SP4.09

Glass Transition of Polymers Confined at the Nanoscale

Yong Yang, Jiong Shen, *L. James Lee

Department of Chemical and Biomolecular Engineering The Ohio State University Columbus, OH 43210, USA

In nanocomposites, electronic thin films, coating, and polymer-based MEMS (Micro-Electro-Mechanical Systems) and NEMS (Nano-Electro-Mechanical Systems) devices, a comprehensive understanding of molecular dynamics of confined polymers at the nanoscale is essential. At the nanoscale, pure polymers show inferior properties compared with the bulk materials. On the other hand, a strong interaction between the solid surface and the adjacent polymer may improve these properties, depending on the entropic and enthalpic effects of the substrate on the polymer chains. In this study, the well-defined systems, polymer thin films/substrate configurations, were used to resemble the interfaces of polymer-substrate and the polymer dynamics (i.e. glass transition temperature, Tg and chain diffusion) in vicinity of the substrate were measured using atomic force microscope with nanoparticles as the probe and neutron reflectivity respectively. Polystyrene (PS) thin films were spun-coat on two types of substrates, highly ordered pyrolytic graphite (HOPG) and silicon (Si) wafer, which have different interactions with PS. The film thickness was changed from 1 Rg (radius of gyration of PS) to 10 Rg so that we could explore the effects of both the polymer-air and the polymer-substrate interactions. The PS on these substrates shows different Tg profiles. The influence of subcritical CO_2 on Tg of those polymer thin films was examined as well. The competing impacts of the entropic confinement (by substrate) and the free-volume increase (by CO₂) were evaluated. These results will provide valuable guides for designing and processing of new polymer nanocomposites, thin film coating, and NEMS devices.