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Physical Aging within Hairy NanoParticle Assemblies H. KOERNER, AFRL-WPAFB, M. BOCKSTALLER, A. DANG, C. MAHONEY, K. MATYJASZEWSKI, C.-M. HUI, Carnegie Mellon U, R. VAIA, AFRL-WPAFB, AFRL-WPAFB TEAM, CARNEGIE MELLON U COLLABORATION — Polymer grafted nanoparticles provide solutions to overcome dispersion challenges in conventional polymer-inorganic nanocomposites (NCs). While most research has focused on blends of these hairy nanoparticles (HNPs) into polymer matrices, recent work has demonstrated substantial promise for solvent- or matrix-free assemblies of HNPs (aHNPs). Significant progress has been made in understanding the relationship between the structure of the polymer corona at intermediate and high graft densities and the morphology, mechanical properties and melts dynamics of the assembly. However, very little is known about the behavior of aHNPs with low graft densities (σ<0.05 nm^{-2}) of high molecular weight chains that are above entanglement (>60kDa). Such aHNPs contain more than 30 vol% inorganic, with maximum separation between particle surfaces less than 10 nanometers. For such materials, we discuss the physical aging characteristics from enthalpy relaxation experiments of these highly confined poly(styrene) and poly(methylmethacrylate) grafts. Physical aging is substantially suppressed in the low σ (σ<0.05) regime, as compared to conventional NCs at similar nanoparticle loadings. Furthermore, relaxation rate, distribution and fragility indicate that aHNPs with high σ exhibit behavior deep within the glass similar to conventional NCs and their neat polymers, however deviate substantially from Arrhenius behavior as Tg-T approaches 0.

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