Fall 11-11-2015

Physical aging and glass transition of single component nanocomposites

Hilmar Koerner

Air Force Research Laboratory, hilmar.koerner.1@us.af.mil

PHYSICAL AGING AND GLASS TRANSITION OF SINGLE COMPONENT NANOCOMPOSITES

Hilmar Koerner
Air Force Research Laboratory
USA
hilmar.koerner.1@us.af.mil

Matrix free assemblies of polymer-grafted, "hairy" nanoparticles (HNP) exhibit novel morphology, dielectric and mechanical properties, as well as providing means to overcome dispersion challenges ubiquitous to conventional polymer-inorganic blended nanocomposites. Physical aging of the amorphous polymer glass between the close-packed nanoparticles (NPs) will dominate long-term stability. However, the energetics of cooperative relaxation of tethered chains confined within the interstitial spaces in single component nanocomposites is unknown. Herein, we compare glass transition temperature (Tg) and physical aging behavior of matrix free assemblies of HNPs (aHNPs) to conventional NP-polymer blends, across different nano-silica loadings (0-50 v/v%) and brush architecture of grafted polystyrene chains in aHNPs. At low to intermediate silica volume fraction, the Tg of blended nanocomposites is independent of silica content, whereas for aHNPs the Tg decreases with silica content, implying that chain tethering decreases local segment density near the NP interface irrespective of chain composition, molecular weight or polymer-NP interactions. In contrast, the Tg of the aHNPs is higher than linear polystyrene of comparable molecular weight to the graft, implying that cooperativity is constrained. Within the glass (T<Tg), local segment relaxation near Tg is retarded irrespective of polymer-silica tethering. This arrested enthalpy recovery rate is less hindered than comparable processes in neat PS, however. This leads to the emergence of a cross-over temperature Tx, at which the enthalpy recovery process of the bulk glass becomes dominant in aHNPs and blended nanocomposites. Differences in structural recovery of aHNP and blended nanocomposites occur only at the highest silica loadings (~ 50 v/v%), where enthalpy recovery for aHNPs is substantially suppressed relative to the blended counterparts. The virtually absent physical aging within aHNPs at high loadings is independent of brush architecture (graft density or molecular weight of tethered chains) and indicates that impact of chain tethering on structural relaxation starts to evolve at particle-particle surface separations on the order of the Kuhn length. aHNPs therefore represent a highly stable alternative to traditional nanocomposite blends at the highest inorganic loadings, which are essential for optoelectronic applications, with minimal susceptibility to property creep due to physical aging.