Exploring Nanoscale Viscoelasticity with a Surface Coupled Scanning Probe Microscope

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Viscoelastic properties dictate a material's ability to withstand loads over time and dissipate various forms of energy. In nanoscale materials, such as nanoparticles, nanocomposites and copolymers, viscoelastic properties can vary substantially over distances of a few nanometers, with characteristics very different than bulk counterparts. The need for rigorous viscoelastic measurement tools capable of probing the nanoscale and providing robust, quantitative property measurement is thus significant. With a periodic stress state, and quantification rooted in frequency determination rather than absolute displacement, viscoelastic contact resonance force microscopy (VE-CRFM), an advanced scanning probe microscopy method, is uniquely suited to the task. In VE-CRFM, the storage modulus, loss modulus and loss tangent of the probed material are determined from variations in the resonance frequency and quality factor of the coupled tip-sample system.

Here, we will discuss the development of VE-CRFM from experimental protocols to theoretical models. We will show how measurements can be performed in air and liquid environments, while still providing accurate quantification. Two recent developments within VE-CRFM will be discussed in detail. The first employs VE-CRFM as a local, in-situ probe of photorheological changes in polymer materials. A 405 nm laser is used to induce photopolymerization of the volume immediately beneath the tip. The fast mechanical bandwidth of the contact resonance enables transformation of the viscoelastic properties to be resolved with sub-millisecond temporal resolution; far faster than afforded by conventional rheological methods. In situ viscoelastic nanorheology is demonstrated on a rubber-to-glass transition and during voxel-scale cure of an additive manufacturing resin. In addition to demonstrating this new rheological tool, we will exhibit a new method of VE-CRFM wherein data are deliberately resolved at a constant CR frequency for all pixels in the image, rather than letting frequency vary. In existing CR methods, the variation in CR frequency leads to a nonmonotonic relationship between quality factor and material damping – making intuitive interpretation of raw data difficult. Furthermore, the variation in frequency means that viscoelastic properties (which themselves are frequency dependent) are measured at a different frequency for each pixel in the image. This calls into question whether observed variations are because of intrinsic differences in dissipation, or simply a result of the frequency change. We achieve constant CR frequency by varying the static load and hence contact stiffness in a force volume map while exciting the cantilever near the contact resonance frequency. The force at constant CR frequency becomes a measurable parameter that can be directly used to quantify variations in elastic modulus while the quality factor becomes an intuitive and monotonic function of loss tangent.