine hardeners were used (230 and 400) g/mole. The DGEBA/D400 system gelled in 30 min, while the DGEBA/D230 resin system gelled in 15 min. When the slower gelling resin was used, the fluorescence shift during cure was

While many techniques are available to study polymer films and surfaces, very few can probe buried polymer/substrate interfacial regions, which are critical in composites, nano-composites, biomaterials, electronics, paints, coatings and adhesives. A technique was developed to probe this interfacial region by localizing a fluorescent dye on the substrate surface. The current work is focused on applications to glass-reinforced composites, but the technique will be extended for micro-electronics applications to probe interfacial acidity of photo-resist polymers adhered to bottom anti-reflective coatings.

independent of the FLSCA/GPS layer thickness (right most graph below). These data show that the composition profile in the interfacial region is influenced by the competition between diffusion of resin monomers into the silane layer, and the reaction kinetics, which slow the diffusion process. Using the transition from incomplete penetration (0.5- $\mu\text{m}$  thick layers) to complete penetration (0.3- $\mu\text{m}$  thick layers), the diffusion constant for resin monomers into the silane layer was estimated to be in the range of ( $10^{-12}$  to  $10^{-13}$ )  $\text{cm}^2/\text{s}$  estimated from  $D \sim L^2/t_{\text{gel}}$ , where  $t_{\text{gel}}$  is the resin gel time. The dotted lines represent the total fluorescence shift when the layers were immersed in hardener only. Since the amine on the hardener



will react with the epoxy functionality these lines represent the maximum fluorescence shift that is expected from equilibrium penetration of the resin and silane layer. The work has resulted in several publications (*J. Coll. Interface Sci.* 221, 75, **2000**; *Langmuir* 16, 8145, **2000**; *Macromolecules* 34, 2225, **2001**; *Optics & Lasers Eng.* 35, 91, **2001**; *Polymer Composites*, in press; *J. Coll. Interface Sci.*, submitted).

The technique will be extended to interfaces in microelectronics including the photoresist and anti-reflective coating (ARC) interface. To probe the acidity in the interfacial region, acid sensitive fluorescent probes will be grafted to the ARC layer.

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# Materials for Wireless Communication

Today, wireless technologies constitute one of the most important growth areas in the global electronics industry. The current revolution in wireless communications would not have been possible without the discovery and development of oxide ceramics exhibiting the coincidence of high, temperature-independent resonant frequency with low dielectric loss. Technically important ceramic materials fall into two major dielectric categories: bulk ceramics for base station resonators/filters and those needed for low-power, miniaturized hand-held devices. Paramount in achieving smaller and lower cost devices are guidelines that facilitate the rational design of advanced materials to provide temperature stability, frequency, and size-reduction requirements for the next generation of devices for cellular, PCS, and many other niches of the wireless communications industry.

A collaboration between the Ceramics Division and the Electrical and Electronics Engineering Laboratory at NIST on ceramic materials for base station applications includes experimental determination of selected complex-oxide phase diagrams integrated with in-depth structural (x rays, electrons, neutrons), crystal-chemical, spectroscopic, and dielectric property characterization. The objective of this multidisciplinary project is to determine the fundamental relationships between phase chemistry, crystal structure, and dielectric performance at wireless frequencies.

Another project in the Ceramics Division uses first-principles calculations to elucidate the roles of cation order-disorder and ferroelastic phenomena in determining the phase relations and physical properties of complex ceramic oxide systems. These calculations are used to predict cation ordering phenomena, physical properties, and how they vary with chemical composition. Critical experiments are performed to test the predictions.

Microstructural modeling and experimental studies are also under way to determine the dimensional changes in low-temperature-cofired ceramics used for portable communication devices. Processing models were identified by a large segment of industrial producers as being crucial to reducing the time currently needed to design and produce components. Wireless devices, often hand-held, are especially susceptible to mechanical damage; assuring the reliability of electronic products is especially critical for such devices. Work in the Materials Reliability Division includes development of noncontact acoustic metrology to characterize wireless materials in both thin-film and bulk form. Also, the mechanical properties of thin films are investigated using laser-ultrasonic methods to generate and detect surface acoustic waves. The elastic property information obtained will result in improved predictive modeling of film performance. In addition, resonant-ultrasonic techniques are applied to new piezoelectric materials for SAW devices, used extensively as oscillators in hand-held devices.

Researchers in the Polymers Division developed a new test method that permits dielectric measurements of film substrates at frequencies of 1 to 10 GHz. The project is exploring the relationships between dielectric properties and structure in a variety of polymer resins, blends and composites, e.g., hybrid materials based on polymer resins and ferroelectric ceramics. Microstructural modeling and experimental studies are being undertaken to determine the effect of polarizability of the polymer matrix on the apparent dielectric permittivity of the composite. A need for models and measurement techniques has been identified by a large segment of industrial producers as being crucial in new designs and in reducing the development time of new products. A consortium involving the National Center for Manufacturing Science (NCMS) and industry has been organized to help address these issues.

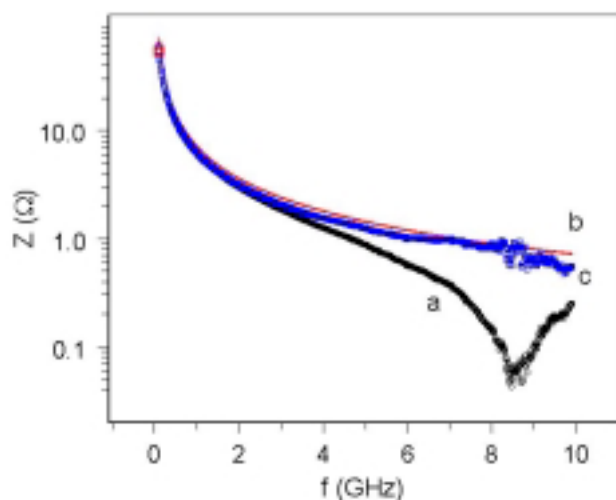
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## Dielectric Metrology for Polymer Composite Films in the Microwave Range

Jan Obrzut

Novel dielectric hybrid materials based on organic resins and ferroelectric ceramics with high-dielectric constants are being developed by the industry to advance miniaturization and functional performance of high-speed electronics. These materials are being used to construct integrated passive devices and de-coupling capacitance films with low impedance that are embedded within chip substrates and printed circuit sub-assemblies. This new material approach is essential as current methods based on discrete components cannot provide adequate solutions at frequencies above 1 GHz, which are critical for wireless communications technologies. The goal of this project is to provide the microelectronics industry with an accurate measurement technique of permittivity for dielectric films at microwave frequencies above 1 GHz and to develop a fundamental framework to identify the key structural and molecular attributes that control dielectric properties of polymer composites.



**Figure 1.** Broadband impedance data for polymer composite film having permittivity of  $34.6 - j 1.6$ . (a) conventional results (b) results calculated for a thin-film capacitance, (c) determined by our new testing procedure.

*Development of the Integrated Passive Device technology for high-speed electronics critically depends on the ability to measure the dielectric permittivity and on the ability to control the dielectric properties from the material's microstructure. This project provides the microelectronics industry with an accurate technique to measure permittivity at microwave frequencies and a fundamental framework to identify the key structural and molecular attributes that control dielectric properties of polymer composite films.*

During the past year we focused on a broadband measurements procedure for film substrates that would be suitable for adaptation as a new industry standard method. The test methods currently in use are lumped-element approximations limited to frequencies below a few hundred megahertz, especially in the case of high-dielectric constant films. Our new broadband measurement methodology is based on observation and analysis of the fundamental propagation mode in a film specimen terminating a coaxial transmission line. Using this test technique, the impedance characteristic and the dielectric permittivity of high-dielectric constant films can be accurately measured at frequencies from 100 MHz to 10 GHz with the precision required by wireless technologies (Figure 1). To enable measurements at frequencies above 20 GHz we are collaborating with the NIST Radio Frequency Division on full mode analysis.

In partnership with the IPC Standard Test Committee Task Force for Embedded Passive Devices we designed the standard test protocol and made arrangements with co-sponsoring member companies for round-robin evaluation.

This project also explores the relationships between dielectric properties and structure in polymer resins, blends and composites. The microwave dielectric properties of several polymer-ferroelectric ceramics composites have been evaluated. Microstructural modeling and experimental studies are under way to determine the effect of polarizability of the polymer matrix on the apparent dielectric permittivity of the composite.

Models and measurement techniques developed in this study were identified by a large segment of industrial producers as being crucial in material design and in reducing the development time of new products.

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# Multiphase Polymeric Materials

The Multiphase Polymeric Materials Program develops realistic measurement and characterization platforms for multiphase polymeric materials that use a combination of experimental measurements and theory and modeling tools to provide realistic and highly optimized output. These measurement and characterization tools and platforms are intended to help industries in pre-production evaluation, materials characterization, and performance prediction, as well as to provide data for process design.

In order to achieve the performance requirements in modulus, stiffness, toughness, temperature, chemical and environmental stability, desired appearance and touch, most polymeric materials in use are either phase separated blends with two or more components, and/or filled with particles or short/long fibers. The challenge in using multiphase polymeric materials extends from processing design, through structure and properties prediction and characterization, to service life prediction. This program is designed to use theoretical and computational modeling tools in conjunction with characterization measurements to form realistic and workable tool sets.

Specifically, characterization techniques will be developed and used to generate relevant databases or constitutive relations to be used as input for more realistic theory and modeling and to bridge the gap in current tools. Current theoretical and computational tools are capable of modeling fine length scales such as nanoscale molecular dynamics simulations, microscale self-consistent field or density functional methods, and meso-scale time dependent

Ginsburg-Landau or Cahn-Hilliard-Cook techniques. On the other hand, macroscopic part sized finite-element-flow calculations and Object Oriented Finite element analysis (OOF) for properties calculations and virtual testing are much coarser grained tools. A seamless connection between these two sets of computer tools is not available to provide realistic materials properties for design, prediction and characterization.

This program is working currently on three materials characterization projects to provide:

(1) phase separation/crystallization results together with interfacial characterization and rheological data to form constitutive relations as input for finite-element-flow modeling, and characterization of phase structure;

(2) structure, dynamics, and modulus characterization in high surface area particle-filled polymers and blends for performance characterization and validation of multiscale computer modeling; and

(3) fiber tow characterization and failure results as input to finite-element-based mechanics and performance evaluation. All three projects are linked to future applications of OOF to polymer research on property prediction and virtual testing.

MSEL researchers work with industrial partners through informal collaborations, Cooperative Research and Development Agreements (CRADAs), and consortium arrangements. Industrial partners include resin suppliers, system suppliers, parts producers, members of the automotive industry, and offshore oil platform companies.

**Contact Information: Charles C. Han**

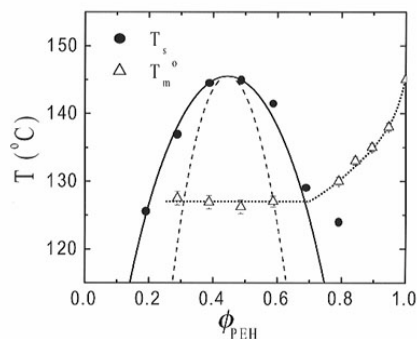
# Constitutive Relationship of Polymer Blends for Process Modeling Needs

Howard Wang, Charles C. Han

The first stage of this project is to obtain detailed and quantitative understanding of the phase transitions in a polyolefin blend. Then the focus will shift to the dynamics of phase separation in the presence of crystallization and non-equilibrium phase behavior under shear flow. A pair of commercial olefin polymers, metallocene-catalyst synthesized statistical copolymers of ethylene/hexene (PEH) and ethylene/butene (PEB), were selected as model materials. The PEH component is crystallizable. Research on the model system results in the following findings:

## Measurement of Phase Transitions

Modified optical techniques were used to identify the boundary of liquid-liquid phase separation (LLPS) because the almost identical refractive index of the blends components and slow kinetics made conventional optical methods difficult. The LLPS boundary has been determined using crystallization induced contrast. Incoherent and coherent light scattering, light transmission, atomic force microscopy (AFM) and differential scanning calorimetry, are used to exploit the crystallization morphology from previously homogenous or segregated blends. The blend exhibits an upper critical solution temperature of 146 °C. The composition dependence of the LLPS boundary follows the prediction of Flory-Huggins theory for binary polymer mixtures. The equilibrium melting temperature of the blends decreases from 145 °C for pure PEH with increasing PEB concentration in the miscible phase, whereas it remains relatively constant within 2-phase region (figure left).



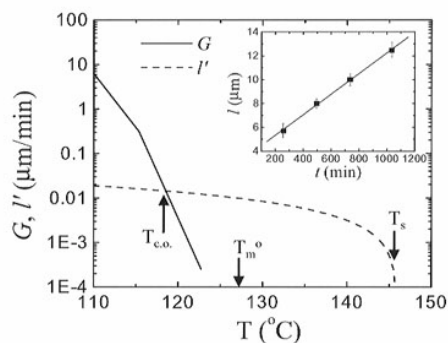
Process modeling may facilitate design of optimal conditions for processing polymer blends provided that the complex structure and behavior of these materials are treated adequately. Techniques and methodologies are developed to define and characterize necessary rheological, morphological and interfacial properties for multiphase polymer blends as a function of processing parameters, composition, phase miscibility, and crystalline structure growth. Constitutive relationships are formulated either as a database or in combination with analytical expressions for process modeling needs.

## Competing Kinetics

The kinetic interplay between crystallization and phase separation in a polymer blend has been examined. By controlling the relative quench depths for liquid-liquid phase separation and crystallization, the growth kinetics of the characteristic length scales of the simultaneous ordering processes show a crossover from crystallization dominated to phase-separation dominated behavior. Based on a scaling argument for late-stage spinodal decomposition, we conclude that this kinetic crossover is inevitable in a blend for which the critical temperature of liquid-liquid phase separation is above the equilibrium melting temperature of the blend, as shown in the figure below.

## Crystallization Morphology

Morphology development during competing LLPS and crystallization, and during crystallization in a previously segregated blend, either under quiescent conditions or under shear flow, is investigated using time-resolved small-angle light scattering, time-resolved small- and wide-angle x-ray scattering (SAXS and WAXS), optical microscopy (OM), and AFM. To date, comprehensive OM, SAXS and WAXS measurements on pure PEH and critical blends at different isothermal temperatures have been completed. AFM measurements on crystal morphology at selected temperatures are also made.



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## Modeling of Interfaces and Interphases of Polymeric Systems

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*A computational software tool is developed for predicting the microstructure evolution of polymer blends in injection molding operations for industrial users. The injection molding of polymer blends is carried out generally while the components are phase separated in which drops of one phase are dispersed in a matrix phase. The detailed morphology that develops during flow depends on the fluid mechanical deformation history, component rheological properties, and blend thermodynamics. The utility of the computational method is enhanced through a fundamental understanding of the interplay between the various process parameters and blend microstructure.*

We currently are engaged in a project to predict the microstructure that forms during the injection molding of polymer blends. Blend mixtures usually enter an injection molding cavity, well mixed and quenched, from an extruder. However, upon entering the cavity, the drops are highly sheared and break-up into finer and finer sizes near mold walls, and coarsen towards equilibrium sizes in regions of low shear. This leads to a non-uniform “skin-core” microstructure in the final part, which highly affects the properties. In order to predict the properties, one must be able to model the morphology that develops during flow. Our approach to this problem involves modeling flow at several length scales. Microscale models which simulate multiphase flow are used to predict detailed drop morphology. However, such models are too computationally demanding to model an entire injection molding process. Thus, volume averaged macroscale models, which use phase-averaged materials properties and micromodels to predict average material structure, are used to predict mold filling. By using such models in tandem, one can get a good approximate picture of the drop morphology. Complementing model development, experimental work

provides viscosity and drop size measurements as a function of shear rate and composition in blend mixtures.

Progress in modeling microstructure evolution resulted from a microflow simulation for binary mixtures based on the multiphase momentum balance and a Ginzburg-Landau free energy for the chemical potential in the chemical species balance. The model equations are solved together with the continuity equations, using a spectral finite element method. Figure 1 shows the evolution of a randomly dispersed initial phase into a discrete layered structure during shear flow. In the absence of flow the initial state coarsens into discrete drops. The simulation shall be extended to non-Newtonian flows in the next phase of the work.

An experimental component of this project is an exhaustive rheo-optical study of a variety of polymer blend systems under simple shear flow. By varying such parameters as the viscoelasticity of the components, the proximity to a critical point, and the interfacial tension between the phases, we are accumulating an experimental database to help guide these simulations. The primary measurement techniques are light scattering, optical microscopy and rheometry.

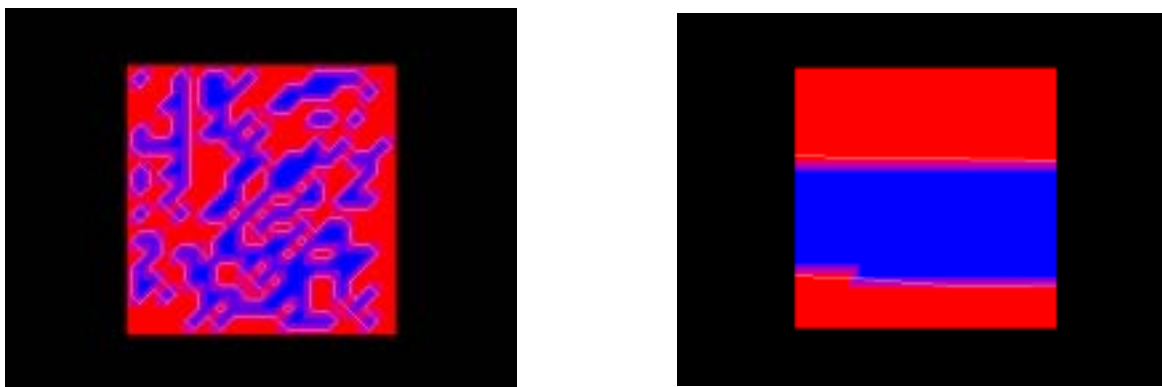


Figure 1. Evolution of binary microstructure during shear flow. (Left) Initial condition: randomly dispersed two-phase structure. (Right) Near steady state under shear flow, the phases form a layered structure.

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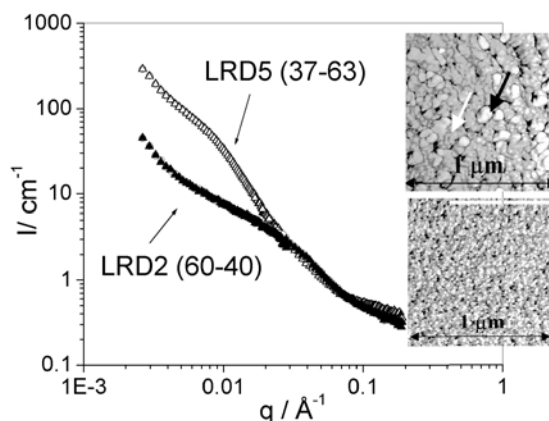
# Synergistic Interactions in Polymer-Nanoparticle Composites

Gudrun Schmidt, Francis W. Starr, Erik K. Hobbie, Charles C. Han

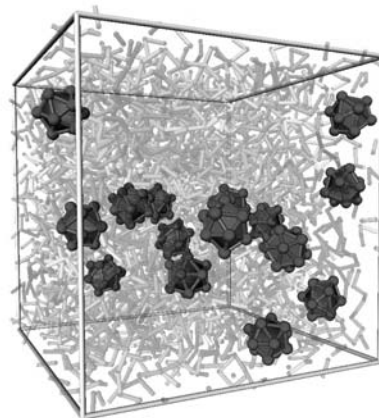
*Inorganic fillers frequently are used to enhance polymer properties. New attributes may be achieved with nanoparticulates provided that the underlying science is developed. Polymer nanocomposites are important in many diverse industrial processes. Potential applications derived from synergistic behaviors and hybrid properties of polymer-nanoparticle composites include data storage and optical and electro-rheological materials for display devices. The objectives of this project are to set new directions and provide fundamental understanding of polymer-nanoparticle interactions and how they dictate the properties of different materials.*

Shear-induced structural ordering in materials containing clay is a new problem encountered in nanocomposite-based materials. The shear orientation of viscoelastic polymer-clay solutions was studied by means of rheology, flow birefringence and small-angle neutron scattering (SANS) under shear. The polymer chains are in dynamic adsorption/desorption equilibrium with the clay particles to form a “network”. The elastic behavior of the network was characterized by constant stress, oscillatory shear, and stress relaxation experiments. Experiments under steady flow characterized the transient behavior of the network. With increasing steady shear rate a pronounced minimum in birefringence was observed at a critical shear rate showing that clay platelets orient first, then polymer chains start to stretch. The shear rate dependent viscosity exhibited near power-law behavior and no corresponding critical feature. While birefringence detects orientational effects on a microscopic-length scale, rheology averages over macroscopic changes in the sample. The same degree of orientation could be achieved under constant shear rate or constant stress conditions.

Simulations of a polymer melt surrounding a symmetric nano-particle have already shown the important role played by nano-particle/polymer interactions on the changes in the structure, dynamics, and glass transition of the melt. Continued work on these systems shows the importance of changes in the surface geometry and the surface-to-volume ratio on the relaxation of chains near the surface. Simulations focused on larger systems are probing the role interactions play in the dynamic clustering and dispersion of nano-particles within the melt. Our results indicate that clustering is very sensitive to changes of both the particle/particle and particle/polymer interactions. Additionally, shear flow, such as that experienced during injection molding, can alter the clustering properties of the particles. Finally, these particles also alter the blend phase diagram, an area of future consideration. Separately, we have also undertaken simulations of a carbon nanotube filled polymer melt in an effort to explore changes introduced by filler asymmetry.



**Figure 1. Concentration dependence of SANS intensity from polymer-clay nanocomposite samples is correlated with AFM. LRD2-bulk (40% PEO, 60% clay) and LRD5-bulk (63 percent PEO, 37 percent clay).**



**Figure 2. Snapshot of molecular dynamics simulation showing a configuration of dispersed nano-fillers embedded in polymer melt.**

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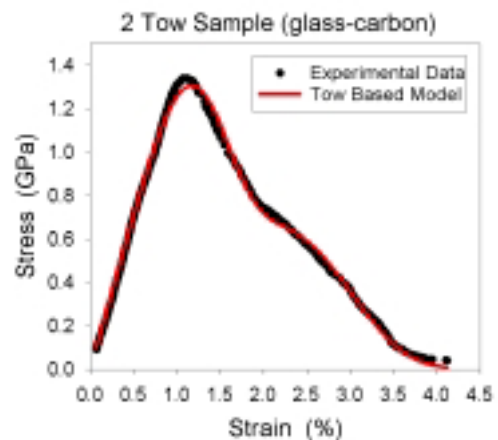
# Structure-Property Characterization and Modeling

The goal of this project is to provide industry test methods, reference data, and predictive models for advanced polymeric material by understanding the role of microstructure in performance. This technology will enable fabricators and users of these materials to develop superior products for applications in transportation, infrastructure, aerospace, and off-shore oil exploration.

Donald L. Hunston, Charles C. Han

To achieve the goals of the project, research is conducted in three tasks. First, techniques are developed to characterize the microstructural features in complex multicomponent polymeric systems. Second, existing measurement techniques are adapted or new methods are generated to determine properties in materials with complex microstructure. Finally, models are formulated to relate the performance of such materials to the properties of their constituents and the microstructure that is present. Where appropriate, Object Oriented Finite Element Analysis (OOF) is employed to incorporate the measured microstructure into the models. The methods developed in the three tasks then are applied to model systems that are relevant to industrial needs.

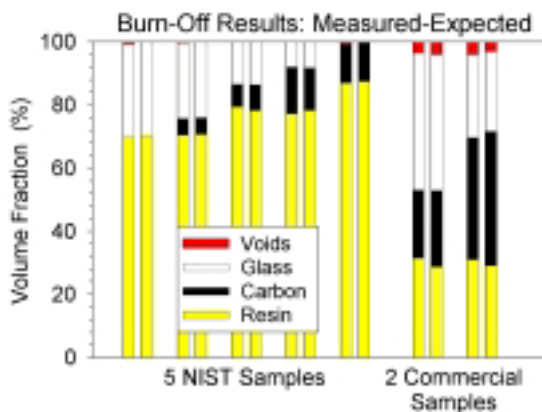
Hybrids are polymers reinforced with two or more different types of continuous fibers. By combining two fibers it is often possible to achieve significantly better trade-offs among various properties and between cost and performance. For this reason, hybrids are a prime candidate for use by the construction industry in composite bridge design and by the oil industry in off-shore drilling platforms. NIST is working with the Composites Engineering and Applications Center at the University of Houston to bridge the gap between laboratory tests and industrial applications. Recent results in this program are discussed below.



**Microstructure Determination:** Microscopy has been used to determine fiber arrangement, void content, and void distribution in hybrid composites, but fiber concentration and mix are difficult to quantify. Consequently, a modification to the burn-off test was developed to assess these features. The procedure has been verified with tests on samples of known concentrations (see figure left).

**Test Method Development:** The Iosipescu test was used to measure the shear moduli of hybrid composites. This test has now been used to characterize the behavior of the model hybrid composites that were characterized in the Microstructure Determination task. Tensile properties were also determined.

**Modeling:** To predict the moduli determined above, a tow-based finite element model was developed. Based on properties of the constituents, both the tensile and shear moduli were modeled successfully as shown in above figure. The actual microstructures determined in the Microstructure Determination Task were used in the model. The work is now being extended to failure behavior. With a tow-based approach, the complete stress strain curve for this sample could be predicted based on the behavior of a single glass and a single carbon fiber.



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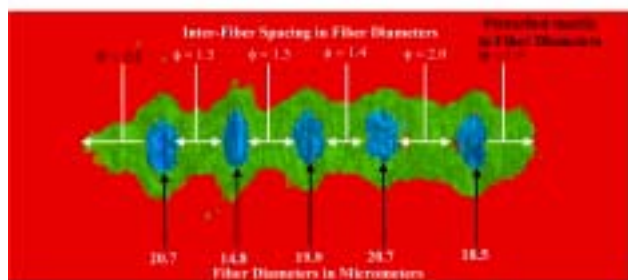
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# Mechanics of Fiber and Nano-Filled Composites

Gale A. Holmes, Charles C. Han

It is recognized that single fiber tests are inadequate in predicting failure in 3-dimensional structures. Our efforts are transitioning from 2-D multi-fiber arrays to 3-D fiber arrays. The current data, however, focuses only on 2-D multi-fiber model composites.

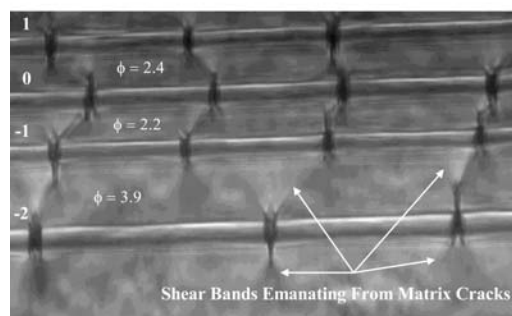
In Figure 1, the inter-fiber spacings between four of the five fibers in a 2-D array are between (1.4 to 1.5) fiber diameters. Capitalizing on optical coherence tomography's (OCT's) unique ability to see changes in matrix stresses, the area immediately surrounding the fibers (> 2 fiber diameters) was observed to have a different intensity than the bulk resin (< 2 fiber diameters). This intensity change reflects the residual curing stresses that occur due to the close proximity of the fibers. This change in intensity is not observed in single-fiber fragmentation specimens.



**Figure 1. Isosurface plot of a multiple E-glass fibers (blue) embedded in DGEBA/m-PDA matrix (red). Green region surrounding the fibers denotes residual curing stresses. Data obtained using optical coherence tomography.**

The initial 2-D multi-fiber arrays consisted of embedded fibers coated with 11-aminoundecyl trichlorosilane (11-AUTCS) deposited using self-assembled monolayer (SAM) technology. The SAM technology is being used in a companion micromechanics project to probe the effect of covalent bonding, mechanical interlocking, and physico-chemical interactions on the transfer of shear stresses at the fiber-matrix interface.

*Failure prediction is critical to the use of fiber-reinforced composites in many applications. Multi-fiber model composites are being used to conduct fundamental studies into the nucleation of failure in fibrous composites. Current results have revealed that the nucleation of critical flaws in unidirectional fibrous composites may depend on the time-dependent redistribution of stress by the viscoelastic matrix. Although their role in flaw nucleation is not understood clearly, shear deformation bands have been detected between fiber breaks and residual curing stresses have been detected in the matrix by optical coherence tomography.*



**Figure 2. Fiber break patterns from E-glass/DGEBA/m-PDA 2-D multi-fiber array (stressed). The interfiber spacing is denoted by  $\phi$ .**

Consistent with epoxy-compatible industrial coatings, the 11-AUTCS coating exhibits matrix crack formation in addition to fiber-matrix debonding during fiber fracture. Initial investigations revealed the presence of 45° shear deformation bands emanating from the crack tips when specimens are under tensile load (see Figure 2). The shape of the matrix cracks surrounding each fiber break is similar to unsymmetrical penny-shaped cracks. It is known that penny-shaped cracks in a material subjected to uniaxial tensile loads generate 45° deformation shear bands that form relative to the tensile axis at the crack-tip. The deformation bands emanating from the crack tips in Figure 2 may relate to this phenomenon. The location of the penny-shaped flaws within the composite is controlled by the spatial population of flaws in the embedded fiber and the stress transfer efficiency at the fiber-matrix interface. The influence of these shear bands on the non-aligned fiber break patterns shown in the figure is not known. It is believed at this point that these bands may be an important key to understanding the role that the viscoelastic matrix plays in nucleating critical flaws in fibrous composites.

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# Poly-OOF: A Virtual Experimental Tool for Polymer Research

The understanding of the relation between the morphology and properties of a polymer mixture is still lacking. Our objective is to develop a morphology-adaptive approach that allows scientists and engineers to explore the behavior on the scale of the microstructure and compare that behavior to macroscopic properties.

Martin Y.M. Chiang, Charles C. Han

Most polymer blends exhibit a phase separation that leads to a heterogeneous morphology. The scale and type of the morphology determines the properties of the polymer blend. However, understanding the relation between the morphology and the properties of polymer blends is still lacking. In order to explore this relation, we performed computational studies that combine simulation of phase separation with generic finite element approach through a computer program having the capability of morphology adaptation. This combination of modeling can help to identify the potentials of multiphase material behavior and can serve as a virtual experimental tool. This tool allows scientists to explore behavior on the scale of the microstructure and to compare that behavior with macroscopic properties. Consequently, it can result in reduced material fabrication costs and improved material performance. Currently, our study has been limited to binary polymer blends.

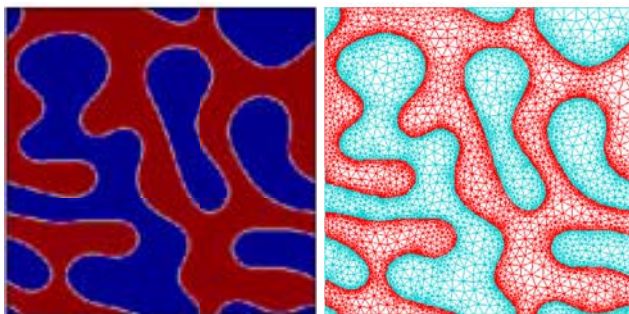


Figure 2. Micrograph of simulated morphology and finite element mesh.

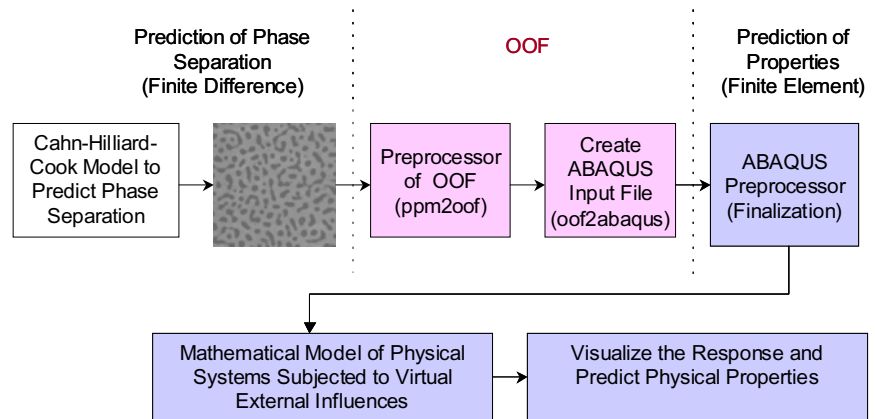


Figure 1. Flow chart of the proposed FEA as a virtual experimental tool.

The procedure of the virtual experiment is illustrated in Figure 1. The phase separation of polymer blends is simulated using a Cahn-Hilliard-Cook model solved with a finite difference scheme. The micrograph of the simulated morphology is automatically adapted through NIST-developed OOF (Object-Oriented Finite Element Program), which converts the information describing the microstructure into a finite element mesh (Figure 2). The resulting mesh is used by a general-purpose finite element program (Abaqus) to formulate a mathematical model of the physical system subjected to virtual external influences. The material properties of the blends can then be calculated and the response visualized to explore the interaction of the components. To date, the elastic modulus and coefficient of thermal expansion have been predicted for a range of simulated microstructures of a phase-separated binary system. Three combinations of material models have been considered that correspond to glassy-glassy, rubbery-rubbery, and glassy-rubbery states of the components of the system.

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# Polymer Characterization

The Polymer Characterization Program provides measurement methods, data, and Standard Reference Materials (SRMs) needed by U.S. industry, research laboratories, and other federal agencies to characterize rheological and mechanical properties of polymers, their processibility and performance, and to improve process control. In response to the critical needs of industry for *in-situ* measurement methodologies, a substantial effort is under way to develop optical, dielectric and ultrasonic probes for use in extrusion and injection molding. Improved methods for determining molecular mass distribution of polymers are developed owing to the dramatic effect it has on processibility and properties. Mechanical properties and performance are significantly affected by the solid-state structure formed during processing. Importantly, unlike many other common engineering materials, polymers exhibit mechanical properties with time dependent viscoelastic behaviors. As a result, the program also focuses on techniques that measure the solid-state structure and rheological behavior of polymeric materials.

Chromatographic techniques, which require calibration by standards of known molecular mass, are the principal methods for determining molecular mass distribution. Because calibration standards are lacking for most polymers, crude approximations must be used to interpret chromatographic data. Recent program activities exploit advances in mass spectrometry using matrix-assisted laser desorption ionization to develop the method as a primary tool for the determination of the molecular masses of synthetic polymers, with particular emphasis on commercially important polyolefins. Advances are sought in measurements of the solid-state structure of polymers, including optical coher-

ent tomography, inelastic neutron scattering, and sum frequency generation spectroscopy.

The extrusion visualization facility combines in-line microscopy and light scattering for the study of polymer blends, extrusion instabilities, and the action of additives. Current research focuses on understanding and controlling the “sharkskin instability” in polymer extrusion. Fluorescence techniques are developed to measure critical process parameters, such as polymer temperature and orientation that were hitherto inaccessible. These measurements are carried out in close collaboration with interested industrial partners.

The polymer industry and standards organizations assist in the identification of current needs for SRMs. Based on these needs, research on characterization methods and measurements are conducted leading to the certification of SRMs. Molecular standards are used primarily for calibration of gel permeation chromatographs, the principal method employed by industry for assessing molecular mass and molecular mass distributions. Melt flow standards are used in the calibration of instruments used to determine processing conditions for thermoplastics. Non-Newtonian rheological standards are also developed to exhibit the typical polymeric behaviors of shear thinning and normal stresses; these standards are also used for calibration of rheological instruments and for research into improved measurement methods. Reference biomaterials are produced for test method harmonization, assessment of new materials, and generation of reference data.

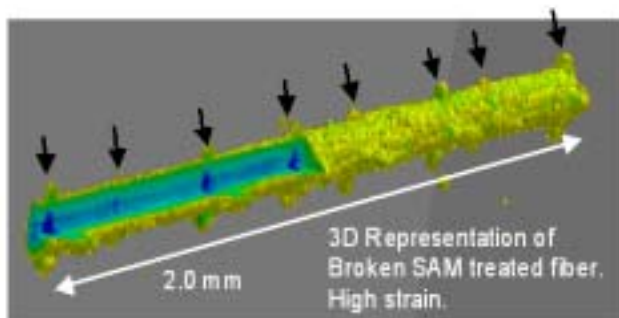
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# Optical Coherence Tomography

Joy P. Dunkers

*We have adapted optical coherence tomography (OCT), a new method for medical imaging, to the realm of material science. More specifically, we apply OCT for meso-scale, volumetric characterization of polymer composites, birefringence, polymer blends, biomaterials and ceramic coatings that cannot be obtained by any other technique. A volumetric representation of the internal structure of the above materials in the micrometer- to millimeter-size scale is often required to understand how various properties of interest are interrelated.*

Optical coherence tomography (OCT) is a non-invasive, non-contact optical imaging technique that allows the visualization of microstructure within bulk materials. OCT uses a near-infrared low coherence source and a scanning fiber optic interferometer for depth discrimination. Reflections generated from material heterogeneity are collected as a function of depth. A requirement for this type of tomography is that the material be transparent to near infrared light,



**An OCT image of the multiple breaks of a glass fiber embedded in polymer matrix. The breaks in the fiber become visible in OCT through the stress-induced birefringence of the matrix material. The locations of the breaks are marked by arrows in the figure.**

making many polymer systems excellent candidates. The imaging is performed by collecting back-reflected light generated from heterogeneities within the sample. The higher the refractive index mismatch at a boundary, the stronger the return reflection at any given depth. Thus, OCT has the ability to distinguish different types of features. OCT is attractive because of its high sensitivity, which enables a typical sample to be imaged at depths anywhere from 0.5 mm to 4 mm. The resolution of the system is 10  $\mu\text{m}$  to 20  $\mu\text{m}$ . Recently, resolutions of 3  $\mu\text{m}$  have been reached with state-of-the-art lasers, electronics and optics. Additionally, OCT systems have been built that are

polarization sensitive (PS-OCT) and these systems gather information about sample birefringence.

OCT has been used historically for medical imaging. We are bridging the gap between materials science and medicine by using OCT to non-destructively elucidate the meso-scale structure of heterogeneous polymeric systems, including biomaterials and polymeric composites. An advantage of OCT is the ability to image biomaterials, such as tissue engineering products, in aqueous medium to mimic their natural state. Critical characterization challenges in tissue engineering scaffolds are to quantify pore size, size distribution and tortuosity and to relate these variables to some measure of the success of cell growth. By generating scaffolds with systematic variations in pore size and pore connectivity, cell growth can be studied quantitatively. In this work, samples made of polycaprolactone and poly(ethylene oxide), PEO, blends were annealed to various times at 75  $^{\circ}\text{C}$ . Then, the PEO phase was removed by dissolving in water. Pore size distribution and tortuosity of these materials were obtained successfully from OCT results. Given the success of this initial work, the next phase of this project will consist of relating the cell growth to the 3-D pore structure of scaffolds generated with systematically varying microstructure.

Two issues in the area of composites were addressed using OCT. Reinforcement microstructure affects the success of a composite part during the manufacturing process. OCT was used to image the reinforcement microstructure and thereby provide insight into the flow characteristics of the resin inside the mold. Secondly, OCT was used to identify various damage modes within a glass-reinforced composite. An example is given in the figure where the breaks along the glass fiber are marked by the arrows. The birefringence in the polymer matrix surrounding the breaks is responsible for the optical contrast. In the near future our OCT system will be upgraded to include a polarization sensitive capability. Effort will be directed to quantify birefringence in 3-D. In addition, data dropout from sample birefringence will be compensated for, to provide an increased image depth in deformed samples.

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# Polyolefin Mass Spectrometry

William E. Wallace

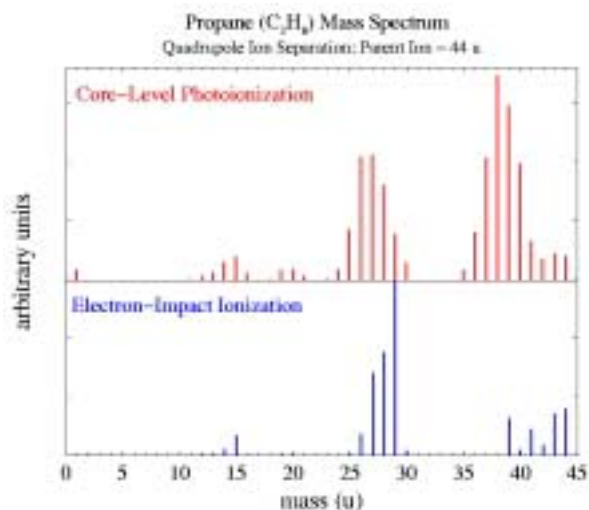
New methods of traditional metal cationization on fully saturated polyethylenes are explored in collaboration with Professor Liang Li of the University of Alberta. In this work, silver is used as the metal cation as is typical for synthetic polymer mass spectrometry; however, instead of using the usual organic acid matrices finely divided cobalt powder is substituted. Mass spectra of intact oligomers up to 5000 u have been measured, indicating intact parent in cationization by silver is possible; however, fragmentation ions are always present complicating spectral interpretation. It is well-known that most metal ions will insert into C-C bonds leading to fragmentation on the time scale of the experiment.

A chemical modification method has been developed in the Polymers Division that allows mass spectrometry to be performed on saturated hydrocarbon polymers. Two synthetic steps are involved: selective bromination of the polymer, followed by conversion of the brominated site to a charged ammonium or phosphonium group. A strong mass spectrum was produced from the modified polymers while the unmodified and the brominated polymers produced no signal at all. This concept has been termed the “covalent cationization method” and has also been demonstrated on unsaturated olefins such as polystyrene and polybutadiene. It is envisioned that this method may become applicable to all types of polymers complementing, or possibly replacing, the metal cationization methods already in use.

Physical ionization methods are also considered. Removal of valence electrons by electron or photon irradiation typically results in excess energy imparting to the molecule and subsequent scission of the C-C bonds. This leads to an abundance of fragment ions. Working with Daniel Fischer (Ceramics Division) using the NIST vacuum-ultraviolet beamline U7A at the National Synchrotron Light Source at Brookhaven National Laboratory (Upton, N.Y.) carbon *core* electrons were ejected from gas-phase alkanes. The photon energy can be tuned to promote Auger relaxations from the C-H bonds and not from the C-C bonds to avoid chain fragmentation. Figure 1 shows a comparison of core-level photoionization and electron-impact ionization for propane.

Saturated hydrocarbon polymers, polyethylene and polypropylene, are the most widely used of all synthetic polymers. Their molecular-mass distribution (MMD) is critical in determining performance properties. Mass spectrometry is currently the most promising method for obtaining accurate, absolute MMDs; however, polyethylene and other polyolefins have not been amenable to mass spectrometric characterization due to the ineffectiveness of conventional methods of cationization. The Polymers Division has addressed this challenge with three distinct cationization approaches: traditional metal cationization, chemical modification, and physical ionization.

The photoionization does bias the mass spectrum toward proton loss compared to the electron-impact ionization; however, residual vibrational energy in the room temperature propane combined with overlap in the valence-electron orbitals leads to not insignificant C-C bond scission.



**Figure 1. Comparison of core-level photoionization with 287.5 eV photons ( $C\ 1s \rightarrow C-H\ \sigma^*$  transition) and electron-impact ionization with 70 eV electrons for propane. The parent ion at 44 u is seen in both spectra. The core-level photoionization is dominated by ions at 38 u to 40 u created by the loss of hydrogen atoms while the electron-impact ionization is dominated by C-C bond cleavage as evident from a major peak at 29 u corresponding to  $C_2H_5^+$ .**

### Industry Interaction:

Discussion of measurement needs and future collaborations on polyolefins with Dow Chemical, ExxonMobile, and Union Carbide is in progress.

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## Fluorescent Sub-Micrometer Probe Molecules with Starlike Architecture

Ronald C. Hedden, Barry J. Bauer

*Rapid advances in nanostructured materials technology motivate development of new methods for structural characterization. We are developing fluorescent polymeric markers for use as probes of sub-micrometer features in membranes, polymer blends and biomaterials. Fluorescent star-shaped polymers with effective sizes in the 10–100 nm range have been targeted as model probes. The detection of fluorescent probes using advanced optical techniques could lead to new methods in polymer structural characterization.*

Fluorescent sub-micrometer probe molecules are needed to characterize structures and transport properties of membranes, polymer blends and biomaterials. An ideal fluorescent probe would exhibit monodisperse size, versatile solubility, high luminescence, minimal photobleaching, and stability under conditions of varying temperature, solvent and pH. Taken together, these criteria are rather demanding making the development of model probes a challenge.

With the goal of fluorescent probes in mind, we prepared and characterized a new class of highly branched, star-shaped polymers containing fluorescent tags. These stars have well-defined structures with effective solution-phase diameters on the order of 10–100 nm (0.01–0.1  $\mu\text{m}$ ). The stars can be tagged with either an organic fluorophore or with fluorescent semiconductor nanocrystals (“quantum dots”). The attractive features of these novel probes include controllable polymer architecture and tunable photophysical properties.

Stars are prepared by attachment of monofunctional poly(ethylene glycol) (PEG) “arms” to poly(amidoamine) (PAMAM) dendrimer “cores”.

Dendrimers are layered, treelike polymers that contain many functional endgroups. The number of dendrimer endgroups increases geometrically with the dendrimer “generation,” or number of layers. The maximum number of PEG arms that may be attached is equal to the number of dendrimer endgroups. A PAMAM Generation 4 star may have up to 64 arms, and a PAMAM Generation 7 star may have up to 512, for example. PEG was chosen for the “arms” due to its versatile miscibility with water, organic solvents and many polymers.

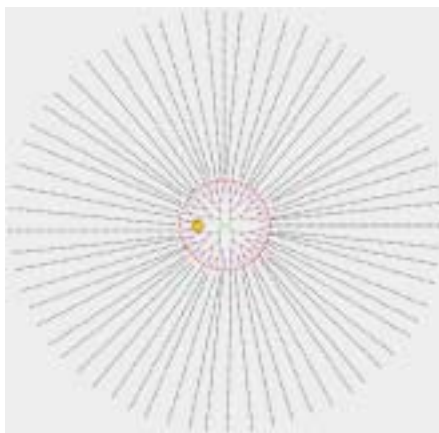
Using a standard synthesis, we have labeled the stars with organic fluorophores. Stars with less than the maximum

number of arms contain unreacted primary amine endgroups, which function as reactive sites for the attachment of organic dyes. The labeled stars are highly luminescent and color-tunable, but organic fluorophores often exhibit poor resistance to photobleaching.

Semiconductor nanocrystals, such as CdS or CdSe, are an alternative type of photobleach-resistant fluorescent

marker. PAMAM dendrimers interact strongly with many types of metal ions, including  $\text{Cd}^{2+}$ , allowing attachment of CdS nanocrystals to the star polymer cores. We have prepared successfully highly fluorescent star-CdS nanocomposites and characterized their physical properties. Gel permeation chromatography and small-angle neutron scattering experiments indicate that the CdS nanocrystals may be introduced without disturbing the size distribution of the stars. Although it has not been straightforward to achieve color tunability, these materials are a milestone in the development of photobleach-resistant fluorescent probes.

Current work focuses on testing fluorescent star polymers as probes. Researchers at NIST (Boulder) are characterizing mass transport in membranes by novel combinatorial methods using fluorescent probes. To facilitate this study, we are developing a series of fluorescent stars with well-defined sizes and independent emission spectra. We are also interested in observing the behavior of the stars in immiscible polymer blends using advanced optical microscopy techniques. We will determine whether the stars migrate to phase boundaries to help explain how highly branched polymers affect the properties of immiscible blends.



**Figure 1. Schematic diagram of a novel fluorescent probe: dendrimer-star polymer containing a CdS nanocrystal.**

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## Standard Reference Materials

Charles M. Guttman, Carl R. Schultheisz

Standard Reference Materials and Reference Materials are issued to address needs of the producers, processors and users of polymers for calibration and for performance evaluation of instruments used in the control of the synthesis and processing of polymers, as well as benchmarks for comparisons of measurement methods and development of new materials. Recently produced Standard Reference Materials include polyethylene of narrow mass distribution certified for mass average molecular mass and intrinsic viscosity and a nonlinear fluid standard for rheological measurements. In addition, the first reference biomaterial, RM 8456, an orthopedic grade ultra-high molecular weight polyethylene, UHMWPE, was issued for use in development of improved test methods for wear and as a benchmark for development of improved materials. Radiation cross-linking of UHMWPE is being pursued by the orthopedics products industry for improved wear resistance products. Better test methods for degree of cross-linking are under evaluation by ASTM through interlaboratory comparison on irradiated samples produced from RM 8456. NIST participated by providing specimens of RM 8456 in a form suitable for the interlaboratory comparison. In anticipation of continuing need for Reference Material UHMWPE for radiation studies NIST is issuing orthopedic grade UHMWPE cubes for radiation cross-linking tests and analysis. This Reference Material is produced from RM 8456.

Among polymer standards provided by NIST are those certified for melt flow, the primary characteristic of a polymer melt used by both producers and processors of polymers to determine the required characteristics of processing equipment. The NIST melt flow standards are referenced in ASTM test method for melt flow for use in assessing laboratory proficiency. Stock of SRM 1473, a melt flow standard, will be depleted in a few months. To address the continuing need for this standard a new batch of resin, from the same source as that used to produce SRM 1473, is certified for melt flow. Current standard test method for melt flow extends to temperatures and flow

*Reference Materials (RM) and Standard Reference Materials (SRM) are produced to address needs of the producers, processors and users of synthetic polymers for calibration of instruments, assessment of laboratory proficiency, test method development and materials development. An orthopedic grade ultra-high molecular weight polyethylene RM is prepared in the form of cubes for irradiation studies. Recertification of a melt flow standard and certification of a non-Newtonian fluid for rheological properties assist polymer processors and producers. The first polymer molecular mass standard is produced with the complete mass spectrum as ancillary data.*

rates under which polymer melts typically degrade, thereby affecting the reliability of the result. Test conditions are determined under which a thermally stabilized resin would have sufficient stability to render melt flow measurements more meaningful. A high temperature, high flow rate melt flow standard would be used for performance evaluation under these conditions.

SRM 2490, a non-Newtonian polymer solution for rheological measurements, was issued for use in calibration and performance evaluation of instruments used to determine viscosity and first normal stress difference in steady shear, or to determine the dynamic mechanical storage and loss moduli and shift factors through time-temperature superposition. Discussions with potential customers of SRM 2490 revealed the need for a second non-Newtonian fluid designed for calibration and performance evaluation of rheometers that lack the stringent temperature control required for calibration with SRM 2490. A suitable polymer fluid, poly (dimethylsiloxane), has been procured to meet these requirements. We will conduct homogeneity measurements followed by certification for non-Newtonian viscosity and the first normal stress difference over a range of temperatures and shear.

SRM 2888, polystyrene possessing a narrow molecular mass distribution, is certified for mass average molecular mass by light scattering. The number average molecular mass determined by high-resolution NMR and mass spectrum measured by matrix-assisted laser desorption/ionization (MALDI) mass spectrometry (MS) are provided as ancillary data. This material was used in an interlaboratory comparison of mass distribution measurement by MALDI MS. The results of the analysis of data submitted by the 18 participating laboratories were published in the journal *Analytical Chemistry* (*Anal. Chem.* 2001, 73 1252-1262). Additional information on the interlaboratory comparison is given in the accomplishment section of this report under the title "Polymer Mass Distribution by Mass Spectrometry."

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Interlaboratory Comparison, Industrial Participants: Lab Connections, Eastman Chemicals, Air Products, 3M, ICI, Charles Evans & Associates, Hercules, Bruker Daltonics, Zeneca, Union Carbide, DuPont

# Quantitative Mass Spectrometry of Synthetic Polymers

Charles M. Guttman

## Sample Preparation

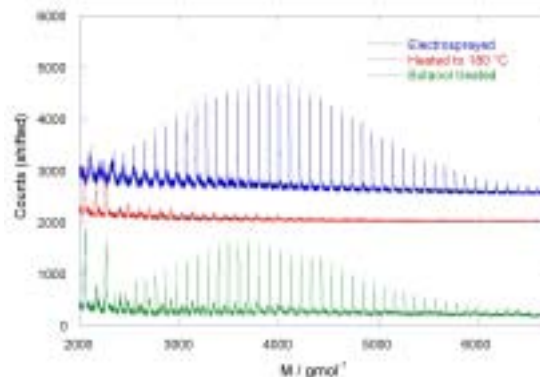
For synthetic polymers samples, MALDI TOF MS can yield quantitative information about end groups, repeat units, molecular masses and molecular mass distributions. Accurate quantitative measurements require equimolar responses for all sample species in the mass range over which a sample is distributed.

Efforts to modify MALDI sample preparation techniques for synthetic polymers with the goal of increasing sample homogeneity and the equimolar peak signal intensity have met with modest success. The usual sample preparation method involves hand-depositing on the sample plate. This sample preparation technique leads to variations in MALDI signal intensity as the ablating laser beam scans across the sample, indicating sample inhomogeneities on the size of the laser spot (25  $\mu\text{m}$ ). An electrospray sample preparation technique showed improvement in the statistical variation of MALDI intensities as long as the sprayed coating was thick.

Experiments were conducted also to address sample morphology in the nanometer scale with the goal of determining if optimal MALDI signal was obtained when analyte molecules were molecularly dispersed in the matrix. This question derives from the premise that the lack of MALDI signals from polyolefins may relate to their segregation from the matrix owing to rapid crystallization under the sample preparation conditions used. Small-angle neutron scattering has been used to measure the size and level of dispersion of synthetic polymers in MALDI samples prepared by electrospraying. In dithranol, a common matrix, deuterated polystyrene (PSD) was found by SANS to form aggregates of size greater than 20 nm. The size of the aggregates appears to be unaffected by the solution concentration of PSD in sample preparation, at least over the concentration range typically used. This suggests that reproducible MALDI results may be obtained without molecularly dispersed polymers.

*The molecular mass distribution (MMD) of a polymer has profound effects on how it is processed and the resultant properties. Recent advances in matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry (MS) suggest that it is possible to obtain the MMD of undegraded polymer molecules with molecular masses up to 300,000 g/mol. Experiments in this project are directed to the use of MALDI to obtain the measurement of the absolute molecular mass distribution of synthetic polymers.*

More definitive results were obtained on a new type of matrix for MALDI, tri- $\alpha$ -naphyl benzene, that forms both glass and crystalline states. By SANS it was shown that PSD is molecularly dispersed in the glass, but segregated in the crystalline state. Figure 1 below shows that the MALDI signal is inferior when PSD is dispersed molecularly in the glass compared to the MALDI signal obtained when PSD is phase separated.



## Baselines in Data Analysis

To derive quantitative results from MALDI spectra care must be given to treatment of the baseline, particularly in spectra where the signal does not return to the same minimum value between each oligomeric peak. A common feature in the MALDI spectrum of synthetic polymers is the appearance of a broad featureless hump that underlies the spectral data. The broad hump is usually offset to the higher mass side with respect to the envelope of the peak distribution and it may extend beyond the highest mass identifiable oligomeric peak. Including the hump as part of the polymer signal in the analysis can affect significantly derived moments of the distribution (for comparisons with other methods, for example). In a set of definitive experiments it was shown that the broad hump results from fragmentation products and polymer-matrix adducts. For this reason the proper treatment is to eliminate the broad hump from spectral data to obtain the MMD and its moments.

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# Support for the Biomaterials Integrated Products Industries

John Tesk

Approximately \$140 billion are spent annually on health care measurements associated with biomedical devices, quality control and many other diagnostic and therapeutic procedures. NIST workshops have identified needs for reference biomaterials (RBMs, 1998) and reference biomaterial properties data (RBMPD, 2000). Among these were reference bars of medical grade Ultrahigh Molecular Mass (weight) Polyethylene (UHMWPE). NIST has responded by stocking a supply of UHMWPE RM 8456 which became available in October 2000. At the 2000 RBMPD workshop, participants identified a major need for a national biomaterials properties database system. Properties of the database system include portals with data from different sources, one with data as supplied by manufacturers of biomaterials and biomedical devices, another with data from testing laboratories such as those of the FDA, and a NIST database with data from the literature and from certificates that accompany NIST Reference Materials (RMs) and Standard Reference Materials of biomaterials. A property of the NIST database is that it contains critical evaluations of the properties included. Certificate data for reference biomaterials was seen as an important source for critically reviewed properties database. An alliance was formed with several intraocular lens and biomaterial companies, and two major university eye clinical centers for the development of intraocular lens reference materials and reference data. Alliances are being pursued for a tissue engineered products reference scaffold and for the development of additional orthopedic reference materials.

*NIST workshops have established the needs of the medical devices industry (BIPIs) for reference materials, test methods, and reference data. In this project a continual assessment is made of the technical needs of BIPIs to inform NIST management for program planning. Leadership is taken to help form alliances, within and outside of NIST, to respond to those needs. Needs are explored through participation on numerous standards boards and their committees, on committees/boards of professional societies and academic institutions, and via liaisons with NIH, FDA, the American Academy of Orthopaedic Surgeons, and the American Dental Association.*

Participation and leadership in standards organizations are seen as other means for assessing the needs for other RMs and RBMPD. Collaboration continues with industry and an ASTM committee for the development and supply of UHMWPE reference cubes that can be used for swelling measurements for the determination of crosslink density as a result of ionizing radiation (crosslinking affects wear resistance and durability of orthopedic joint implant bearing surfaces).

A workshop on Standards for Biomedical Materials and Devices was identified by NIST major operating units at a meeting convened by the Materials Science and Engineering Laboratory, as a means for establishment of a NIST-wide strategy for work on standards in support of the biomedical devices industry. The Polymers Division held a major role in the organization and operation of the workshop, which was held on June 13, 2001. The workshop identified action items for NIST early follow-up in support of the biomedical materials and devices industry, and items for consideration of future NIST responses to the industry's needs for standards.

Publications were also pursued to provide greater visibility of NIST to the BIPIs community. An invited paper on the proceedings of the RBMPD workshop was published in the July issue of the *Journal of Biomedical Materials Research, Applied Biomaterials*.

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## Control of Extrusion Instabilities

*Polymeric materials have become ubiquitous in the modern economy because they are comparatively easy to process. However, polymeric materials exhibit complex and sometimes catastrophic responses to the forces imposed on them during manufacturing. These instabilities limit the rates at which the materials can be processed. In this project we seek new measurement technologies to understand and control processing instabilities.*

Kalman B. Migler

The understanding and control of extrusion instabilities is hampered by the lack of experimental techniques that provide real-time data at sufficient spatial and time scales. We recently have upgraded the Extrusion Visualization Facility so that it can operate at high-speed/high magnification. Using our new capabilities, we collected an abundance of data that clarifies several of the uncertainties



regarding the nature of the sharkskin instability (see accomplishment report). Buoyed by that success, we are opening efforts to study the “gross melt fracture instability”, to develop new metrology to quantitate the polymer processing additive coating process, and to probe the correlation between instabilities and molecular architecture.

### Sharkskin and Gross Melt Fracture

Using the extrusion visualization facility, we examine the flow behavior of the polymer as it is extruded through a capillary rod. High-speed microscopy of the material as it exits the tube reveals that the molten material tears at its surface just at the exit from the tube. The central core of the material extrudes at high speed while the surface region tears, peels off and then joins the central core (see Figure).

Current work is examining an extrusion instability known as gross melt fracture. This is characterized by severe distortions in the extruded material. Traditionally, it is believed that this instability occurs in the region where the material narrows down from a large diameter to a small one, well upstream of the capillary exit. However, we recently have discovered that the exit region may be of importance. We have discovered that the material undergoes transient-spontaneous cavitation in the exit region of the tube during gross melt fracture. We intend to understand cavitation and its implications for gross melt fracture control.

### Measurement of In-situ Coating Process

Polymer Processing Aids (often fluorocopolymers) eliminate sharkskin by reducing the extensional deformation of the polymer as it exits the die. In order to work, the fluoro-copolymer must first coat the die’s internal surface. This coating process is critical to product performance, yet there are no in-situ quantitative measures of the coating. Here, we seek a new measurement technique for the coat-

ing of a fluoropolymer additive based on evanescent wave induced shifts in optical reflection. We propose to measure quantitatively the formation and growth of the fluoro-polymer layer onto the solid wall through use of total internal reflection. When the fluoropolymer starts to coat the internal wall, the conditions of total internal reflection will be met and dramatic changes in optical reflection are predicted. The thickness of the fluoropolymer layer at which this technique first becomes effective is determined by the penetration depth of the evanescent wave (the exponentially decaying light that does not become reflected). For the materials used here, the effects of the wall will be felt when its thickness is approximately 100 nm, which is exceptional for an optical measurement.

### Molecular Architecture and Extrusion Instabilities

One of the great challenges in rheology is to elucidate the connection between molecular architecture and rheology, and to apply this knowledge to the study of flow instabilities. This question is particularly important because recent synthetic strategies allow for precise control of the molecular architecture, such as long chain branching and molecular mass distribution. We are starting a project to use and develop our measurement tools to examine critical flow parameters at the onset of various extrusion instabilities. We will correlate these measurements with characterized materials that have systematic variations in architecture.

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3M Canada Co., 3M Company, Dyneon LLC, Dow, MMI



# Real-Time Process Monitoring

Anthony J. Bur

## Optical Technique

Over the past several years we have concentrated our attention on the development and use of optical techniques involving light transmission and fluorescent molecular probes. We have instrumented extrusion and injection molding machines and shown how optical sensors can provide a wealth of information about the resin under processing conditions. When selected fluorescent probe molecules are added to the resin, we can use them to monitor resin temperature and molecular orientation. The fluorescent probes are mixed with the resin at very low concentrations, less than  $10^{-5}$  mass fraction of dye in the resin.

A class of fluorescence molecules called band definition dyes is used to measure temperature. We have discovered several dyes that survive processing temperatures up to 300 °C. They are benzoxazolyl stilbene (BOS), perylene, and bis(di-tert-butylphenyl)-perylene dicarboximide (BTBP). These dyes display their fluorescence in distinct spectral bands that have individual temperature dependence. The basis for measuring temperature is the temperature dependence of the shape of the fluorescence spectrum.

The fluorescence temperature measurement method is used in collaborative programs with three industrial R&D laboratories—Exxon/Mobil Films, DOW Chemical, and Data-point Labs. At Exxon/Mobil we are monitoring the temperature of biaxially stretched polypropylene films that contain the fluorescent dye BTBP.

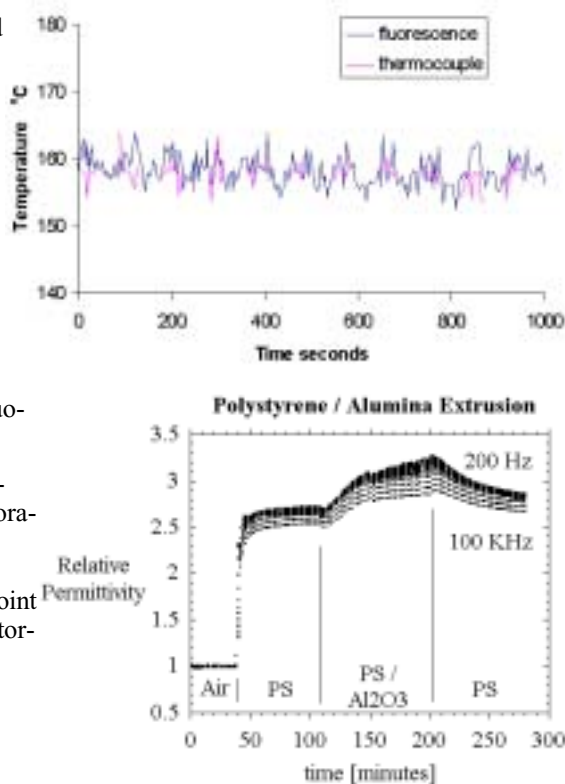
*Real-time, on-line measurements of resin materials properties are desirable not only because they preempt the need for post processing characterization but also because they can be used to monitor resin conditions, to detect problems with processing parameters and to control the process. In this project, we are developing measurement techniques based on optical, dielectrics, and ultrasonics techniques. The work involves the design and construction of sensors and the application of these sensors to real-time process monitoring.*

The temperature measurement is obtained from the BTBP fluorescence spectrum by measuring the ratio of intensities at 544 nm and 577 nm. The biaxial stretching must be carried out between 155 °C and 162 °C. Typical steady-state monitoring is shown in the upper figure. The standard uncertainty for the temperature measurements is 2 °C.

## Dielectric Measurements

In collaboration with Chemical ElectroPhysics Corp. (CEP), we have carried out in-line dielectric measurements during extrusion of filled polymers. CEP's in-line dielectric cell has a ring design with the inner surface of the ring containing interdigitated electrodes. The cell is contained in a temperature control housing and is attached to the exit of an extruder. By applying a small voltage to the electrodes, a fringing field intercepts the resin flowing through the ring. Associated circuitry in conjunction with calibration of the instrument yields measurements of permittivity and conductivity. Real-time measurements of filled polymers are used to monitor filler concentration, transition times between resin loadings, and the dielectric properties of the melt.

Consider the data shown at left for processing of polystyrene filled with aluminum oxide. The data are a plot of relative permittivity versus time for processing of polystyrene filled with 20 percent by mass aluminum oxide powder. The uncertainty in permittivity measurements is 0.01.



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# Micro-scale Processing

*Micro-scale processing is an emerging technology with applications in the optical, medical, and “lab-on-chip” industries. However, many concepts developed for macroscopic processing break down in this regime. The goal of this work is to advance the technology infrastructure to support the growth of these industries.*

Kalman B. Migler

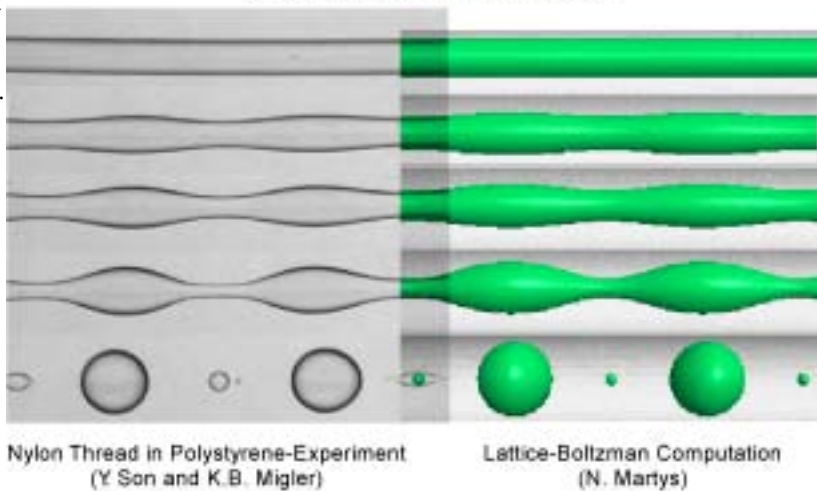
We are exploring the effects of confinement and the breakdown of mixing that occur in the micro-scale regime. The two sub-projects described below are designed to bring the synergistic advantages brought by polymer blending into the fabrication of small-scale structures.

### Confinement and Stability of Liquid Threads

It has been known since the 19th century that a liquid thread immersed in a fluid is unstable—it breaks into a sequence of droplets. Recently we have shown that it is possible to stabilize the thread by confining it between two parallel walls. This result is important in emerging micro-fluids technology as well as in micro-injection molding. By combining experiments, interfacial area calculations, and Lattice-Boltzman numerical simulations (See Figure), we systematically explore the relevant parameter space. The emerging confluence between the experimental and numerical results will allow us to model and optimize the behavior in complex geometries before building actual devices.

Further application of this work has led to the development of an improved method for the measurement of interfacial tension that combines the advantages of existing techniques while eliminating their disadvantages. We thus believe that it will become the method of choice for interfacial tension measurements in polymer blends.

### Rayleigh-Tomotika Instability



Nylon Thread in Polystyrene-Experiment (Y. Son and K.B. Migler)

Lattice-Boltzman Computation (N. Martys)

### String Structures in Confined Blends

Last year, we reported the unexpected discovery of string formation in sheared polymer blends that occurs when the droplet size becomes comparable to the gap width. Now, we are exploring the consequences of this finding and the range of conditions over which it is valid. We find that string formation is

extremely robust, occurring over a wide range of micro-scale processing conditions. We have observed it over a wide range of compositions, with string formation occurring at volume fractions as low as 5 percent, over a range of viscosity ratios from (0.1 to 10) and over a range of elasticities. We find that extreme care must be taken to ensure the string morphology is appropriate to the application. Our work also points the way to potential uses of the technology, for example to produce scaffolds in tissue-engineered products.

We also report the discovery of layering transitions that occur when the shear rate is too high to produce the string structure. We observe that the droplets organize into one, two, or three layer systems as they are sheared. These results further emphasize the profound changes that are induced by confinement.

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Viscoelastic behavior of polymers  
Dendrimers and dendritic polymers  
Functional biomaterials

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Synthetic and polymer chemistry  
Dental composites, cements and adhesion  
Initiator systems  
Interfacial coupling agents  
Remineralizing polymer systems

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Polymer thin films  
Dewetting  
Combinatorial measurements

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Polymer electrostriction

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Gas and vapor transport in polymers  
X-ray scattering  
Computer applications in polymer measurements

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Polymer synthesis thermal characterization  
Neutron, x-ray and light scattering  
Dendrimers, metallic ions nanocluster

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Crystallization in thin films  
Optical light scattering  
Controlled/living polymerizations

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Polymer analysis by size exclusion  
Chromatography  
Mass spectrometry of polymers

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Adhesion  
Dental composites  
Novel monomer synthesis

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Mass spectrometry of polymers  
Chemical modification  
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Dielectric properties of polymers  
Fluorescence and optical monitoring of polymer processing  
Piezoelectric, pyroelectric polymers  
Viscoelastic properties of polymers

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Polymer thin films  
Tissue engineering

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Microanalytical analysis techniques  
Phosphate chemistry  
Ion-selective electrodes

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

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Polymer morphology  
Phase behavior of block copolymers  
Polymer blends

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Engineering mechanics of polymer-based materials  
Bi-material interface
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Ferroelectric polymers  
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Phase transitions  
Glasses  
Polymers at interfaces
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Transport properties of polymer solutions and suspensions  
Polymers at interfaces  
Scaling and renormalization group calculation
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Fiber optic spectroscopy  
Infrared microspectroscopy of polymers
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Calcium phosphate compounds as dental materials  
Effects of solution and biological molecules on precipitation of calcium phosphates  
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Phase separation kinetics of polymer blends

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Shear mixing/demixing and morphology control  
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Static, time resolved, and quasi-elastic scattering  
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Siloxane polymers: synthesis and properties of  
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Polymer fractionation  
Gel permeation chromatography

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Multiphase polymer systems

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Small-angle neutron scattering  
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Polymer processing  
Polymer blends  
Polymer-clay processing

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Internal stress of composition due to polymerization

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Refractometry  
Intrinsic viscosity

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Failure and fracture of polymers  
Polymer composite interfaces

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Failure, yield and fracture of polymers  
Nonlinear viscoelasticity  
Molecular rheology  
Physics of polymer glasses  
Rubber thermodynamics and mechanics  
Mechanics of composites

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Biodegradable polymer blends  
Phase-separation and wetting properties of thin films  
Combinatorial methods for coatings

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Effects of shear and pressure on phase behavior  
Fluorescence and optical monitoring of polymer processing  
Liquid crystals  
Shear-induced two phase structures  
Polymer slippage

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Automated measurement design  
Computerized data analysis and programming  
Electrical properties of polymers

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Interfacial interactions via electrochemical and infrared spectroscopy  
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Mechanical properties via nondestructive methods

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Small-angle neutron scattering  
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Filled polymers  
Rheo-optical behavior of polymers

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Viscoelastic flow modeling  
Flow in porous media  
Lattice Boltzmann methods
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Wide-angle and small-angle x-ray scattering  
Block copolymer phase behavior
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Photo-polymerization
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Polymer mixing and compounding  
Liquid crystalline polymer/thermal plastic polymer mixing
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Vacuum deposition of metals  
Calibration of polymer transducers  
Microcomputer interfacing  
Fluorescence measurements
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Polymer-clay interaction  
Light and neutron scattering
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Physics of polymer glasses  
Polymer rheology
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Structure and dynamics of polymer solutions  
Light scattering and fluorescence photobleaching recovery
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Polymer phase transitions
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Cytotoxicity  
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Bone marrow cell lineage/trafficking

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Liposome studies

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Polymer crystallization behavior  
Thin-film block copolymer behavior  
Nanofilled polymer behavior  
Electron, atomic force, x-ray and light microscopies

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Polymer crystallization  
WAXD and SAXS of polymeric materials  
Thermal expansion measurements  
Thermal analysis of polymers  
Dielectric measurements and behavior

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Elastic and inelastic neutron scattering  
X-ray and neutron reflectivities  
Polymer thin films

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Polymer processing  
Polymer phase behavior  
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Polymer adhesion  
Surfaces and interfaces  
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Polymers and polymer composites  
Polymerization of expanding monomers  
Fluorinated polymers  
Polymerization kinetics

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Slow dynamics in soft condensed matter  
Molecular dynamics simulations and parallel computing

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Calcium phosphate biomaterials  
Topical fluoridation  
De- and remineralization

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Bond strength characterization  
Casting of alloys  
Strength of dental systems  
Thermal expansion and properties of dental materials  
Finite element studies  
Porcelain-metal systems  
Weibull analysis  
Wear testing, orthopaedic materials  
Reference biomaterials

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Chemistry of calcium phosphate compounds  
Remineralization studies  
Standard reference materials

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Solid-state NMR of polymers  
Measurement of polymer morphology at the 2–50 nm scale  
Pulsed field gradient NMR

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Polymer interfaces  
Scattering of light, neutrons & x rays  
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Interfacial phenomena  
Scanning-probe microscopy

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Fluorescence spectroscopy  
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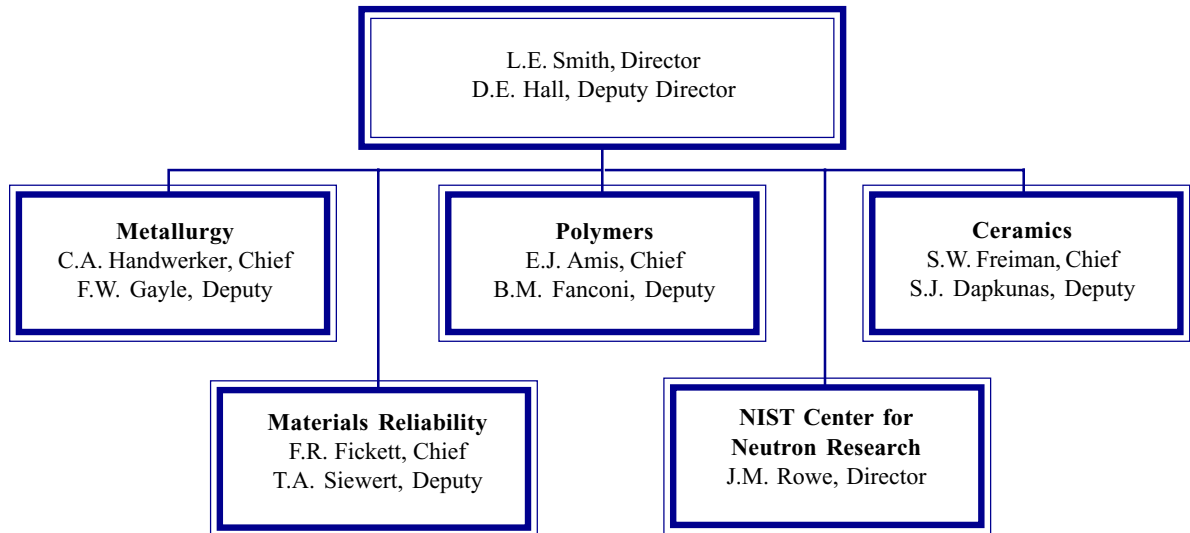
Dynamic light scattering  
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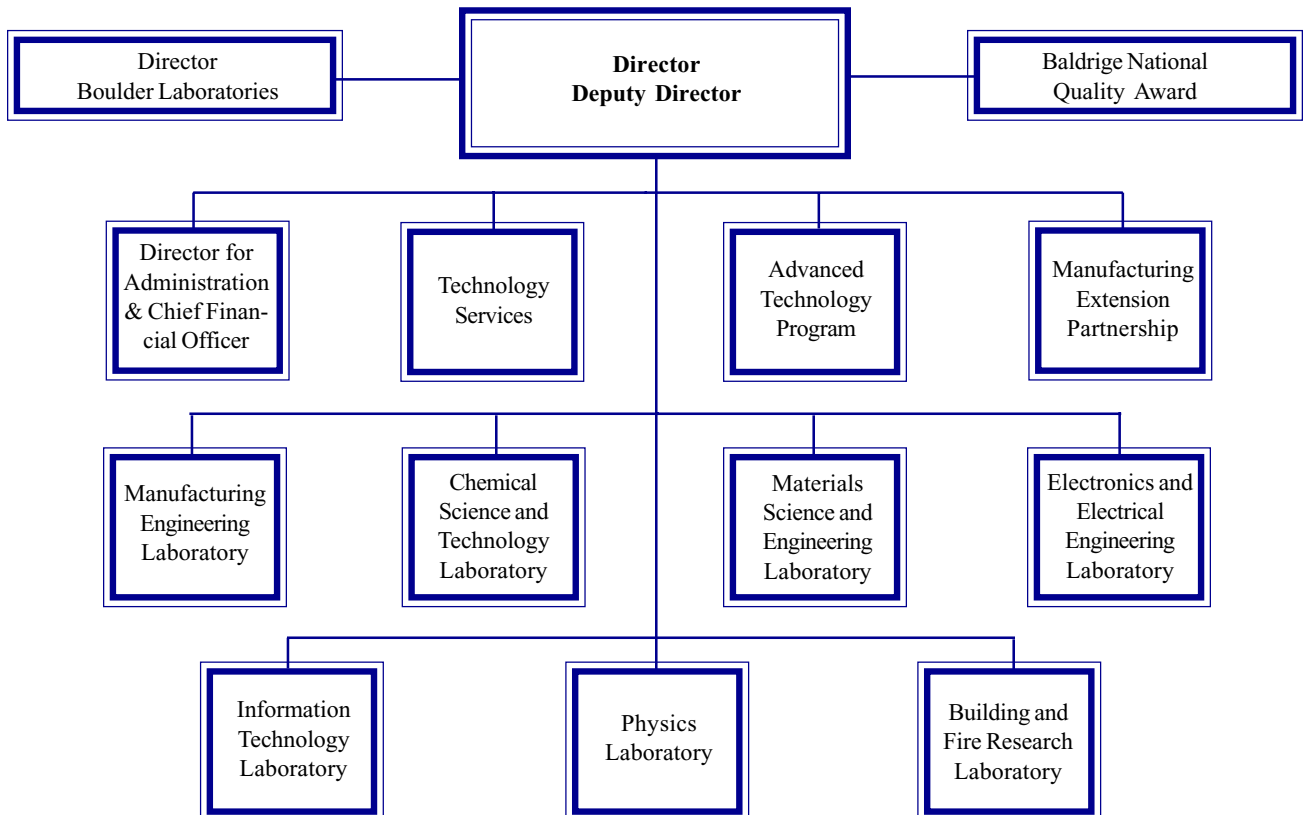
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# Organizational Charts

## Materials Science and Engineering Laboratory



## National Institute of Standards and Technology



# Organizational Charts

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**NISTIR 6796—POLYMERS DIVISION: FY 2001 PROGRAMS AND ACCOMPLISHMENTS**

