

Introduction

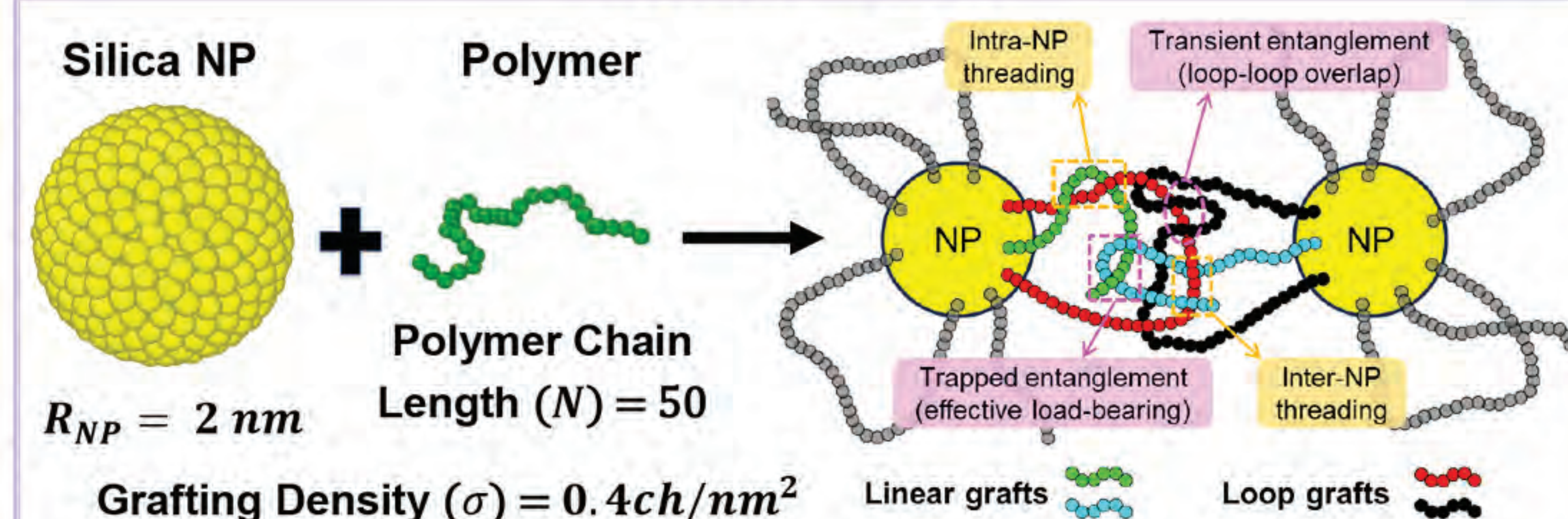


Figure 1. Covalently grafting polymer chains onto the surface of a nanoparticle (NP).

The dispersion of **linear** polymer-grafted nanoparticles (gNPs) within a neat polymer matrix – forming a grafted nanoparticle composite (gNPC) – offers enhanced mechanical properties over conventional nanocomposites, owing to their superior nanoparticle dispersion and stronger interfacial interactions via the grafted polymer chains.^[1] **Properties = $f(N, \sigma, R_{NP}, \Phi_{NP})$**

Project Aim: To elucidate how graft-chain topology – specifically **loop architectures** (Fig. 1) – governs the miscibility and mechanical behavior in gNPCs through coarse-grained (CG) molecular dynamics (MD) simulations.

Methodology

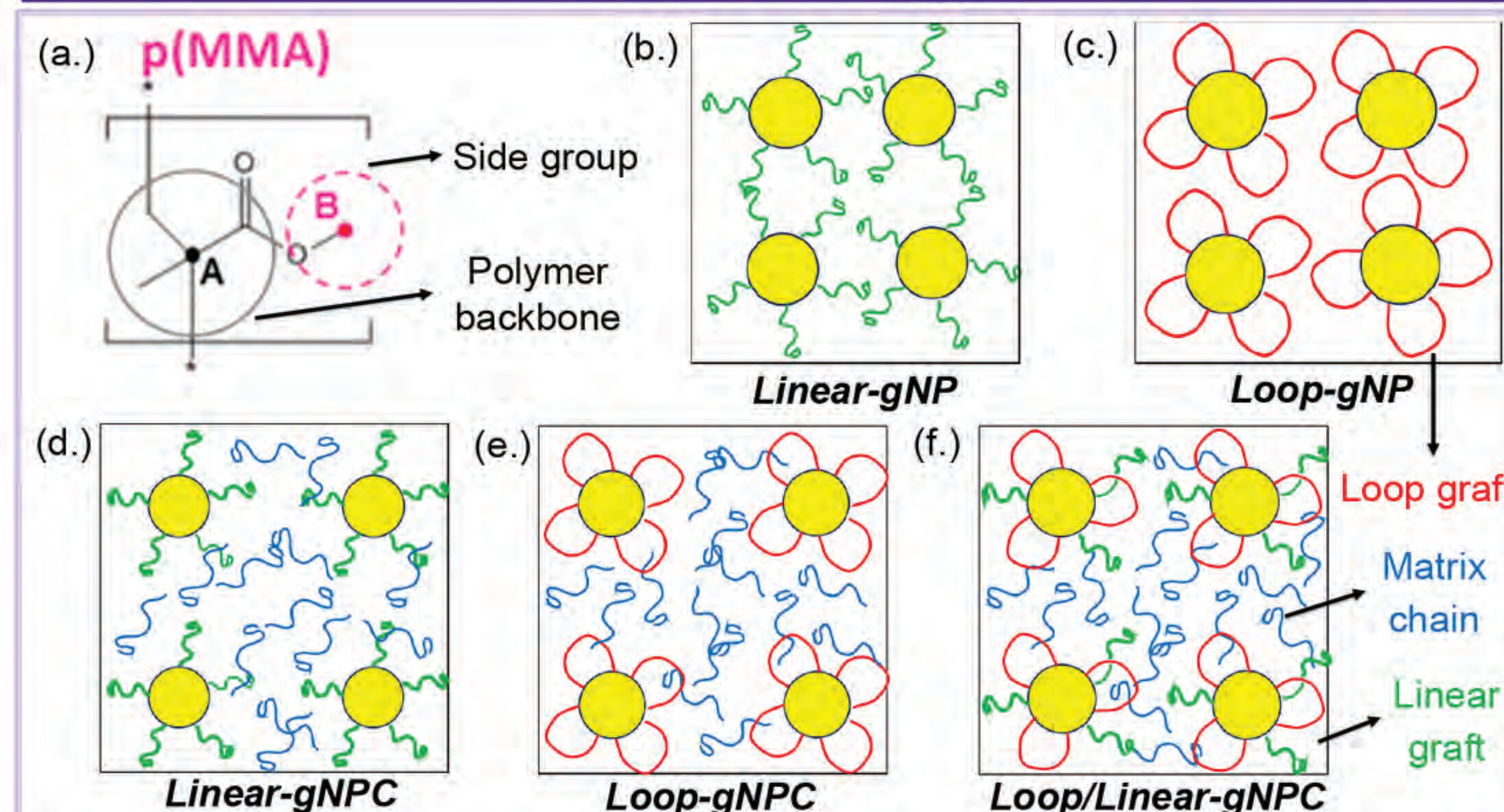


Figure 2. (a) CG mapping of polymethyl methacrylate (p(MMA)) monomer, ^[2] (b-f) schematic representations of the gNP and gNPC system architectures. The CG model is ~200 times faster than all atomistic models. Bonded and non-bonded interactions are defined using harmonic and Lennard-Jones potentials, respectively.

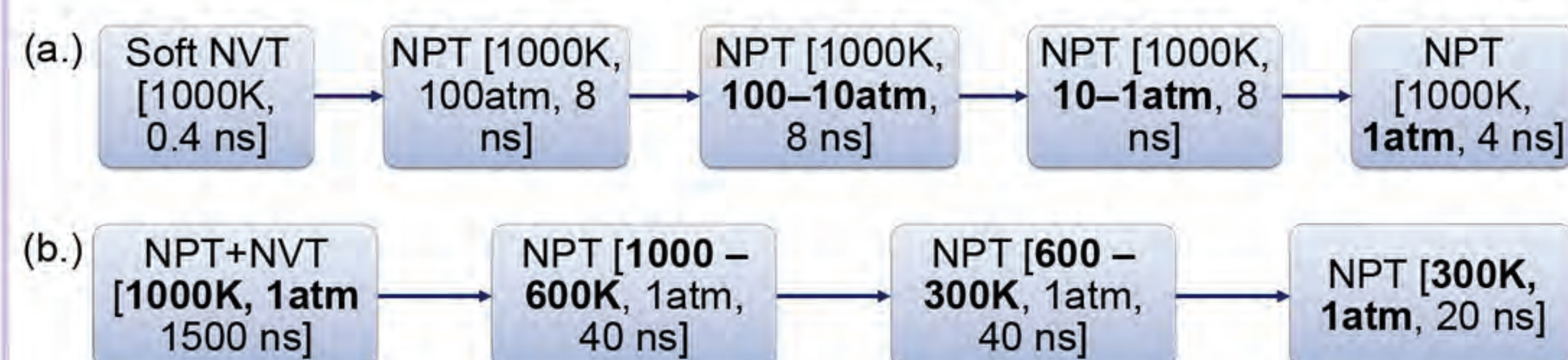


Figure 3. Equilibration Protocol; (a) Generation, (b) Equilibration and Quenching.

Results and Discussion

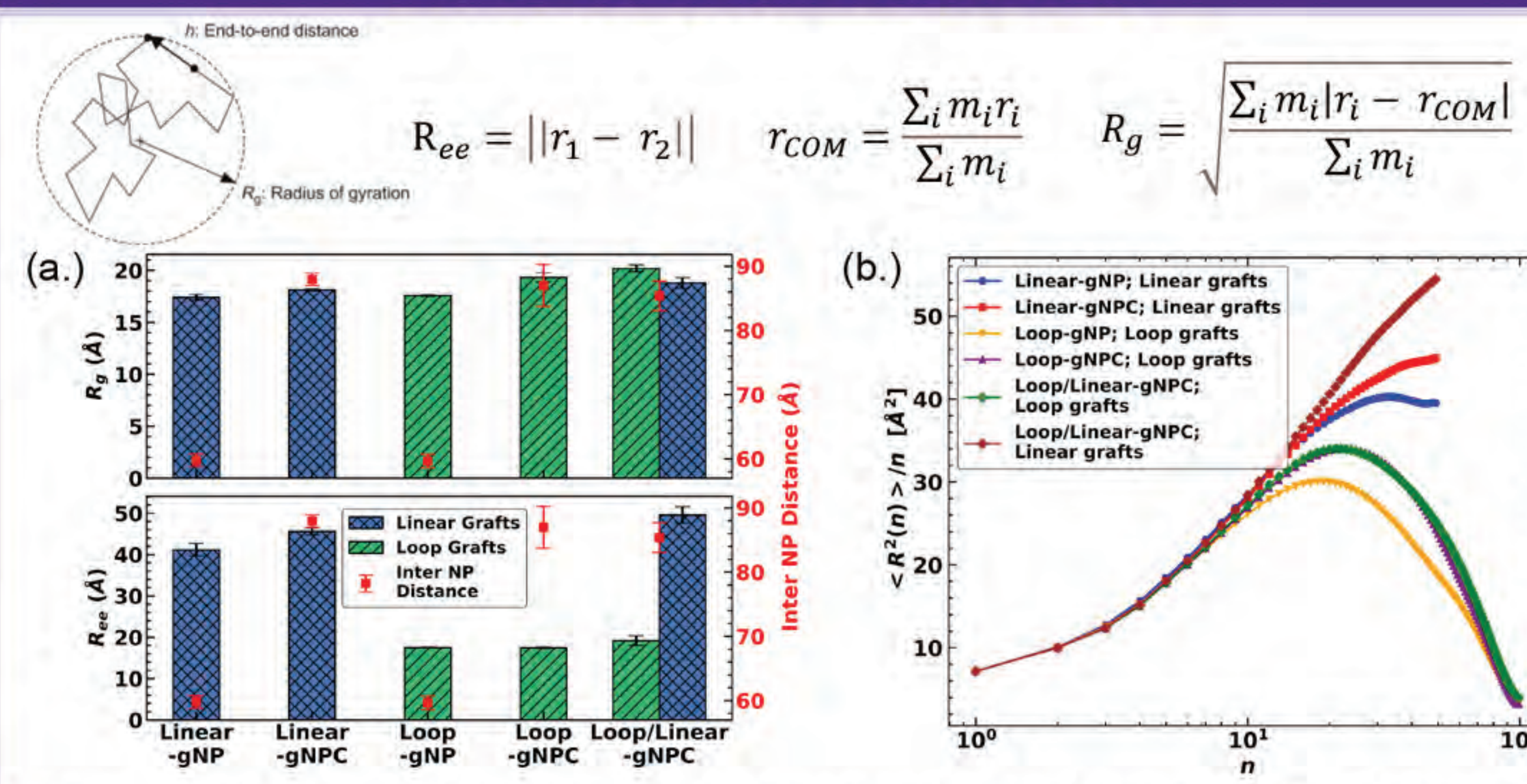


Figure 4. (a) Radius of gyration (R_g , top) and end-to-end distance (R_{ee} , bottom) of linear and loop polymer grafts in simulated gNPs and gNPCs. Red symbols denote the average inter NP distance. (b) Mean-squared internal distance (MSID), $\langle R^2(n) \rangle / n$, as a function of segment size $n = |i - j|$ along the grafted polymer chains, averaged overall monomer pairs with $i < j$ and $j \in [1, N]$.

Enhanced interfacial interactions in **Loop/Linear-gNPC** promote radially extended and swollen graft conformations, thereby facilitating superior NP dispersion compared to single-graft topology systems (Fig. 4).^[3]

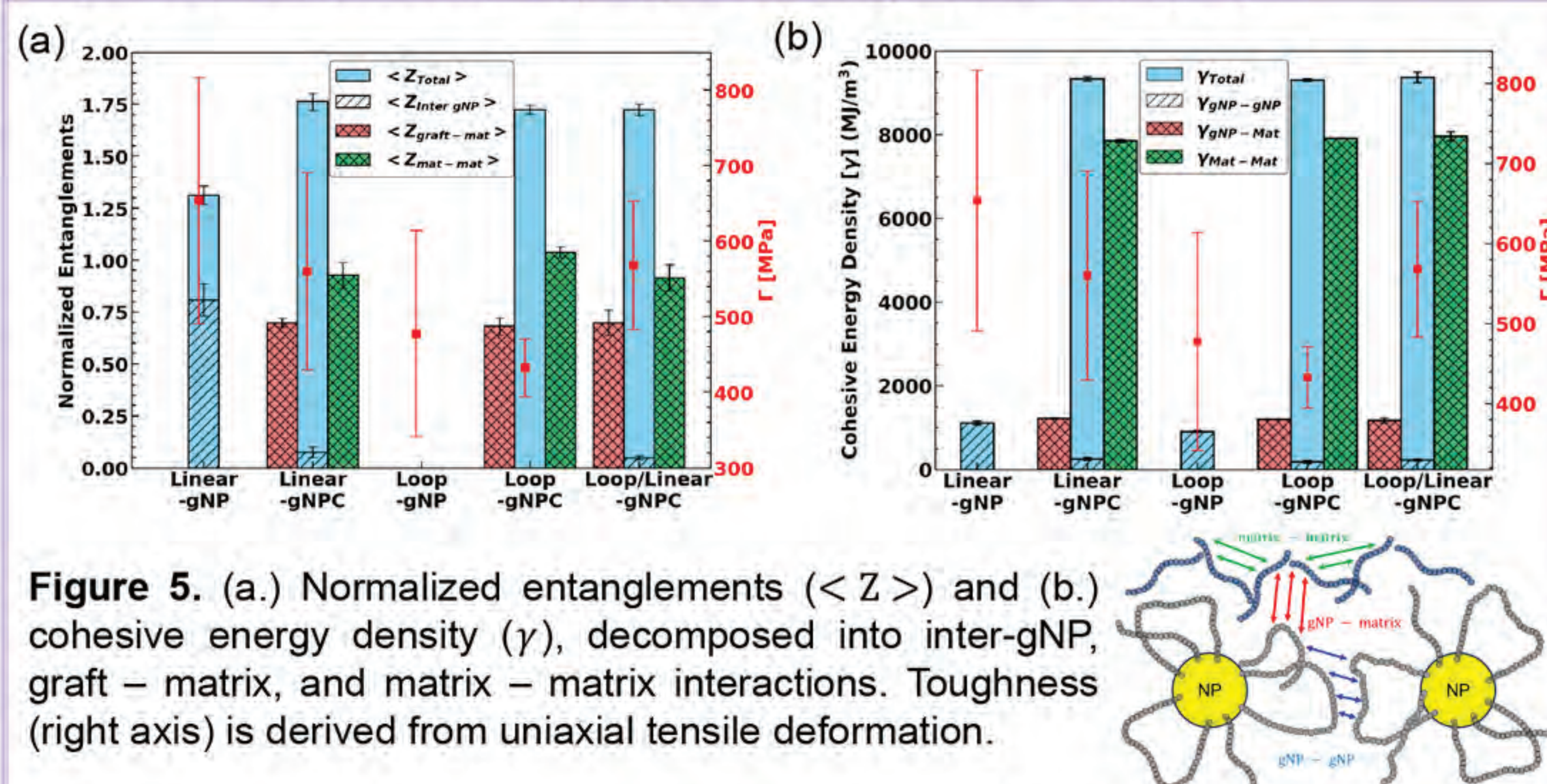


Figure 5. (a) Normalized entanglements ($\langle Z \rangle$) and (b) cohesive energy density (γ), decomposed into inter-gNP, graft – matrix, and matrix – matrix interactions. Toughness (right axis) is derived from uniaxial tensile deformation.

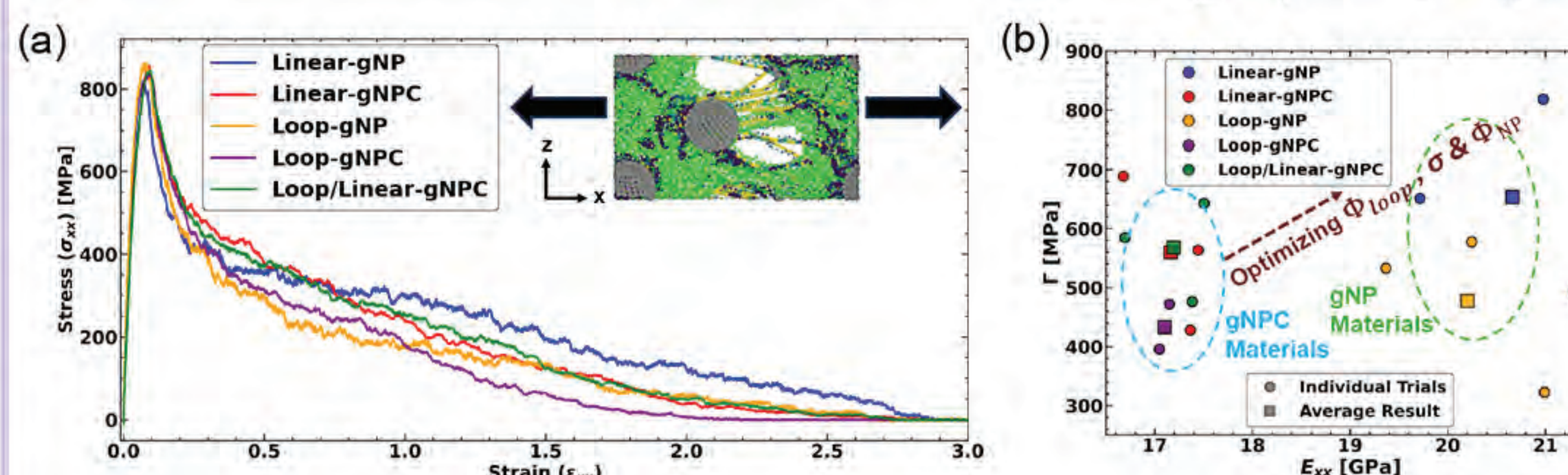


Figure 6. (a.) Stress-strain response of various graft topologies under uniaxial deformation ($\epsilon_{xx} \leq 3$). (b.) Ashby plot of Toughness (Γ) versus Young's modulus (E_{xx}).

Marginal variation in miscibility and mechanical behavior between **Linear-gNPC & Loop/Linear-gNPC** (Fig. 5 and 6); attributed to low particle loading (10 wt.%) across all gNPCs and short grafts.

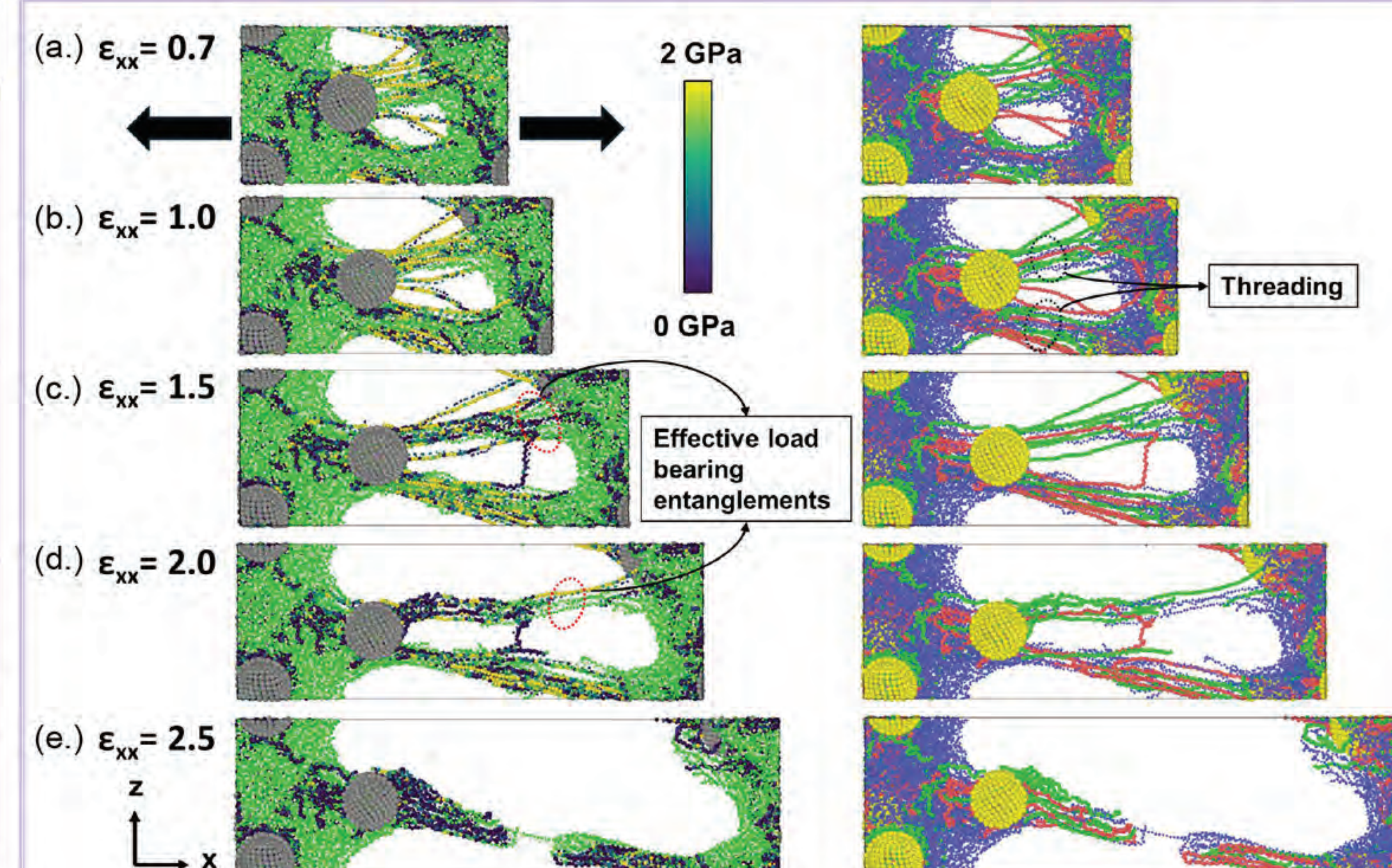


Figure 7. Stress contour maps (left) and chain-resolved representations (right) of the Loop/Linear-gNPC system during tensile deformation at axial strains (ϵ_{xx}) of (a) 0.7, (b) 1.0, (c) 1.5, (d) 2.0, and (e) 2.5.

- Loop/Linear-gNPC achieves toughness of ~ 568 Mpa via load-bearing cross-fibrils formed by topological blending of loop/linear grafts and linear matrix chains (Fig. 7).
- Loop-gNP stretchability stems from high loop fraction ($\Phi_{loop} > \Phi_{loop}^*$), facilitating extensive loop – loop overlap.

Conclusion

- ✓ Loop/linear topological graft blend and matrix interfaces surpass conventional Linear-gNPC in overcoming dispersion and miscibility limitations.
- ✓ Beyond the swelling induced by the free linear matrix, additional swelling of the loop grafts through threading with linear grafts enhances conformationally entropic mixing in the blended Loop/Linear-gNPC.^[3]
- ✓ Established Φ_{loop} as a critical design parameter, alongside σ and Φ_{NP} , for optimizing nanohybrid mechanical performance.

$$\text{Properties} = f(N, \sigma, R_{NP}, \Phi_{NP}, \Phi_{loop})$$

Acknowledgements

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References:

- [1] Schmitt, M. et al. Faraday Discuss. 186, 17–30 (2016).
- [2] Hsu, D. et al. Journal of Chemical Theory and Computation 10, 2514–2527 (2014).
- [3] Grest, G. S. et. al. ACS Polym. Au 3, 209–216 (2023).