This project targets mathematical and computational underpinnings of a predictive capability for high performance, nano-composite (HPNC) materials. The overall goal is two-fold: 1st we develop theory, models, and numerical algorithms for the HPNC processing pipeline, starting with composite information, through flow processing, and finally to multi-functional property characterization; 2nd we implement these mathematical tools to predict measurable and significant features of HPNC materials.
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The materials we consider are nano-rods and nano-clays in aqueous and polymeric solvents, which are technology targets for multi-functional properties ranging from electrical, thermal, mechanical, and barrier (low permeability of liquids and low diffusivity of gases). We have made progress in the theory and models for flow processing and effective properties, in the analysis, numerical algorithms and simulations of the models, and in scientific understanding of nano-composite materials. A current high profile project relates to nano-particle contacts, which are significant even at extremely low volume fractions (~1%) due to the extreme aspect ratios of nano-particles. The role of contacts, and percolation thresholds, across composition and processing space is critical to property characterization, and is now experimentally implicated as a dominant effect. The PI is collaborating with Dr. Richard Vaia, AFRL/MLBP, Wright-Patterson AFB, Dayton, OH, on this critical issue; Vaia has directed the PI's focus on effective properties, providing both the experimental evidence for causal effects as well as feedback on predictions coming out of our modeling group.

During and as a consequence of flow processing, the nano-particle ensemble is theoretically described in terms of an orientational distribution function (PDF). In extension-dominated flow, such as fiber processing, features of the PDF have been shown by the authors in previous contracts to be predictable and controllable. In film and mold-filling processing, anomalous dynamical responses of the nano-ensemble and generation of spatial gradient morphology have been the subject of intense experimental, theoretical and computational scrutiny for the past two decades. The theory has simply not been available to make predictions of relevance to technology, and in particular, the mathematical community has only recently engaged these challenges. Forest and collaborators have made significant progress on a controlled understanding of model experiments in which the flow is shear-dominated, representative of film and mold processing, in the coupling of extensional and shear flow components, in the role of confinement through molecular anchoring on solid boundaries which leads to gradients in...
the PDF of the nano-ensemble and significant flow feedback (nonlinear shear bands). We have recently generalized the Doi-Hess-Marrucci-Greco models and predictions to incorporate an imposed magnetic field, which may serve as a controller during processing to shape the PDF and rid the ensemble of deleterious orientational shear-dominated features. We have further made significant advances in mapping flow-induced PDFs of the nano-ensemble to effective properties, both for homogenized averaging properties and recently for nano-particle cluster and percolation dominated properties. All of these projects are linked together, serving as a basis for an eventual control strategy that bridges composition, processing, effective properties, and performance evaluation.

Specifically, we build theory, models, and simulations that provide the link from control parameters: composition (viscous solution or polymer matrix plus nano-elements), processing flow type and rates, and confinement conditions (device lengthscales as well as solid boundaries); to multi-functional material properties.

A significant obstruction in the production pipeline is control over anisotropy and heterogeneity of performance properties in nano-composites, which arise on lengthscales between the molecular and device scales. These property features are clearly a consequence of the orientational morphology of the anisotropic nano-inclusions, which are typically long rod-like or thin platelet molecules with aspect ratios between 20 and 2000. At present, these anisotropic ensembles and spatial morphologies of the nano-inclusions, and subsequently of the effective properties of materials, are viewed as problematic. However, these features are only possible in soft matter materials, and offer potential keys to novel materials. We currently have theory, modeling, and simulation predictions with a host of the relevant chemical composition and processing physics built in. Other physics and chemistry are not on solid theoretical foundation yet, such as non-uniform mixing of the nano-elements and a polymeric solvent rather than a viscous liquid, we have made progress in incorporating them into the framework.

In our approach, the design and control pipeline is divided into a sequence of fundamental theory and computation problems:

- Molecular potentials and process controls determine the micron-scale, physical structures due to molecular orientational distributions generated in films and molds, as well as stored elastic stresses in these viscoelastic composites. The mathematical theory and models, analytical solution methods, and numerical simulation tools for these orientational anisotropy and structure properties and associated stored stresses are central components of our research over the funding period of F49620-03-1-0098. The extension of the numerical algorithms for processing to full 2D and 3D physical space, and their implementation and understanding into a coherent picture, are key projects in the renewal FA9550-06-1-0063.

- Once the micron-scale molecular morphology is characterized, either as a numerical database, analytical scaling properties, or an experimentally determined dataset, the next challenge to mathematics and computation is the determination
of effective material performance properties. Since there are millions of molecules in a cubic micron, clearly one must develop scale-up methods based on the molecular orientational distribution, molecule properties, the solvent or matrix properties, and the geometry of the material (film thickness, mold shape). Here we have teamed with Robert Lipton, Louisiana State University, to marry the results of composite homogenization theory with our molecular structure morphology results. This gives the effective anisotropic composite property tensor, parametrized by composition and processing parameters, which we have now published in 4 major articles supported by F49620-03-1-0098. Through interactions with R. Vaia, we have identified HPNC systems where percolation and contacts among nano-particles are dominant in properties, as opposed to homogenized averaging. This feature is a high priority of our current efforts in the renewal contract FA9550-06-1-0063.

- The last stage in the pipeline is a direct solve for the performance features of the film, using the mechanical, thermal, electric, piezoelectric, permeability property tensor(s) of the nano-composite, which are the variable, anisotropic coefficients in an elliptic, second- or fourth-order operator, together with realistic boundary conditions the materials are exposed to during performance conditions. We have only begun to run simulations for this purpose.

- Finally, a control wrapper is necessary that measures performance properties, evaluates them based on a cost functional which penalizes departure from desired properties, and then gives feedback to which composition and processing parameters can minimize cost and thereby achieve desirable performance features. This capability is realistic within the next 3-5 years, and is the central focus of the sub-contract FA9550-06-C-0017 with Nonlinear Control Strategies.

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19. A numerical study of unsteady, thermal, glass fiber drawing processes, (with H. Zhou), Communications in Mathematical Sciences, Volume 3(1), March (2005).


Submitted refereed research articles and web-posted preprints


33. A correspondence principle between Stokes flows of viscous and viscoelastic fluids, (with I. Klapper, K. Xu), JNNFM, to be submitted, March, 2006.

34. Monodomain dynamics for rigid rod & platelet suspensions in strongly coupled...
37. Extension of the Ferry shear wave model for viscoelastic characterization to finite depth, wave reflection, and nonlinearity, (with S. Mitran, B. Lindley, L. Yao), JNNFM, to be submitted, March, 2006.

Honors & Awards Received by the PI
Grant Dahlstrom Distinguished Professor of Mathematics, UNC, 2003

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Presentations (since 2003 that acknowledge AFOSR support)


4. 2003, “What’s math got to do with nano-materials?”, UNC-Chapel Hill Mathematics Graduate Visions Seminar, April 14


9. 2003, "Laminar flows of nematic polymers: high performance materials in the making", Florida State University, Mathematics Colloquium, September 22


11. 2003, "Multiscale challenges in soft matter materials", American Mathematical Society Regional Meeting, University of North Carolina, October 20


23. 2004, “A modeling thrust: Modeling the nano-composite pipeline for nano-composite materials”, NASA BiMat URETI annual review, Langley, VA, October 8

24. 2004, “Toward predictive capability in medicine”, UNC Vice Chancellor’s Workshop on Nanomedicine, Chapel Hill, NC, October 12


30. 2005, “Nano-composite materials”, UNC Chapel Hill, Department of Mathematics Colloquium, Chapel Hill, NC, April 7


Technology Assists

The Forest group has established the only proof-of-principle results on HPNC materials whereby effective properties are directly linked to composition and processing phases. These results have led to contacts from two technology companies, Moldflow Corporation and Fujiyama Polymer Research, both of whom are interested in applications of our property characterization tools.

Key Accomplishments

The Forest group has several successes which are recognized as significant accomplishments in referee reports, communications from journal editors, and in our property bifurcation diagram making the cover graphic of the December, 2005 issue of Advanced Functional Materials. These successes are summarized as follows:

Processing: Phase diagrams of the stable ensemble probability distribution functions (PDFs) of nematic polymers across processing parameter space. Results include PDF databases and scaling properties versus geometry and volume fraction of the nano-particles, flow type and flow rate, confinement geometry, driving conditions (drag versus pressure) and boundary anchoring conditions. New theory and models, new algorithms, and new identification of phenomena and transition behavior have been published and recognized.

Property Characterization: Volume averaged conductivity and mechanical properties versus processing-induced PDFs, and percolation phenomena based on processing-induced PDFs, of nematic polymer nano-composites. Results include effective property tensors in the form of databases and scaling properties versus geometry and volume fraction of the nano-particles, flow type and flow rate, confinement geometry, driving conditions (drag versus pressure) and boundary anchoring conditions. Extensions of existing homogenization theory have been development, along with new algorithms, and
identification of new phenomena and transition behavior have been either published or will be submitted in the upcoming month.

Graphics and powerpoint slides, with annotations, of these accomplishments have been forwarded to the cognizant program officer, Dr. Arje Nachman, and can be modified and updated upon request.