

Microscopic Characterization of Fracture Mechanisms in Polystyrene Grafted Nanoparticle Assemblies: The Role of Film Thickness and Grafting Density

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Assemblies of polymer-grafted “hairy” nanoparticles (HNPs) are of current interest for a wide array of mechanical, photonic and electrical applications. In contrast to nanoparticles dispersed in a free polymer matrix, the grafted polymer determines particle spacing and circumvents nanoparticle agglomeration. HNPs are prepared by surface-initiated ATRP/RAFT polymerization. The thickness (monolayer or multilayers), and the order of nanoparticles assembly in HNPs films are controlled by the solution concentration and preparation methods (drop-casting and flow coating assembly at the air-water interface). The extent to which these grafted polymers are entangled determines the robustness and strength of the HNP assembly. As these polymer-grafted “hairy” nanoparticles (HNPs) are a relatively new class of materials, investigation of fundamental failure mechanisms have been limited [1,2]. Here in, we discuss the craze (nucleation and growth) and crack (fracture) process in thin film assemblies of polystyrene-grafted HNPs under strain using static (bright field, HAADF-STEM, tomography) and in-situ TEM and AFM techniques. Results show that crack processes dominant for HNPs assemblies with low grafting density, but crazing process occurs for assemblies with high grafting density. As with linear polystyrene, molecular weight and strain rate also impact the transition from crack to craze. These correlations between HNP architecture and assembly deformation and failure modes refine the HNP design space for the synthesis and fabrication of assemblies with excellent mechanical properties.

Here we discussed the effects of film thickness and tethering density on failure mechanisms in HNPs and presented *ex situ* TEM observation of hairy polystyrene grafted SiO₂ nanoparticle assemblies with two different grafting densities (aHNP-PS-1 and aHNP-PS-50) after straining in tension. Tab. 1 shows the molecular characterization and glass transition values of grafted polystyrene (T_g^{PS}) for aHNP-PS-1 ($\sigma = 0.57$) and aHNP-PS-50 ($\sigma = 0.07$) respectively. The glass transition temperatures of the two aHNP-PS-X samples were found to be constant although the two σ values are significantly different. Fig. 1 shows TEM images of aHNP-PS-1 and aHNP-PS-50 films, each with a nominal film thickness of 150 nm, indicating significant microstructural morphology changes of the HNP film are driven by the extent of PS grafting on the silica nanoparticles (σ values). Fig. 2 a-c shows failure microstructures of PS grafted HNPs films with thicknesses ranging from 22 nm to 1340 nm. Plastic deformation consisting of perforated sheets containing silica nanoparticles dominates in thin HNP films with thickness less than 200 nm and silica NP seems not to participate the formation of craze microstructure. Crazes form in the thick film case (Fig. 2c). The decrease in the rate of craze initiation and propagation in thick film might be driven by solid plastic constraint in thickness direction caused by the presence of high modulus silica nanoparticles ($E^{SiO_2} = 70$ GPa). Crack microstructures dominate the morphologies in the low σ aHNP-PS-50 film [3].

References:

- [1] Kumar, S. K.; Jouault, N. *Macromolecules* vol. **46** (2013), p. 3199
- [2] Jaeger, H. M; Wang, Y. *et al* *Faraday Discuss.* vol. **181** (2015), p. 325

[3] The authors acknowledge support from the Air Force Research Laboratory

Fig. 1 Molecular and thermal characterizations of PS @ SiO₂ NPs assemblies

aHNP ($r_0 = 8 \text{ nm} \pm 35\%$)	f^{SiO_2}	N graft	σ (chains/nm ²)	T_g (°C)
aHNP-PS-1	0.97	2200	0.57	102
aHNP-PS-50	50	192	0.07	102

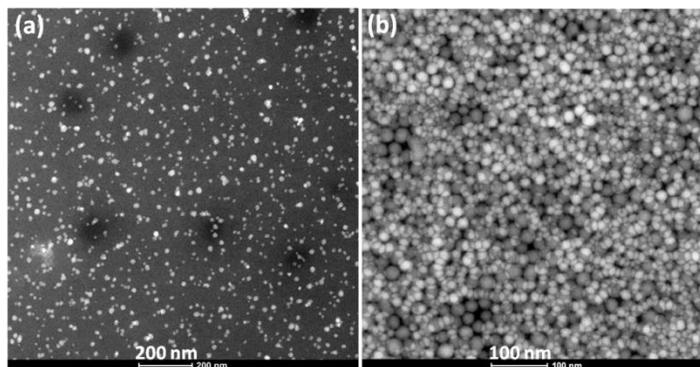


Fig. 2 TEM images of (a) aHNP-PS-1 thin film and (b) aHNP-PS-50 thin film, respectively.

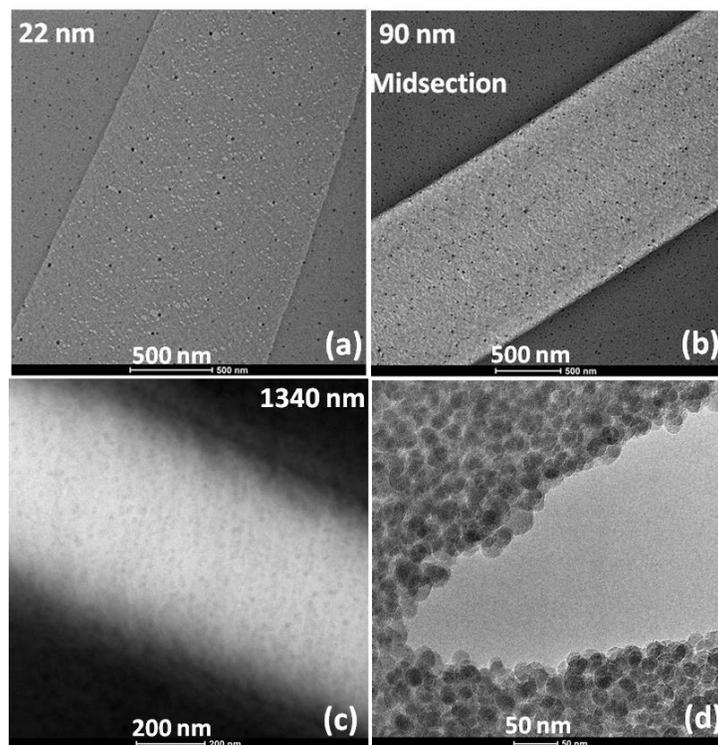


Fig. 3 (a-d) TEM images of strained PS @ SiO₂ films. Plastic deformation in the form of a perforated sheet morphology dominates in (a) aHNP-PS-1 film with the thickness of 22 nm and (b) aHNP-PS-1 film with the 90 nm thickness. Crazing morphology forms in (c) aHNP-PS-1 film with a 1340 nm thickness. Cracking forms in (d) aHNP-PS-50 thin film.