NIRT: Influence of Nanoscale Structure and Dynamics on the Deformation of Polymer Glass Nanocomposites
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Polymer glasses play a role in technology that no other type of material can fill. Polymers can be molded into any desired shape with relatively little energy input and when cooled can form "tough" solids. These materials are seen in everyday use as "bullet-proof glass", compact disks, safety glasses, automobile headlamp covers, aircraft windshields, etc. as well as in a host of engineering applications. In contrast to other types of solids, polymer glasses can show high impact resistance and, even though they are stiff, can often be significantly deformed without breaking. Even though polymeric glasses are impressive engineering materials, there are considerable opportunities to improve their properties, particularly their strength and failure properties. Recent evidence indicates that reinforcement of polymer glasses with nanoscale particles (i.e. nanocomposites) can produce materials with strength and failure properties that are substantially improved and, given current understanding, cannot be produced in any other manner.[2] The two key questions are: *What are the fundamental mechanisms that control the deformation of glassy polymer nanocomposites? Given these mechanisms, what is the optimum size, volume fraction, surface interaction, etc. of the nanoparticles that should be employed to engineer a nanocomposite with a given combination of mechanical properties?* To answer these questions, our NIRT brings together expertise in the fields of polymer deformation and continuum mechanics, materials theory, materials simulation, and glassy dynamics. In addition, we are engaged in a strong outreach program targeting high school students from under-represented groups.

Synthesis of PMMA-silica nanocomposites. We have been working to produce nanocomposites of non-aggregated silica particles in poly(methyl methacrylate) (PMMA), adapting the method of Sunkara et al. [3]. Silica particles of narrow size distribution were produced via the Stober method [4]; the particle surface was modified with the silane modifying agent (3-acryloxypropyl)-trimethoxysilane following Philipse and Vrij [5]; the modification was verified by solubility characteristics and elemental analysis. These particles have been transferred into the monomer with little aggregation. Nanocomposites produced by polymerizing the monomer/particle mixture will be used in both mechanical and optical experiments.

Viscoelastic properties of PMMA and nanocomposites. Linear and nonlinear single and two-step creep experiments have been performed on lightly-crosslinked PMMA. A master curve obtained from the linear creep experiments is consistent with literature data. Measurements on nanocomposites will commence shortly. The thermo-viscoelastic model (TVEM) of Caruthers et al. [6] is the only thermodynamically consistent constitutive model with a demonstrated ability to predict a wide range of relaxation phenomena in glassy materials (including yield, stress/volume/enthalpy relaxation, nonlinear stress-strain behavior, and physical aging). An efficient C++ code has been developed to implement TVEM for various deformation/loading and thermal histories. Preliminary validation of the code has been carried out using available literature data for PMMA. TVEM will use experimental data for nanocomposites in the linear regime to generate predictions for non-linear deformation and for deformation-induced mobility.

Experimental measurements of deformation-induced mobility. We have built an apparatus to measure the deformation-induced mobility of polymer glasses and nanocomposites. Previously we have shown that the reorientation of a dye molecule (on the time scale of thousands of seconds) can be used to monitor the segmental dynamics of a polymer melt.[7] Here we utilize this method to measure mobility during tensile deformation of a free-standing film. In preliminary experiments on a lightly cross-linked PMMA glass, we have observed deformation-induced mobility from T_g-10 K to T_g -30 K. Generally we observe the largest changes in mobility if the sample is deformed at a lower temperature. At a given temperature, mobility enhancements correlate better with strain rate than with stress or strain. More interestingly, small increases in the strain rate can give rise to dramatic mobility increases. At T_g – 18 K, when the strain rate is lower than 10^{-5}/s, no mobility enhancement is observed. However, once the strain and strain rate cross threshold values, the mobility increases dramatically. Up to now, the largest change in mobility is about a factor of 200 (equivalent to a temperature increase of ~12 K). After removing the stress, we observe that the enhanced mobility disappears slowly. Building on this recent progress, experiments on PMMA/silica nanocomposites are being initiated. We are eager to use measurements of deformation-induced mobility to uncover the microscopic mechanisms of the nanoscale filler effect.

Microscopic theory of relaxation and deformation in polymer glasses and nanocomposites. Recently developed statistical mechanical theories of supercooled polymer melt dynamics [8] and nonlinear viscoelasticity of nanoparticle suspensions [9] have been generalized to create a microscopic theory of relaxation, elasticity, mechanical properties, and physical aging of polymer glasses. Below T_g the density fluctuations which control segmental barrier hopping become partially frozen and follow a nonequilibrium temperature dependence [10]. A consequence is the crossover from highly non-Arrhenius behavior in the supercooled regime to apparently Arrhenius relaxation below T_g, in accord with experiments [11]. Deformation reduces the effective free energy barrier for hopping, thereby accelerating the segmental relaxation process, softening the elastic modulus and ultimately resulting in yield and plastic flow. Quantitative applications of the theory to PMMA glasses result in temperature and strain rate dependent stress-strain curves and yield points in good agreement with experiment. The key physical effect is deformation-induced reduction of the segmental relaxation time that is larger for colder glasses and/or at higher strain rates, consistent with our experimental measurements. We are generalizing our approach to treat creep experiments to allow direct comparisons with ongoing experiments. The dynamic consequences of heterogeneous nanodomains, and extension of the theory to glassy polymer nanocomposites, are also under active study.

A theory for physical aging has also been developed based on a simple kinetic model for the equilibration of collective density fluctuations via activated barrier hopping. Power law, stress-dependent aging of the relaxation time are predicted with apparent exponents that depend systematically on temperature and aging time.

Computer simulations of nanocomposite deformation and yield. We have examined both melt and glass polymer nanocomposite regimes. In the melt, we have implemented an entanglement search algorithm that permits calculation of the number of entanglements (or the so-called entanglement length) of a polymeric melt in the absence and in the presence of nanoparticles. We find that a small concentration of nanoparticles (from 5 to 10% volume) can

reduce significantly the molecular weight between entanglements, thereby leading to a material with a higher plateau modulus. The effect of nanoparticles on entanglement appears to be relatively robust and, for well dispersed nanoparticles, relatively insensitive to the details of the particle-polymer interaction. In the glassy region, our results to date have shown that polymeric glasses are mechanically heterogeneous. Stiff domains are usually surrounded by soft domains. When the glass is deformed, it is the soft domains (having a near-zero elastic modulus) that lead to plastic events. Such plastic events are highly localized for small deformations (or strains), but their frequency increases with strain until an "avalanche" of events results in the overall, macroscopic plastic yield of the material[12]. Contrary to intuition, we find that nanoparticles strengthen the glass by decreasing the mechanical heterogeneity of the material. Nanocomposites are more mechanically homogeneous and, upon deformation, local plastic events are less frequent and occur at higher strains[12].

Education and outreach program. Our NIRT works with a University of Wisconsin-Madison program known as PEOPLE (Pre-college Enrichment Opportunity Program for Learning Excellence) to increase the likelihood that minority and low-income high school students matriculate to colleges and universities. During the summer of 2006, our NIRT designed and staffed a three-week class on polymer materials, with an emphasis on applications relevant for computers. We had 15 high school juniors from the PEOPLE program in our two-hour per day course. The curriculum for our course and documentation of our summer activities can be found at: http://www.chem.wisc.edu/~ediger/outreach.htm. The PEOPLE program seeks to increase the size of the pipeline bringing under-represented groups to post-secondary education. Program details can be found at http://www.peopleprogram.wisc.edu/. This program is one of only a few nation-wide that engages a large group of students early and interacts with that same group continuously until they finish high school. To our knowledge, it is the only program that offers a full tuition grant as an incentive to graduates. More than 90% of PEOPLE graduates go on to college – in the absence of this program, only about 35% of these students would be expected to enter college. In the last four years, UW-Madison has enrolled more than 120 graduates of the PEOPLE program and retention rates are excellent.

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