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Effects of Polydispersity on the Glass Transition Dynamics of Aqueous Suspensions of Soft Spherical Colloidal Particles

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Abstract : The zero shear viscosity (η_0) of a suspension of hard sphere colloids characterized by a significant polydispersity (≈10%) increases with increase in volume fraction (ϕ) and shows a dramatic increase at $\phi=\phi g$ with the system entering a colloidal glassy state. Fragility which is the measure of the rapidity of approach of these suspensions towards the glassy state is sensitive to its size polydispersity and stiffness of the particles. Soft poly(N-isopropylacrylamide) (PNIPAM) particles deform in the presence of neighboring particles at volume fraction above the random close packing volume fraction of undeformed monodisperse spheres. Softness, therefore, enhances the packing efficiency of these particles. In this study PNIPAM particles of a nearly constant swelling ratio and with polydispersities varying over a wide range (7.4%-48.9%) are synthesized to study the effects of polydispersity on the dynamics of suspensions of soft PNIPAM colloidal particles. The size and polydispersity of these particles are characterized using dynamic light scattering (DLS) and scanning electron microscopy (SEM). As these particles are deformable, their packing in aqueous suspensions is quantified in terms of effective volume fraction (ϕeff). The zero shear viscosity (η_0) data of these colloidal suspensions, estimated from rheometric experiments as a function of the effective volume fraction ϕeff of the suspensions, increases with increase in ϕeff and shows a dramatic increase at ϕeff = ϕ_0. The data for η_0 as a function of ϕeff fits well to the Vogel-Fulcher-Tammann equation. It is observed that increasing polydispersity results in increasingly fragile supercooled liquid-like behavior, with the parameter ϕ_0, extracted from the fits to the VFT equation shifting towards higher ϕeff. The observed increase in fragility is attributed to the prevalence of dynamical heterogeneities (DHs) in these polydisperse suspensions, while the simultaneous shift in ϕ_0 is ascribed to the decoupling of the dynamics of the smallest and largest particles. Finally, it is observed that the intrinsic nonlinearity of these suspensions, estimated at the third harmonic near ϕ_0 in Fourier transform oscillatory rheological experiments, increases with increase in polydispersity. These results are in agreement with theoretical predictions and simulation results for polydisperse hard sphere colloidal glasses and clearly demonstrate that jammed suspensions of polydisperse colloidal particles can be effectively fluidized with increasing polydispersity. Suspensions of these particles are therefore excellent candidates for detailed experimental studies of the effects of polydispersity on the dynamics of glass formation.

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