Nanoscale infrared spectroscopy for polyolefins – from reverse engineering to monolayer research.

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We have developed a novel form of nanoscale infrared spectroscopy that can perform chemical analysis on complex polymeric samples with nanometer scale spatial resolution. Combining atomic force microscopy and infrared spectroscopy (AFM-IR)[1] the technique uses the tip of an AFM cantilever probe to detect the sample's local photothermal expansion due to the absorption of infrared light at specific wavelengths at spatial resolution orders of magnitude finer than conventional IR microspectroscopy.[2] Measuring absorption as a function of wavelength creates an IR absorption spectrum that acts as a chemical fingerprint to characterize and identify chemical components, even in complex heterogeneous polymer materials. In some cases it has been possible to fully reverse engineer polymeric materials via AFM-IR analysis.[3] Mapping IR absorption spatially over a sample at different wavelengths can be used to create maps of nanoscale chemical composition to visualize the distribution of different chemical components. The AFM-IR technique has also been used to study thermally induced changes in chemical composition. Local molecular orientation can also be studied by performing AFM-IR measurements under different polarization conditions. In this presentation we will share applications of AFM-IR in polymer materials sciences including polyolefin blends, composites, fibers and multilayer films. We will also discuss a recent resonance-enhanced version of the AFM-IR technique that enables it to be used on monolayers and ultra-thin films. [4]

We will also discuss two other nanoscale characterization techniques that Anasys pioneered which are nanoscale thermal analysis (nanoTA) and nanoscale dynamic mechanical spectroscopy via Lorentz Contact Resonance (LCR). In the nanoTA technique, an AFM probe has an embedded heater and can heat locally at the nanoscale to obtain Tg ad Tm information at the nanoscale. In the LCR technique, we can rapidly obtain contact measure and map mechanical properties of heterogenous materials with nanoscale spatial resolution and a very large dynamic range of material stiffness. LCR works by interacting a static magnetic field with current flowing through a U-shaped, self-heatable AFM cantilever. The Lorentz interaction between the AC current and the magnetic field field produces a oscillating force directly at the tip of the AFM cantilever. By sweeping the frequency of the AC current, a nanomechanical spectrum of the sample material can be obtained. The LCR spectra provide the ability to rapidly discriminate and identify different material components in heterogeneous materials and nanostructures. The self heatable LCR cantilever probes can also locally manipulate the sample temperature to enable temperature dependent measurements of mechanical properties. We will present applications of LCR nanomechanical spectroscopy in areas including polymer blends, composite materials, semiconductors, and graphene research.

References:

1. A. Dazzi, R. P., F. Glotin, and J. M. Ortega. Opt. Lett. 2005, 30, 2388-2390.
2. Dazzi, A.; Prater, C. B.; Hu, Q.; Chase, D. B.; Rabolt, J. F.; Marcott, C. Appl. Spectrosc. 2012, 66, (12), 1365-1384.
3. Eby, T.; Gundusharma, U.; Lo, M.; Sahagian, K.; Marcott, C.; Kjoller, K. Spectroscopy Europe 2012, 24, (3), 18-21.
4. Tip-enhanced infrared nanospectroscopy via molecular expansion force detection, Feng Lu, Mingzhou Jin and Mikhail A. Belkin, Nature Photonics 8, 307–312 (2014). doi:10.1038/nphoton.2013.373.