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Dependence of local dynamics on the chain length of grafted molecules

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Nanoparticles can be utilized to induce restricted spatial mobility in the polymer and smaller molecules. However, a simple blend of nanoparticles with the organic molecules leads to phase separation and hence is unsustainable. Grafting the molecules on nanoparticle surface addresses this problem efficiently. The grafting induces significant alteration to the conformation and dynamics of the molecules. We discuss two cases here: polymer molecules grafted on iron oxide nanoparticles i.e. long molecules and oleic acid grafted on iron oxide nanoparticles i.e. short chains. We study these systems using a combination of Quasielastic neutron scattering (QENS) and dielectric spectroscopy. We observe a molecular weight dependent average dynamics in grafted polymers. For lower molecular weight, the dynamics of grafted polymer is decelerated as compared to the pure polymer. On the other hand, for higher molecular weight, the dynamics of grafted polymer is faster. We invoke a detailed analysis method using distribution of relaxation times to fit the data which unearths the presence of both faster as well as slower segments in all the nanocomposites. On the other hand, in case of oleic acid, the dynamics is restricted to uniaxial rotation when grafted on nanoparticles. We show that even below the crystallization temperature of pure oleic acid, rotational dynamics is observed in case of grafted oleic acid. However, there is selective rotation of bonds depending on temperature. A modified uniaxial rotation diffusion model is able to capture these temperature dependent dynamics of the grafted oleic acid system.

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