

Dynamic Heterogeneity and the Behavior of Glass-Forming Materials at the Nanoscale

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Sindee L. Simon¹, Gregory B. McKenna¹, Edward L. Quitevis¹, Ranko Richert²

¹Texas Tech University, ²Arizona State University

The principle aim of the present NIRT project is to understand how spatially dynamic heterogeneity in polymeric and small molecule glass formers is influenced by confinement or constraints imposed at the nanoscale, and how this in turn, influences the relaxation of molecular and thermodynamic properties. Current activities include development of nanoconfinement and freeze-drying techniques, development of new rheological techniques to measure the properties of ultrathin polymeric films, the development of the fluorescent probe experiments, and the use of microemulsions as soft confinement in solvation dynamics studies, as well as outreach and educational efforts.

Nanoconfinement will include "soft" confinement of low molecular weight glass-formers in crosslinked rubber. Such nanoconfinement templates are currently being developed using dicumyl peroxide, a quantitative crosslinking agent for polyisoprene, to make polyisoprene networks. The crosslink density will be calculated from the amount of crosslinker used; in addition, the crosslink density will be experimentally determined based on the degree of swelling and on the melting point depression of low-molecular weight solvents, the latter of which occurs when the crystals in the crosslinked network cannot grow because they are restrained by the network structure. Past work from one of the PIs has shown that crystal sizes are close to those expected from the distance between the crosslinks.¹ At the present, a graduate student is currently learning the methodologies for making and characterizing crosslinked rubber networks.

In addition to developing a "soft" rubber confinement for low molecular weight glass formers, freeze-dried polystyrene is being studied. Freeze drying offers a potential way to separate the influence of intrinsic size effects, macroscopic confinement effects, and processing effects. During the freeze-drying process, a very dilute polymer solution is frozen and then the solvent is sublimed off. The polymer chains separated in the dilute solution remain so after sublimation because of the slow relaxation rate at temperatures well below T_g . As a result, a T_g depression on the order of 2 to 5 K for linear polystyrene has been observed in previous work of one of the PIs.² Although this depression is significant, a sample with a larger T_g depression might be expected to result in larger differences, for example, in dynamic heterogeneity and in structural recovery. To this end, we examined freeze-dried cyclic polystyrene and found that the T_g depressions were much larger than in the linear material³ as shown in Figure 1. The freeze-drying techniques, originally completed by a post-doctoral researcher, are currently being learned by a graduate student on the project. Dynamic heterogeneity and structural recovery studies on the freeze-dried cyclic polystyrene are planned.

Characterization of the viscoelastic response of materials in ultrathin films is important for understanding the glass transition at the nanoscale, and as part of the NIRT, several new

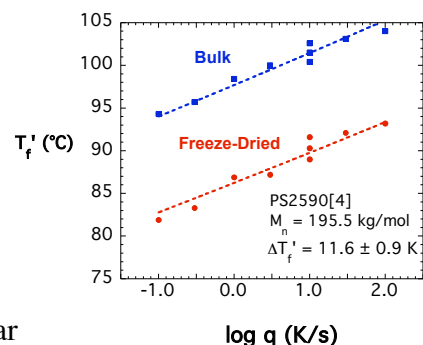


Figure 1. Effect of freeze drying on the T_g depression in cyclic polystyrene.

methodologies are being explored. A novel creep test has been developed⁴ which relies on the imaging capabilities of the atomic force microscope. In essence, the test is a reduction in size of the classical bubble inflation test. Figure 2 shows a regular array of inflated bubbles in an ultrathin film cast on a substrate having regular spaced channels, with the inset showing an enlarged view of a single inflated bubble. Measurement of the bubble height as a function of time at constant inflation pressure yields the creep compliance. Such linear viscoelastic measurements are shown as a function of time and temperature for films of poly(vinyl acetate) (PVAc) at a thickness of 27.5 nanometers in Figure 3. Comparison of the data with the viscoelastic creep data of Plazek for bulk PVAc⁵ suggests that there is little change in the glass transition temperature based on the viscoelastic response although the rubbery creep compliance is considerably lower than for the bulk and appears to depend on film thickness. Corroborating the result that the timescales for the viscoelastic properties of ultrathin films are very similar to those in the bulk is a viscoelastic contact mechanics analysis⁶ of the nanosphere embedding data of Teichroeb and Forrest⁷ on ultrathin polystyrene films. The analysis using the bulk properties of polystyrene gives quantitative agreement with the data as shown in Figure 4, indicating little or no depression in the glass transition temperature. Future work is aimed at performing the bubble inflation and nanosphere embedding techniques in the glassy state in order to determine if confinement in thin films changes the physical aging response.

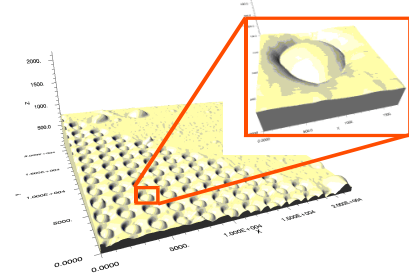


Figure 2. AFM image on 22 micron scan showing the regular array of inflated bubbles, with the inset showing an enlarged view of a single bubble.

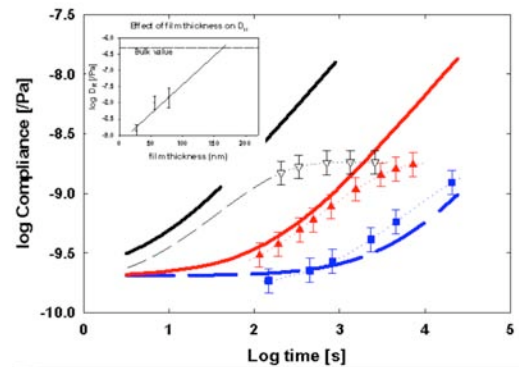


Figure 3. Experimental creep compliance data for 27 nm thick PVAc film (symbols) compared to the bulk values (lines) at 25.5 C (blue), 30 C (red), 35 C (black). The inset shows the log of the rubbery creep compliance as a function of film thickness, with the bulk value indicated by the horizontal line.

In parallel work, an apparatus has been constructed to perform holographic FRAP measurements of the translational diffusion of fluorescent probe molecules in various glass-forming liquids. In holographic FRAP, optical fringes are used to create a photobleached population grating in the sample. Traveling wave fringes are swept across the photobleached population grating using an electro-optic modulator (EOM); the translational diffusion coefficient D_T for the probe molecule is obtained from the decay of amplitude of the modulated fluorescence. The experimental setup was tested by measuring the D_T of the fluorescent probe rubrene in ortho-terphenyl (OTP). The values of D_T obtained in these measurements compare well with previously published values for this system. Preliminary measurements have also been made for the translation diffusion of rubrene in the glass-former sucrose benzoate (SB), which has a $T_g = 332$ K, and a FRAP signal for rubrene in supercooled SB at 368 K is shown in Figure 5. Future

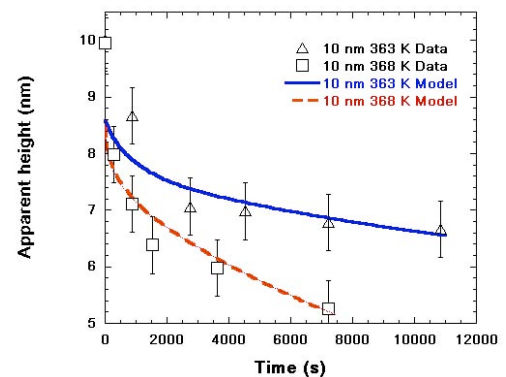


Figure 4. Comparison of calculated and measured 10 nm sphere embedding into polystyrene surface. Experimental data (symbols) from Teichroeb and Forest.

work will involve performing measurements as a function of temperature down to temperatures very near T_g of the glass-formers, both in the bulk and for material confined in the nanopores of crosslinked rubber.

One of the aims of the project is to compare the effects of "soft" and "hard" confinements on dynamic heterogeneity, as measured by solvation dynamics studies, in the vicinity of the glass transition temperature. To obtain soft confinement, we exploit glass-forming microemulsions, where reverse micelles self-assemble in a ternary system composed of the polar (or "water") phase, a surfactant, and a nonpolar (or "oil") phase. For propylene glycol/AOT/decalin doped with suitable chromophores, the dynamics of the intramicellar propylene glycol droplets of 2.6 and 4.6 nm diameter near the glass transition at $T_g = 160$ K can be selectively probed. Contrary to hard confinement to porous glass, the PG droplet dynamics are now faster than the bulk dynamics⁸, as shown in Figure 6. For confinement of PG to diameters near 10 nm, the glass transition shifts by +4.5 K in hard confinement, while the effect reverses to a ΔT_g of -7 K for the 4.6 nm microemulsion droplets, where the extramicellar matrix decalin is approximately 30 K above its T_g of 135 K.

Outreach has included presentations by the PIs on the findings of this project at various national and international meetings, including the American Physical Society and the Society of Plastics Engineers. In addition, Prof. Richert gave seminars at TTU in the fall of 2003 and 2004 and Prof. McKenna gave a seminar in Chemistry at ASU in the spring 2004. Other outreach activities have included helping two sixth-grade students with their science fair projects on sol-gel glasses. In terms of education, one undergraduate researcher, five graduate students, and one post-doctoral researcher are being trained through this grant.

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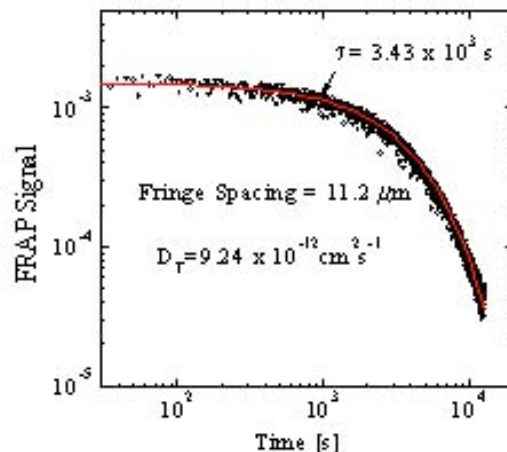


Figure 5. FRAP signal for rubrene in sucrose benzoate at 368 K. The solid red line is a fit to an exponential decay function.

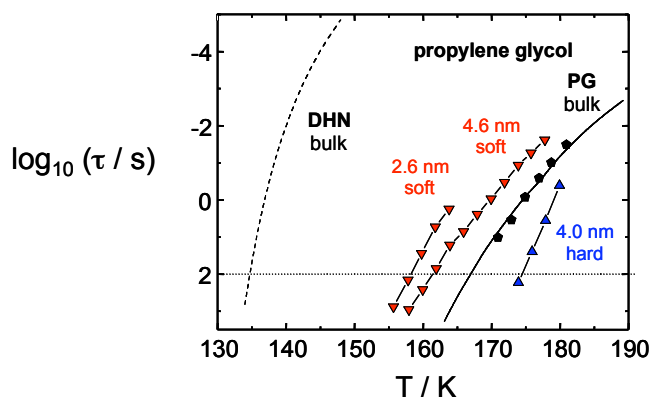


Figure 6. Characteristic solvation relaxation times for propylene glycol in various confinement: Black symbols are for bulk PG, blue triangles for 'hard' confinement to 4.0 nm porous Vycor glass, and red triangles are for 'soft' confinement to the 2.6 and 4.6 nm diameter reverse micelles in the PG/AOT/DHN microemulsion. The dotted line marks the relaxation of bulk DHN, the matrix phase of the microemulsions.