

Study of Polybutadiene/Silica Nanocomposites through Molecular Dynamics Simulations

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The conformations and the dynamics of poly-(butadiene) chains, of various molecular weights, in PB/silica nanocomposites are studied through long-time atomistic molecular dynamics simulations at $T = 413$ K, well above T_g . The effect of the stereochemistry of PB chains is addressed by simulation of cis-1,4-PB/silica and trans-1,4-PB/silica nanocomposites. The model systems contain 30wt % silica nanoparticles of diameter ≈ 4 nm. The nanocomposites are characterized through analyzing (i) interfacial packing and the dimensions of the PB chains; (ii) statistics of the train, bridge, loop, and tail conformations of adsorbed chains and the coupling between segmental orientational dynamics and chain conformations; and (iii) the orientational and translational dynamics of the polymer chains and the desorption kinetics of chains and segments. The dimensions of PB chains, excluding a small fraction of chains that wrap around the NP, are not affected. The segmental and terminal dynamics of PB chains are slower in the nanocomposites than in the respective bulk melts. Moreover, the dynamics of PB chains in the nanocomposites is very heterogeneous and a coupling between the dynamics and the conformation of PB chains is observed: the adsorbed segments (trains) and the chains that have a higher number of contacts to the NPs are more decelerated. The self-diffusion coefficients, D , of PB chains in the nanocomposites are also reduced compared to the respective bulk systems. A clear crossover from the unentangled (Rouse-like) to the entangled (reptation-like) regime is observed based on the calculation of the segmental mean-square displacement and D as a function of the chain length. The deceleration of dynamics in the nanocomposites, in both Rouse and reptation-like regimes, is discussed in terms of a higher effective monomeric friction coefficient. Finally, the correlation times for the desorption of segments and chains are much larger than the segmental and end-to-end-vector correlation times, respectively.

Keywords: polymer nanocomposites; Atomistic Molecular Simulations

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References

- [1] A. F. Behbahani, A. Rissanou, G. Kritikos, M. Doxastakis, C. Burkhart, P. Polinska, V. Harmandaris, *Macromolecules*, 2020, 53, 6173
- [2] G. Maurel, F. Goujon, B. Schnell, P. Malfreyt, *J. Phys. Chem. C*, 2015, 119, 4817.