Nanocomposite Analysis:

Microscopy

- "Characterization of Polymer-Layered Silicate (Clay) Nanocomposites by Transmission Electron Microscopy and X-Ray Diffraction: A Comparative Study" Morgan, A. B.; Gilman, J. W. *J. App. Polym. Sci.* **2003**, *87*, 1329-1338. TEM Examples of all nanocomposite general types (exfoliated, mixed exfoliated/intercalated, microcomposite/immiscible) shown at low and high magnifications included in paper. XRD experimental considerations and how those conditions affect XRD data and interpretation is also discussed. Alternative clay nanocomposite techniques (AFM, NMR, etc.) are briefly reviewed. Paper shows how XRD data alone cannot be used for nanocomposite data interpretation, but how combined with TEM can be far more informative for nanocomposite analysis.
- "Characterization of the Dispersion of Clay in a Polyetherimide Nanocomposite" Morgan, A. B.; Gilman, J. W.; Jackson, C. L. *Macromolecules* **2001**, *34*, 2735-2738. Example of Exfoliated immiscible nanocomposite – clay dispersed by solvent, not in-situ polymerization. Some discussion of how synthesis process leads to nanocomposite structure, especially when synthesis process can lock in a nanocomposite structure (ex – thermosets) or how the process can degrade the alkyl ammonium treatment leading to a particular nanocomposite structure.
- "Three Dimensional Observation of Structure and Morphology in Nylon-6/Clay Nanocomposite" Usuki, A.; Hasegawa, N.; Kadoura, H.; Okamoto, T. *Nano Letters* **2001**, *1*, 271-272. Solvent etching away of polymer (PP Nanocomposite Foam made by supercritical CO2) to show clay plates by SEM.
- "New Developments in Transmission Electron Microscopy for Nanotechnology" Wang, Z. L. *Adv. Mater.* **2003**, *15*, 1497-1514. High resolution TEM (HRTEM), scanning TEM (STEM), and electron energy loss spectroscopy (EELS) techniques discussed. Examples of how the techniques have been applied to various nanosized materials presented. Clay nanocomposites not presented, but several examples with layered materials and carbon nanotubes given.
- "Assessing Organo-Clay Dispersion in Polymer Nanocomposites" Eckel, D. F.; Balogh, M. P.; Fasulo, P. D.; Rodgers, W. R. *J. App. Polym. Sci.* **2004**, *93*, 1110-1117. Nanocomposite characterization paper by XRD and TEM, with some mechanical properties included. Majority of refs in paper old, work not very up to date. Data in paper supports findings in regards to XRD deficiencies observed in "Characterization of Polymer-Layered Silicate (Clay) Nanocomposites by Transmission Electron Microscopy and X-Ray Diffraction: A Comparative Study" Morgan, A. B.; Gilman, J. W. *J. App. Polym. Sci.* **2003**, *87*, 1329-1338. Otherwise, paper of limited usefulness.
- "Micro- and nano-structure in polypropylene/clay nanocomposites" Perrin-Sarazin, F.; Ton-That, M.-T.; Bureau, M. N.; Denault, J. *Polymer* **2005**, *46*, 11624-11634. PP + PPgMA (two molecular weights – 9100 and 330000) + clay (Cloisite 30B or 15A) nanocomposites made by twin screw extrusion. Some masterbatches used. By TEM, best dispersion obtained with Cloisite 15A with 330000 MW PPgMA, no masterbatch use. XRD and DSC data show that some alpha phase crystallites were nucleated by the organoclays. Use of SEM for characterization an interesting part of paper, including image analysis data from SEM vs. TEM at micro, sub-micro, and nano levels where appropriate. Interesting explanations of PPgMA chain length and how it gave the observed organoclay dispersions included in paper.
- "Surface Characterization of Poly(ε-caprolactone)-Based Nanocomposites" Viville, P.; Lazzaroni, R.; Pollet, E.; Alexandre, M.; Dubois, P.; Borcia, G.; Pireaux, J-J. *Langmuir* **2003**,

19, 9425-9433. Polycaprolactone + MMT (Cloisite Na, 25A, or 30B) nanocomposites made by melt compounding (two-roll mill) or in-situ polymerization. Materials characterized by XPS, FTIR, and SPM/TMAFM (scanning probe microscopy, tapping mode AFM). Control samples of pure PCL and pure MMT analyzed first by XPS and TMAFM – may be first reported images of MMT by AFM. Melt intercalated samples shown to be intercalated – intercalated clay plates could be seen by TMAFM with good resolution! FTIR indicated how certain organic treatments interfaced with the PCL matrix, and how the PCL matrix interfaced with the organic treatment, but signals from the MMT itself could not be seen. In-situ polymerized samples show best dispersion, especially with functionalized organic treatments (Cloisite 30B).

- "The role of plasticizer on the exfoliation and dispersion and fracture behavior of clay particles in PVC matrix: a comprehensive morphological study" Yalcin, B.; Cakmak, M. *Polymer* **2004**, *45*, 6623-6638. Extensive paper on PVC + dioctylphthalate + Cloisite 30B nanocomposite. TEM, XRD, and very high quality AFM analysis done. Clay dispersed well into PVC, with exfoliation affected by phthalate content. AFM analysis of clay very useful, showing that AFM can be used for some nanocomposite analysis (tactoids measurements, clay particle shapes).
- "Evaluation of the Structure and Dispersion in Polymer-Layered Silicate Nanocomposites" Vermogen, A.; Masenelli-Varlot, K.; Seguela, R.; Duchet-Rumeau, J.; Boucard, S.; Prele, P. *Macromolecules* **2005**, *38*, 9661-9669. Very good paper showing an image analysis technique for TEM and optical microscopy data, providing better more detailed descriptions besides just "exfoliated/intercalated/mixed". Rheology data + WAXS helped understand how the organoclay dispersed in the PP matrix during melt compounding with single screw, twin screw, and optimized twin screw extrusion.

NMR / EPR

- "NMR Measurements Related to Clay-Dispersion Quality and Organic-Modifier Stability in Nylon-6/Clay Nanocomposites" VanderHart, D. L.; Asano, A.; Gilman, J. W. *Macromolecules* **2001**, *34*, 3819-3822. Clay exfoliation measured by relaxation times of hydrogen that "sees" iron in the montmorillonite clay.
- "Solid-State NMR Investigation of Paramagnetic Nylon-6 Clay Nanocomposites. 1. Crystallinity, Morphology, and the Direct Influence of Fe^{3+} on Nuclear Spins" VanderHart, D. L.; Asano, A.; Gilman, J. W. *Chem. Mater.* **2001**, *13*, 3781-3795. Use of Fe atoms in montmorillonite clay to determine clay dispersion in Nylon-6 matrix.
- "Solid-State NMR Investigation of Paramagnetic Nylon-6 Clay Nanocomposites. 2. Measurement of Clay Dispersion, Crystal Stratification, and Stability of Organic Modifiers" VanderHart, D. L.; Asano, A.; Gilman, J. W. *Chem. Mater.* **2001**, *13*, 3796-3809. Use of Fe atoms in montmorillonite clay to determine clay dispersion in Nylon-6 matrix. Also, degraded alkyl ammoniums (from thermal processing above 200 °C) observed by NMR technique.
- *"Clay intercalation of poly(styrene-ethylene oxide) block copolymers studied by two-dimensional solid-state NMR" Hou, S. S.; Bonagamba, T. J.; Beyer, F. L.; Madison, P. H.; Schmidt-Rohr, K. *Macromolecules* **2003**, *36*, 2769-2776.
- "Solid-State NMR Study of Intercalated Species in Poly(ε-caprolactone)/Clay Nanocomposites" Hrobarikova, J.; Robert, J.-L.; Calberg, C.; Jerome, R.; Grandjean, J. *Langmuir* **2004**, *20*, 9828-9833. Polycaprolactone + laponite or saponite nanocomposites

prepared by in-situ polymerization. Materials characterized by ^{13}CAP NMR to understand how surfactants at clay surface interacted with polymer matrix.

- "Addressing the Interface in Polymer-Clay Nanocomposites by Electron Paramagnetic Resonance Spectroscopy on Surfactant Probes" Jeschke, G.; Panek, G.; Schleidt, S.; Jonas, U. *Polym. Eng. Sci.* **2004**, *44*, 1112-1121. Use of EPR to directly measure and understand interface between polymer and clay organic treatment. Clays used were fluorinated synthetic mica (Somasif) and Laponite, with organic treatments having nitroxyl groups (one with nitroxyl near ammonium, another with nitroxyl at end of long chain away from ammonium). Organoclays analyzed by EPR, and organoclays in PS were also analyzed. Overall clay dispersion is not measured by this technique, only the structure and mobility of the nitroxyl surfactant in relation to the PS or solvent. Some mobility of the clay organic treatment was observed as temperature was increased, but PS intercalation immobilized the anchor region of the surfactant.

X-ray / Neutron Scattering or Diffraction

- "Deformation Behavior of Polyethylene/Silicate Nanocomposites As Studied by Real-Time Wide-Angle X-ray Scattering" Wang, K. H.; Chung, I. J.; Jang, M. C.; Keum, J. K.; Song, H. H. *Macromolecules* **2002**, *35*, 5529-5535. Melt compounding of Cloisite 20A (MMT) + PEgMA nanocomposites. Good clay dispersion obtained. Interesting data on how clay performs at fracture surfaces compared to a PEgMA + silica control. Also interesting XRD data showing how clay changes PE crystallites under strain.
- "3D Hierarchical orientation in polymer-clay nanocomposite films" Bafna, A.; Beaucage, G.; Mirabella, F.; Mehta, S. *Polymer* **2003**, *44*, 1103-1115. HDPE + PEgMA + OrganoMMT clays made by twin screw extrusion. Extensive WAXS and SAXS data studying how clay orients in these films, but no TEM data presented.
- "Characterization of Organically Modified Clays Using Scattering and Microscopy Techniques" Ho, D. L.; Briber, R. M.; Glinka, C. J. *Chem. Mater.* **2001**, *13*, 1923-1931. Dispersion of organomontmorillonites (Cloisite clays) in organic solvents and methods to characterize how the organoclay dispersed in the solvent. Mostly neutron and wide-angle X-ray scatter techniques used.
- "Effects of Solvent Solubility Parameters on Organoclay Dispersions" Ho, D. L.; Glinka, C. J. *Chem. Mater.* **2003**, *15*, 1309-1312. Use of Cloisite 15A (soxhlet extracted) in solvents to determine clay exfoliation. Use of neutron and x-ray techniques showed that solvents that could hydrogen bond with clay prevented exfoliation of clay in that solvent. The two solvents that completely exfoliated the clay (according to SANS, SAXS and WAXS) were chloroform and trichloroethylene.
- "A Small-Angle Neutron Scattering Study of a Commercial Organoclay Dispersion" Hanley, H. J. M.; Muzny, C. D.; Ho, D. L.; Glinka, C. J. *Langmuir* **2003**, *19*, 5575-5580. SANS analysis of Cloisite 15A (1%) in Toluene. Study designed to determine if organoclay completely exfoliates in a solvent. The organoclay did disperse well, but did not fully exfoliate.
- *"An in situ time-resolved XRD-PSD investigation into Na-montmorillonite interlayer and particle rearrangement during dehydration" Wilson, J.; Cuadros, J.; Cressey, G. *Clays and Clay Minerals* **2004**, *52*, 180-191.
- "X-Ray Powder Diffraction of Polymer/Layered Silicate Nanocomposites: Model and Practice" Vaia, R. A.; Liu, W. *J. Polym. Sci. B: Polym. Phys.* **2002**, *40*, 1590-1600.

Extensive paper on the application of XRD to nanocomposite analysis, including theory and equations, explanations of observed patterns and other related topics. The paper includes discussion on interlayer disorder and crystallite size and disorder. An excellent paper one should use when interpreting XRD data from nanocomposite samples.

- "Analysis of Small-Angle Scattering of Suspensions of Organically Modified Montmorillonite: Implications to Phase Behavior of Polymer Nanocomposites" Vaia, R. A.; Liu, W.; Koerner, H. *J. Polym. Sci. B: Polym. Phys.* **2003**, *41*, 3214-3236. Extensive paper on the application of SAXS to organoclay analysis in a solvent. This technique allows one to understand how a clay dispersed in a simple solution could be related to a clay dispersed in a polymer. Discussions on experimental techniques, as well as data interpretation are included. An excellent paper one should use when interpreting SAXS data from suspended clay samples, or attempting to analyze SAXS data from a polymer nanocomposite.
- "Reversible De-Intercalation and Intercalation Induced by Polymer Crystallization and Melting in a Poly(ethylene oxide)/Organoclay Nanocomposite" Sun, L.; Ertel, E. A.; Zhu, L.; Hsiao, B. S.; Avila-Orta, C. A.; Sics, I. *Langmuir* **2005**, *21*, 5672-5676. Use of temperature-dependent synchrotron wide-angle XRD to measure clay d-spacing and polymer crystallite changes. System studied was PEO + Cloisite 10A. Technique could be useful for other polymer clay nanocomposite systems.
- "Assessing organo-clay dispersion in polymer layered silicate nanocomposites: A SAXS approach" Causin, V.; Marega, C.; Mariog, A.; Ferrara, G. *Polymer* **2005**, *46*, 9533-9537. Use of SAXS to quantify clay dispersion in a PP + Cloisite 15A nanocomposite. TEM was collected first and image analysis data on over 200 images was collected. SAXS complimented and matched the TEM data, and quantified it, but SAXS does not eliminate the need for TEM yet.

Dielectric

- "Dielectric spectroscopy during extrusion processing of polymer nanocomposites: a high throughput processing/characterization method to measure layered silicate content and exfoliation" Davis, R. D.; Bur, A. J.; McBrearty, M.; Lee, Y-H.; Gilman, J. W.; Start, P. R. *Polymer* **2004**, *45*, 6487-6493. Nylon-6 nanocomposites analyzed by on-line dielectric measurements while materials were made by twin-screw extrusion. Dielectric results correlated with TEM and XRD results, confirming that dielectric technique (looking at difference between baseline alpha relaxation for Nylon-6 and Maxwell-Wagner relaxation seen for nanocomposite) can be used to quantitate clay concentration in a polymer matrix, but additional values would need to be measured to quantitate clay dispersion in a polymer matrix.
- *"Dielectric properties of nylon 6/clay nanocomposites from on-line process monitoring and off-line measurements" Noda, N.; Lee, Y-S.; Bur, A. J.; Prabhu, V. M.; Snyder, C. R.; Roth, S. C.; McBrearty, M. *Polymer* **2005**, *46*, 7201-7217.
- "Measuring the extent of exfoliation in polymer/clay nanocomposites using real-time process monitoring methods" Bur, A. J.; Lee, Y-S.; Roth, S. C.; Start, P. R. *Polymer* **2005**, *46*, 10908-10918. Nylon 6, 11, and 12 + Cloisite Na, 15A, 20A, 30B nanocomposites prepared by melt compounding and then analyzed by passing through a slit die at the end of the extruder. The slit die had a specialized dielectric sensor (looking at Maxwell-Wagner relaxation) and an optical transmission sensor. Data from the dielectric relaxation and the optical transmission correlated to clay dispersion as observed by TEM. Most usefully –

optical transmittance increased as exfoliation of clay increased (less light scattering from larger clay tactoids).

Spectroscopy (UV/Vis/NIR, FTIR, Raman, etc.)

- "Fourier Transform Infrared Investigation of the Deformation Behavior of Montmorillonite in Nylon-6/Nanoclay Nanocomposite" Loo, L. S.; Gleason, K. K. *Macromolecules* **2003**, *36*, 2587-2590. FTIR study showing the Si-O stretching peak, and its peak shifts. This suggests a method to observe how clays deform relative to the polymer matrix.
- "Optical Probes for Monitoring Intercalation and Exfoliation in Melt-Processed Polymer Nanocomposites" Maupin, P. H.; Gilman, J. W.; Harris, R. H.; Bellayer, S.; Bur, A. J.; Roth, S. C.; Murariu, M.; Morgan, A. B.; Harris, J. D. *Macromol. Rapid Commun.* **2004**, *25*, 788-792. Use of fluorescence dye (Nile Blue A) on imidazolium or ammonium treated MMT in PS, PA-6 nanocomposites prepared by melt compounding. Characterization by XRD, TEM, fluorescence. As clay exfoliated in PA-6, color of polymer nanocomposite changed from purple to red, and spectra from dye changed as well.
- *"Effect of Laponite and a Nonionic Polymer on the Absorption Character of Cationic Dye Solutions" Yurekli, K.; Conley, E.; Krishnamoorti, R. *Langmuir* **2005**, *21*, 5825-5830.

Rheology

- "A rheological method to compare the degree of exfoliation of nanocomposites" Wagener, R.; Reisinger, T. J. G. *Polymer* **2003**, *44*, 7513-7518. Use of rheology to quantify the shear thinning effect for polymer nanocomposites and relation of those results to clay dispersion. SEM data investigating overall clay dispersion given, but no XRD or TEM correlations are presented in the paper.
- "Rheological characterization of polystyrene-clay nanocomposites to compare the degree of exfoliation and dispersion" Zhao, J.; Morgan, A. B.; Harris, J. D. *Polymer* **2005**, *46*, 8641-8660. PS + imidazolium treated clay nanocomposites (with montmorillonite and fluorinated synthetic mica) prepared by solvent blending and fully characterized by TEM and XRD. Rheology used to characterize these materials further, correlating exfoliation vs. microcomposite results to the rheology data. Exfoliated materials do have significantly different rheology profiles when compared to microcomposites.
- "Effect of hydrogen bonding on the rheology of polycarbonate/organoclay nanocomposites" Lee, K. M.; Han, C. D. *Polymer* **2003**, *44*, 4573-4588. PC + Cloisite Na or Cloisite 30B nanocomposites made by twin screw extrusion. FTIR shows that Cloisite 30B disperses better in PC than Cloisite Na+ in PC. Polymer degradation due to clay organic treatment degradation did seem to occur during melt compounding, but to what extent is unknown, and what did appear to occur did not appear to be large. Authors comment (and have evidence to support) that rheology is a useful nanocomposite analysis tool. However, expertise in interpreting the results will be required to make sense of the observations.

Other Papers

- *"Real time exfoliation behavior of clay layers in epoxy-clay nanocomposites" Kong, D.; Park, C. E. *Chem. Mater.* **2003**, *15*, 419-424.
- *"Characterizing clay mineral suspensions using acoustic and electroacoustic spectroscopy" Guerin, M.; Seaman, J. C. *Clays and Clay Minerals* **2004**, *52*, 145-157.

- *"Acoustic and electroacoustic characterization of variable-charge mineral suspensions" Guerin, M.; Seaman, J. C.; Lehmann, C.; Jurgenson, A. *Clays and Clay Minerals* **2004**, *52*, 158-170.
- "Thermally Induced Phase Transitions and Morphological Changes in Organoclays" Gelfer, M.; Burger, C.; Fadeev, A.; Sics, I.; Chu, B.; Hsiao, B. S.; Heintz, A.; Kojo, K.; Hsu, S-L.; Si, M.; Rafailovich, M. *Langmuir* **2004**, *20*, 3746-3758. Analysis of Cloisite 6A (unextracted and extracted to remove excess surfactant), Cloisite 15A and Cloisite 20A clays by XRD, SAXS, DSC, TGA, and FTIR. X-ray measurements done under temperature ranges to see how the clay changed over a temperature range. Much of the data confirms observations from other papers, but provides more concrete data verifying the reactions. Clay organic treatment decomposition observed at 190 ºC, with slight improvement in thermal stability provided by extracting the clay (confirming extraction experiments by Morgan/Harris and Gilman/Davis). DSC measured a melting event for the organic treatment at 35-50 ºC, but no change in XRD pattern detected at this temperature. Modeling of the SAXS data shows how bimodal, unimodal thickness distributions can occur, as well as what happens to the clay when it degrades. The techniques in this paper should be very useful for clay characterization, but their application to polymeric nanocomposites is unknown.