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**Deformation Behavior of Monolayer Assemblies of Polystyrene Grafted Nanoparticles** YANG JIAO, MING-SIAO HSIAO, LAWRENCE DRUMMY, RICHARD VAIA, Air Force Rsch Lab - WPAFB — Assemblies of polymer-grafted nanoparticles (PGNs) are of interest to a wide array of structural, photonic and electrical applications. In contrast to nanoparticles dispersed in a free polymer matrix, the grafted polymer determines particle spacing. The extent to which these grafted polymers are entangled determines the robustness and strength. Here, we investigate the correlation between PGN architecture (nanoparticle radius, graft density, graft molecular weight) and the deformation mechanism of polystyrene-grafted PGNs. In contrast to highly stretched conformations within a dense brush of short chains, the canopy height, h, for PGNs with sparse grafting density (0.05 ch/nm2), scales as h $\approx$ $N^{1/3}$ in as-cast films, and relaxes to h $\approx$ $N^0$ for annealed films. This implies densification and chain relaxation occur due to these volumetrically frustrated PGN designs. An increase in polymerization degree, regardless of grafting density, results in a conformational transition to semidilute polymer brush (SDPB), accompanied by an increase in fracture toughness. Overall, these studies of low graft density PGNs imply that a unique canopy architecture exists that optimizes the critical application requirement of simultaneous maximization of nanoparticle volume fraction and toughness.

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