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14. ABSTRACT

This report details the acquisition of instrumentation to support fundamental research focused on studying the relationships between microstructure, processing and macroscopic properties of polymeric based nanocomposites having reinforcing particles with 0, 1 and 2 dimensional shapes. A close coupling between experimental observations and computational modeling & analysis is essential to develop the understanding needed to take nanocomposite technologies forward. The equipment is being utilized to establish a fundamental knowledge base of the structure-property-processing relations for a wide spectrum of nanocomposite types. Controlled blending of inorganic fillers of a range of morphologies - equiaxial (carbon black, silica); tubular: (carbon nanotubes) or discotic (nano-clay) - into a range of polymeric matrices (semicrystalline, glassy, thermoplastic-elastomer and elastomeric) provides exploration of filler/matrix combinations with a wide range of chemical and physical attributes. The huge surface/volume ratio and the small inter-particle spacings create an unusual situation in which nearly every polymer molecule is interacting with a nearby filler interface.

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Instrumentation For Research on the Microstructure, Processing and Mechanical Performance of Polymeric Nanocomposites

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The following major items of equipment were purchased on this contract as per the original research proposal:

- AFM Dimension 3100 and in-situ mechanical Tester.
- TecMag NMR Console
- DURINT Beowulf Cluster
- Linde Cell Gas Permeability Equipment
- Haake Minilab Micro-twin-screw compounder (2)
- Texture Analyzer Mini Testing machine

Brief reports on the capabilities and usage of these instruments is provided on the following pages. All of the instruments are being used in the ongoing DURINT research program (P.I. Mary C. Boyce), and a detailed list of publications can be found therein.

1. Upgrade of Veeco Atomic Force Microscope (Dimension AFM3100)

We used approximately $82K to upgrade our existing AFM (by adding new z-scan and z-engage drive system) and to custom fabricate a deformation stage for *in situ* testing. The Dimension 3100 scanning probe microscope operates at ambient atmosphere and the technique itself is non destructive. In tapping mode, height images provide topographic profile while phase images provide information of different phases in the system through modulus contrast. The home-built deformation stage was designed by Christian Grippo. The deformation stage has a computer interface and fits underneath the AFM head probe. It deforms the sample to an input strain and creates a digital output stress-strain curve. At the same time, the microstructural evolution can be observed with nanometer resolution by the AFM. This tool allows us understand connections among the morphology, deformation mechanisms, and mechanical properties of nanocomposite materials, which will lead to a better understanding of their mechanical behavior.

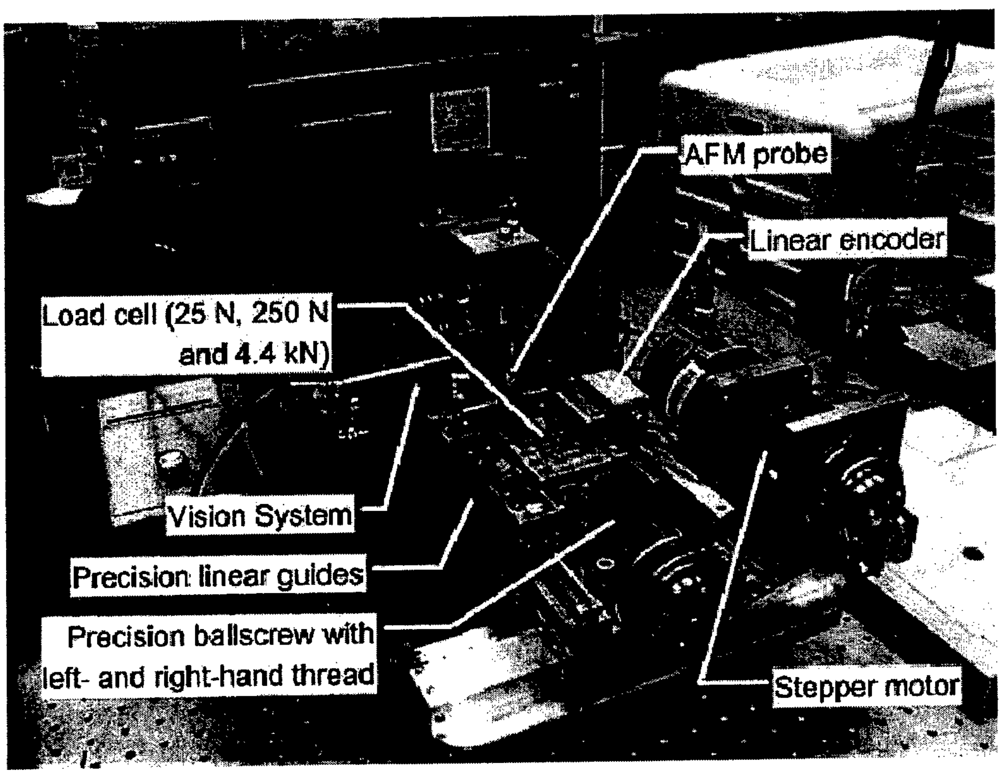


Fig. 2 The tensile testing machine on the Dimension 3100 AFM

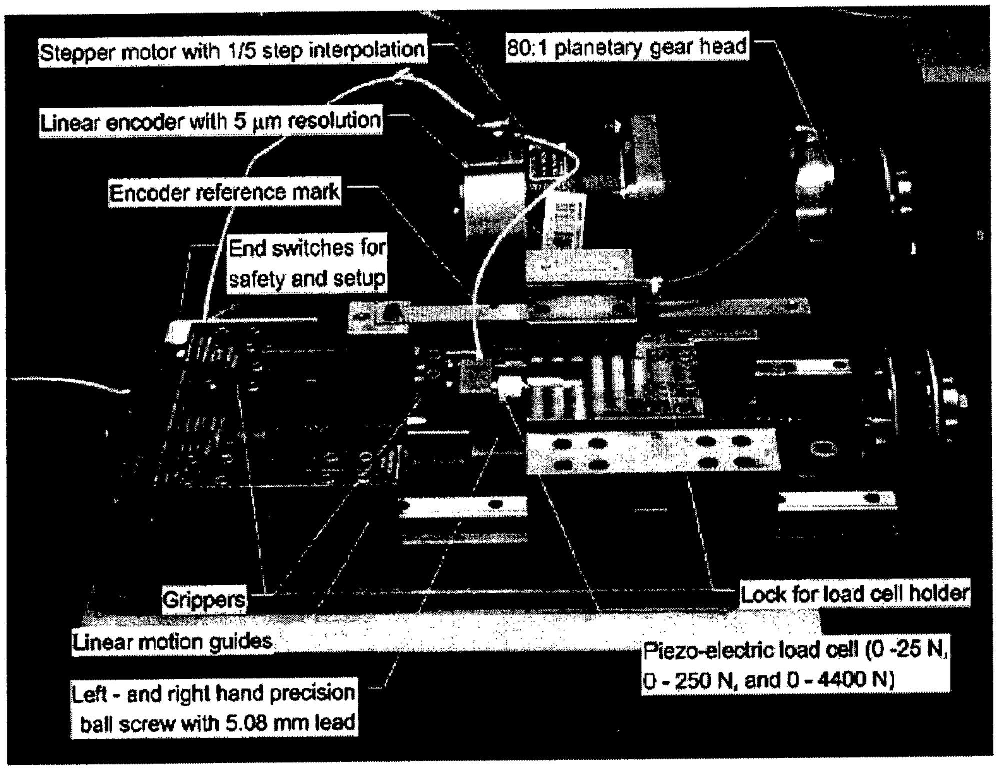


Fig. 3 Major components of the tensile testing machine

2. TECMAG NMR Console

The TecMag dual resonance console was purchased to update instrument control, data acquisition and data analysis from a decade old, homebuilt system. The console included both a synthesizer and a digital receiver. The dual resonance capability of the synthesizer allowed for simultaneous RF pulses over a wide range of frequencies, including 1H and 13C for monitoring the polymer and 29Si for monitoring the clay structure. The independent digital receiver resulted in better signal-to-noise than that of the homebuilt system. Proton spectra, in particular, are susceptible to fast transverse relaxations which can result in a loss of signal if digitization is not sufficiently rapid. This receiver's faster digitization rate, and subsequent increase in bandwidth, allowed for acquisition of 1H spectra with a larger signal to noise ratio lending more confidence to observed spectral changes. The system is integrated with a Compaq 1 GHz computer with Pentium III processor. In addition, NTNMR software was included allowing for a user friendly interface for pulse programming and data analysis. This instrument was used to monitor the spin lattice relaxation (T1) of the protons of 1,4-cis polyisoprene and 1,4-cis polyisoprene nanocomposites during compressive strain. These experiments indicated increases in the molecular mobility of the polymer with an increase in strain, once a threshold of 25% strain had been surmounted. Furthermore, the effect of Laponite clay in this matrix mobility was found to be negligible for particle sizes in the micron scale. However, the presence of the clay increases thermal aging effects of the matrix in comparison to the homopolymer. The changes in molecular motions caused by aging, monitored by 1H NMR, showed a different sensitivity than changes in bulk properties, monitored by mechanical data and gel permeation chromatography. For montmorillonite nanocomposites, the 1H T1 behavior was dominated by the paramagnetic Fe+3 in the clay galleries. Increases in the surface area up to 20% that of the original area were observed depending on the surfactant employed and whether the matrix was crosslinked. This effect of an increase in surface area was complimentary to other techniques such as transmission electron microscopy; however, 1H NMR allowed for quantification of the increase not possible from microscopy.

3. DURINT Beowulf cluster

The new Beowulf cluster is a parallel computation cluster composed of 28 Dell Poweredge 1650, Pentium III processors running at 1.26 GHz with 256 MB SDRAM memory and 18 GB of hard disk. The new processors communicate through a PowerConnect 5012 10GB ethernet bus. The new processors were installed as an expansion to an existing cluster of 32 processors running the Scyld operating system. 70% of the expansion was funded through DURINT. The Beowulf cluster provides the computational hardware to run molecular modeling codes developed within the DURINT research group to study molecular scale structure, dynamics and properties of polymeric nanocomposites. Because of the length scales associated with the nanoparticles of interest to this research effort, simulations which are very large (in terms of number of atoms simulated) by atomistic modeling standards are required; these are performed most efficiently by dividing the computational workload among numerous processors running in parallel. Pentium III processors offer the best performance per dollar for this purpose, with processing efficiencies on the order of 70-90%. The 20 processors attributable to DURINT thus offer about 15x speedup.

To date, the Beowulf cluster has been used to simulate the mechanical properties of a model montmorillonite clay sheet and to study the structure and dynamics of POSS (polyhedral oligomeric silsesquioxane) particles and the surrounding polymer matrix material. In the first case, the simulations provided the first complete, quantitative data for the elasticity of the clay particles, and led to a better recognition of the breakdown of certain concepts of continuum mechanical behavior as length scales approach the sizes of the constituent atoms themselves. The computed elasticities have been used by other members of the DURINT program in finite element modeling of polymer-clay nanocomposites to study their properties as a function of state of aggregation. One paper (O.L. Manovitch, G.C. Rutledge, *J. Phys. Chem. B*, 2003).has been submitted for publication as a result of this work. In the second case, the simulations have provided detailed information used to interpret certain experimental results, in particular NMR results, for cyclopentyl- and cyclohexyl-functionalized POSS nanocomposites.

4. **Custom Scientific gas permeation cell** (Linde Cell)

With temperature control bath and attendant pressure gauge, quick-snap interconnects.

This instrument has been utilized for measurements of steady-state and unsteady transient gas flux (at various temperatures and pressures) through planar membrane film samples (ca 1mm thick) of polymeric materials and polymer nanocomposites. From the steady measurements (the most common and reliable data that can be obtained from this device) we can calculate the steady permeability P, a material characteristic of the membrane. In the case of the heterogeneous nanocomposites one is measuring an "effective permeability" of the material, including an important consideration of the tortuosity, τ, associated with the nanostructured morphology. Because the measured steady permeability reflects both thermodynamic and kinetic issues, one can represent the observed value of P as the product of an equilibrium solubility (S) of the selected gas in the selected membrane and a diffusion coefficient (D) of the gas in the polymer matrix. Thus we consider our measurements in the context of the relation

$$P = DS/\tau \qquad (1)$$

As noted above, the Linde Cell is best suited to make direct measurements of P, but D can be estimated from "lag time" observations in unsteady measurements and S can often be obtained from sensitive weight uptake measurements. The tortuosity τ can be accessed through microscopy and other morphological characterization methods. Thus, measurements of P along with consideration of Eq 1 in the context of other data on the nanocomposites offers a simple, independent consistency check on the material structure as well as a means for obtaining data on an important figure-of-merit issue (gas barrier properties) for the materials.

The permeability data are also important in the overall DURINT program to test the reliability of novel finite element models that have been developed to predict permeability of nanostructured composites. Deviations of the model from measurements will enable us to probe the interfacial material in these new nanocomposites possessing unusually high S/V ratios.

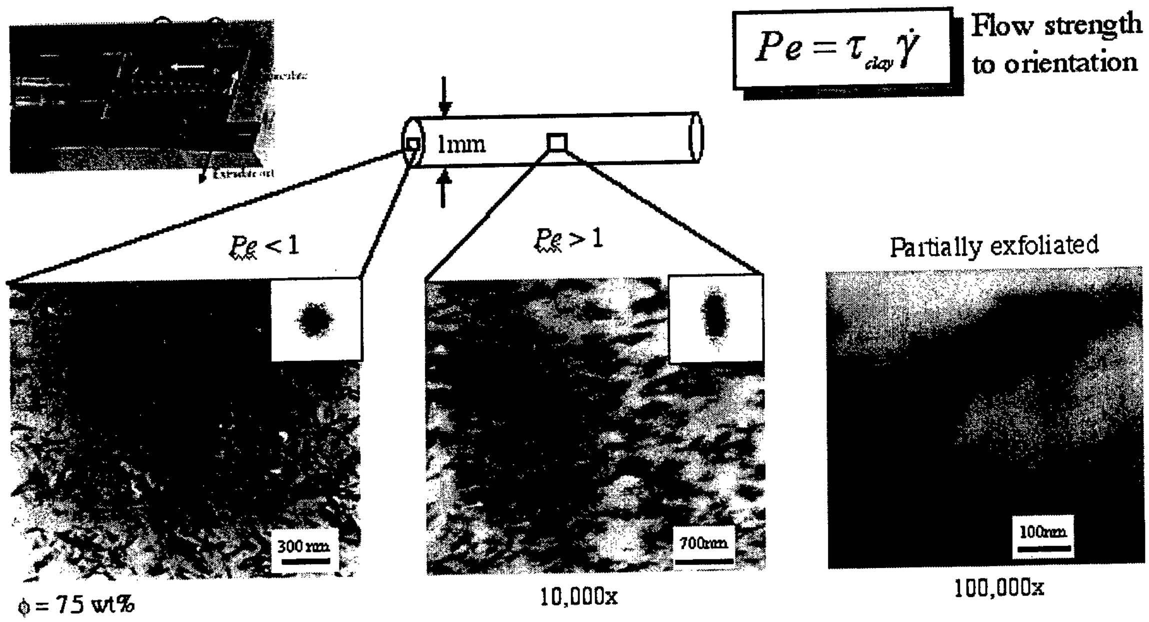
5. Minilab Twin-Screw Microcompounder

In order to process and compound polymeric nanocomposites, we have also acquired a bench-top scale twin screw extruder and compounder (Haake Minilab). This equipment is ideal for preparation of new nanocomposites as it has a very small batch size (5-8grams) and the feed system can handle direct injection of powders (e.g. Laponite, Montmorillonite) and pelleted resin feedstocks (e.g. PMMA, polypropylene). In addition the equipment is instrumented to enable online measurements of the instantaneous torque exerted on the screw and also the shear viscosity of the compounding material (through the use of two flush-mounted pressure transducers P1, P2 indicated in the top left of the picture below). This enables to carry out studies of the total power, mixing time and maximum torque (or stress) exerted on the material.

Some representative examples obtained using a PMMA melt containing 7.5 wt% by weight of Montmorillonite are shown below. The degree of exfoliation depends on the total torque and compounding time (i.e. on the total mechanical energy per gram delivered to the system). In this specific example, a partially exfoliated morphology can be seen through SEM analysis with tactoids containing 3–6 silicate layers still remaining. However, in addition to the morphology, pronounced orientation can also be obtained through processing. This can be described by a dimensionless group, the Peclet number representing the ratio of the natural rotational diffusive time scale of the clay disks (τ_{clay}) compared to the flow time scale ($\tau_{flow} \sim 1/\dot{\gamma}$).

$$Pe = \tau_{clay}\dot{\gamma}$$

Flow strength to orientation



The Brittain group (The University of Akron) also purchased an identical Thermo-Haake Mini-Compounder in order to enable similar compounding studies on new materials to be carried out directly in Akron. Leveraging of available State matching funds also enabled acquisition of a matched DSM Microinjection Molder. To date, the Akron group has primarily used the mini-compounder to test the processability of different nanocomposite formulations. The mini-compounder has been a critical and essential piece of equipment in the Akron laboratory. We have been able to examine the stability of polystyrene, poly(vinyl chloride) and poly(methyl methacrylate) nanocomposites made with different loadings and types of clay. We have been able to study whether the exfoliated state is maintained after processing. Furthermore, the minicompounder helps us screen samples before they are sent to M.I.T. for further study. Several manuscripts are currently in preparation and at least two of them will report our findings on the exfoliation before and after extrusion. For example, we have found for poly(methyl methacrylate)–clay nanocomposites that the hybrid system remains exfoliated before and after extrusion (based on microscopy and X-ray analysis). Furthermore, we have observed that the molecular weight of the polymer matrix does not change after extrusion. These observations are critical to the development of useful and practical polymer–clay nanocomposites.

In current work, we are continuing to utilize the mini-compounder to explore the effect of aspect ratio of the nanocomposite materials. In addition, we are beginning to make dog-bone samples with the microinjection molder for mechanical tests on the most promising nanocomposite samples.

6. Texture Technologies TA.XT2i High Resolution Texture Analyzer

The TA.XT2i is a small lab-scale mechanical testing machine, specifically optimized for imposing tensile deformations extensional 'squeeze flows' on soft solids (such as nanocomposite elastomers, or even liquid precursors). It has a very low range force sensor (5kg total force) which enables rapid testing of very small samples such as the 1mm rods extruded from the MiniLab system (see diagram above). The instrument can also be used to test elastomeric strips. The adaptability of the stage mounting system makes it possible to mount a wide range of fixtures for different test geometries, including squeeze flow, 3-point bend and flexure tests, uniaxial tension on rods and thin films.

Publications and Presentations (to date) using the DURIP Equipment

Ha, Y-H., Thomas, E.L., "Deformation Behavior of a Roll-Cast Layered-Silicate/Lamellar Triblock Copolymer Nanocomposite", Macromolecules, 35, 4419-4428, 2002.

Sheng, N., Boyce, M.C., Parks, D.M., Rutledge, G.C., Abes, J., Cohen, R.E., "Multiscale Micromechanical Modeling of Polymer/Clay Nanocomposites and the Effective Clay Particle", Polymer, accepted , 2003.

Pantano, A., Boyce, M.C., Parks, D.M., "Nonlinear Structural Mechanics Based Modeling of Carbon Nanotube Deformation", Physical Review Letters, Vol. 91, n. 14, 145504, 2003 (CMI/DURINT).

Pantano, A., Parks, D.M., Boyce, M.C., "Mechanics of Deformation of Single and Multi-Wall Carbon Nanotubes", Jnl. Mechanics & Physics of Solids, accepted for publication, 2003 (CMI/DURINT).

Qi, H., Teo, K., Lau, K., Boyce, M.C., Milne, W., Robertson, J., Gleason, K.K., "Determination of Mechanical Properties of Carbon Nanotubes and Vertically Aligned Carbon Nanotube Forests Using Nanoindentation", Jnl. Mechanics & Physics of Solids, March 2003 (CMI/DURINT, in press).

Loo, L.S., Gleason, K.K., "Insights into Structure and Mechanical Behavior of α and γ Crystal Forms of Nylon 6 at Low Strain by Infrared Studies", Macromolecules, 36, 6114-6126, 2003.

Loo. L.S., Gleason, K.K., "Fourier Transform Infrared Investigation of the Deformation Behavior of Montmorillonite in Nylon 6/Nanoclay Nanocomposite", Macromolecules, 36, 2587-2590, 2003.

Lazzeri, A., Thio, Y.S., Cohen, R.E., "Volume Strain Measurements on a $CaCO_3$/PP Particulate Composites: Effect of Particle Size", to appear in Journal of Applied Polymer Science (NSF-MRSEC/Durint).

Parsons, E., Boyce, M.C., Parks, D.M., "An Experimental Investigation of the Large Strain Tensile Behavior of Neat and Rubber-Modified Polycarbonate", submitted to Polymer, June 2003, accepted, in revision October 2003.

Lau, K.S., Bico, J., Teo, K.B., Chhowalla, M., Amaratunga, A.J., Milne, W.I., McKinley, G.H., Gleason, K.K., "Superhydrophobic Carbon Nanotube Forests", accepted, Nano Letters, 2003.

Manevitch, O.L., Rutledge, G.C., "Elastic Properties of a Single Lamella of Montmorillonite by Molecular Dynamics Simulation", submitted to J. Phys. Chem, March 2003; revised Sept 2003.

Yung-Hoon Ha, Younghwan Kwon, Theodora Tzianetopoulou, Edwin P. Chan, Thomas E. Breiner, Mary C. Boyce, Robert E. Cohen and Edwin L. Thomas' "Deformation Behavior of Highly Oriented Exfoliated Clay – Block Copolymer Nano-Layered Composites", submitted to Advanced Materials, in revision, October, 2003

Papers in the works: Several additional papers are also under preparation;
Gallino, A.M., Boyce, M.C., Parks, D.M., Cohen, R.E., "Permeability of Polymer/Platelet Composites: Dependence on Particle Structure and Distribution", to be submitted to Polymer, estimated completion November 2003.

Poliskie, G.M., Gleason, K.K., Cohen, R.E., “Static Uniaxial Compression of Polyisoprene-Montmorillonite Nanocomposites Monitored by ^{1}H Spin-Lattice Relaxation Time Constants”, to be submitted to Journal of Applied Polymer Science, estimated completion November 2003.

Lee, H., Cohen, R.E., McKinley, G.H.,“Nonlinear rheological properties and modeling of PMMA-clay and PS-clay nanocomposites”, In preparation, Journal of Rheology, November 2003.

Lee, H., McKinley, G.H., “Role of Clay-Clay Interactions on extensional Rheology of polystyrene-clay solutions”, in preparation, Polymer, November 2003

Kopesky, E.T., Haddad, T.S., Cohen, R.E., McKinley, G.H., "Thermomechanical Properties of Tethered and Untethered POSS-filled PMMA", to be submitted to Macromolecules, estimated completion December 2003.