Molecular Dynamics Simulations of Nanoparticle-Based Rheology

TING GE, University of North Carolina, GARY GREST, Sandia National Laboratories, MICHAEL RUBINSTEIN, University of North Carolina — We perform molecular dynamics simulations of nanoparticles (NPs) in entangled melts of linear polymers and non-concatenated ring polymers to explore NP-based rheology. As in conventional micro-bead rheology, the generalized Stokes-Einstein relation (GSER) is employed to extract an effective stress relaxation function $G_{\text{GSE}}(t)$ from the mean square displacement of NPs. $G_{\text{GSE}}(t)$ for different NP diameters $d$ are compared with the stress relaxation function $G_{\text{GK}}(t)$ obtained from applying the Green-Kubo formula to a pure polymer melt. By comparing $G_{\text{GSE}}(t)$ and $G_{\text{GK}}(t)$, we demonstrate the slip NP-polymer boundary conditions in simulations. For NPs in linear polymers, a plateau in $G_{\text{GSE}}(t)$ emerges as $d$ exceeds the tube diameter $a$ and approaches the entanglement plateau in $G_{\text{GK}}(t)$ with increasing $d$. A complete overlap of $G_{\text{GSE}}(t)$ and $G_{\text{GK}}(t)$ is not observed for the largest $d \approx 3a$, but is anticipated to occur for $d > 4a$. The progressive coupling of NPs to the bulk viscoelasticity reflects the intriguing interplay between NPs with $d$ moderately larger than $a$ and the entanglement network. For NPs in ring polymers, as $d$ increases towards the spanning size $R$ of ring polymers, $G_{\text{GSE}}(t)$ approaches $G_{\text{GK}}(t)$ that exhibits no entanglement plateau. The $d$-dependence of the local viscoelasticity probed by NPs indicates the coupling between NPs and the relaxation of ring polymers at larger length and time scales with increasing $d$. Finally, $G_{\text{GSE}}(t)$ and $G_{\text{GK}}(t)$ are anticipated to overlap for $d > 3R$, corresponding to the coupling of NPs to the bulk viscoelasticity.

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