CORRELATING THE DEPENDABILITY OF NANOPARTICLE DISPERSION WITH THE PRESENCE OF MATRIX POLYMER IN NANOPARTICLE COMPOSITES

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Introduction

Grafting of polymers on the surface of nanoparticles (NPs) instead of surface coating of nanoparticle with polymers have been shown to lead to better dispersion of nanoparticles is the polymer nanocomposites (PNC). This is due to better steric effect induced by the grafted polymer chains which enhances the dispersion of the nanoparticles in the system. However, although there is a better dispersion of the nanoparticles in the PNCs, which leads enhanced mechanical strength of the PNC material, the presence of the free polymer chains reduces the dispersibility of the NPs due to the entanglements that occurs between the free polymer chains (matrix polymers) and the grafted polymer chains. Thus, some form of aggregation is still experienced by the NPs in the PNCs. We seek to show that by systematically reducing the concentration of the matrix polymers in the system, more dispersion of the nanoparticle can be achieved.

Methodology

Coarse-grained molecular dynamics simulations using LAMMPS parallel MD packages is used in simulating a system which includes solvents, matrix homopolymer chains and nanoparticles grafted with linear polymer chains (PGNPs). Three systems were developed with different but related compositions namely:

- Solvent, matrix polymers and polymer grafted nanoparticles
- Solvent and polymers and polymer grafted nanoparticles
- Solvent and PGNPs with extended polymer grafted nanoparticles

The mean squared displacement (MSD) of the nano-particles in the systems will be calculated to understand the diffusivity of the nano-particles. This will be done to shed light on some dynamic properties of the nano-particles in the system.

Furthermore, the radial distribution function (RDF) will be used to investigate the structural properties of the systems.

System parameters

- Simulations were done in cubic boxes with periodic boundary conditions.
- Coarse grain model was used to model the nano-partcles, grafted polymer and matrix polymer.
- Finite extensible nonlinear elastic potential was used to model all the polymers chains in the system
- Degree of polymerization
  - Matrix polymer = 40
  - Grafted polymer = 10
- All monomers are chemically identical
  - *mass (m) = 1*
  - *intermolecular distance (σ_p) = 1*
- All nano-particles are chemicaly identical
  - *mass (m) = 1*
  - *intermolecular distance (σ_n) = 5*

Polymer grafting

- N_g chains were grafted on the surface of nano-particle such that the grafting density:
  - $\sum_g$ = 0.4 (chains/ σ_p)
- Soft potential was used to ensure good distribution of the grafted chains on the nanoparticles to avoid depletion effects.
- Parking fractions were calculated using:
  - $\eta_T = \frac{\pi}{6}(\sigma_p^3\rho_p + \sigma_n^3\rho_n + \sigma_g^3\rho_g$
- Volume fractions were calculated using:
  - $\phi_T = \sigma_n^3\rho_n / (\sigma_p^3\rho_p + \sigma_n^3\rho_n + \sigma_g^3\rho_g$

S/N	System type	Φnano (with solvent)	Φnano (No solvent)	Φ - sol	NPs	Matrix Poly	Grft-len
1	Sol+mat+pgnp (RED)	0.05	0.1	0.5	40	815	10
2	Sol+pgnp (BLUE)	0.05	0.3	0.83	40	0	10
3	Sol+extpgnp (BLACK)	0.05	0.1	0.5	40	0	36

Table 1: Some parameters of the systems simulated

Results:
Presented below are the results of calculations of RDF and MSD from the three systems that were simulated.

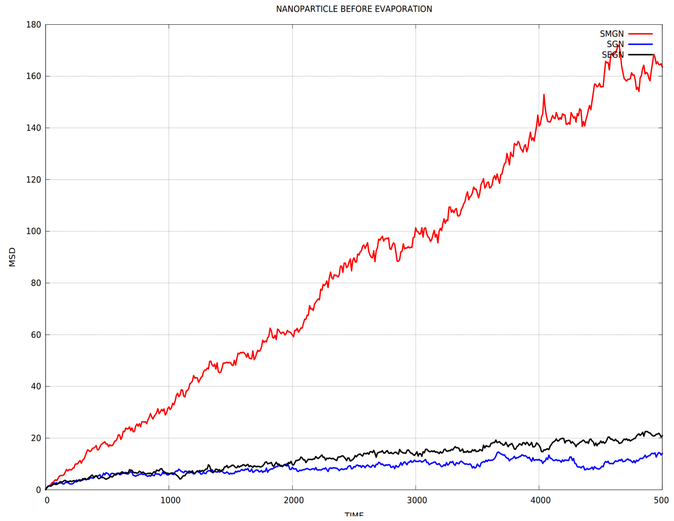

Fig 1: MSD of nanoparticles before evaporation.
The figure shows that we have the highest displacement in system with matrix polymers. This can be attributed to improved steric effect on the nanoparticles.

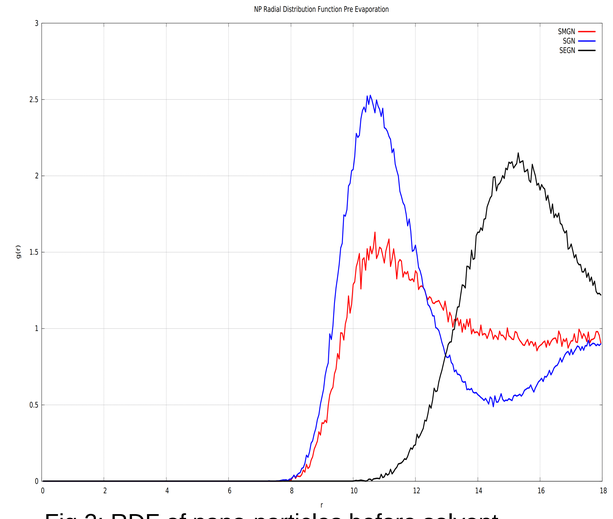

Fig 2: RDF of nano-particles before solvent evaporation.
Wide peak in system 1 agrees with results from Fig1 i.e we have good dispersion in system 1.

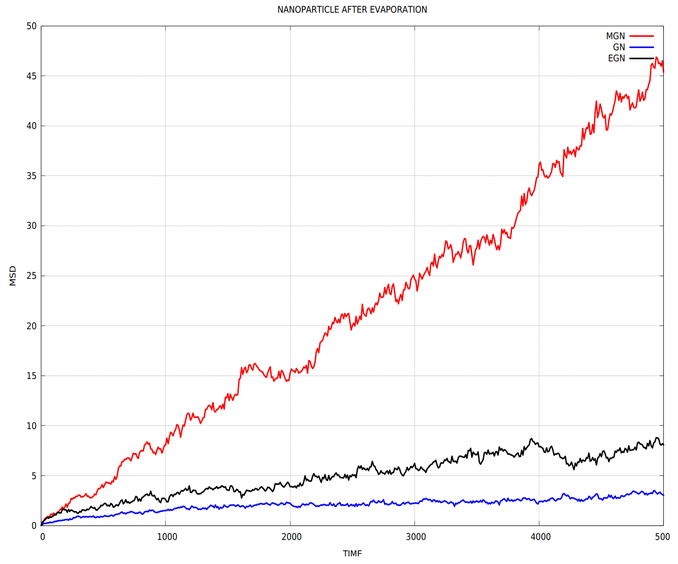

Fig 3: MSD of nanoparticles after evaporation.
Improved dispersion of nanoparticles seen in system 3 can be attributed to the more effective steric effect due to longer polymer chain.

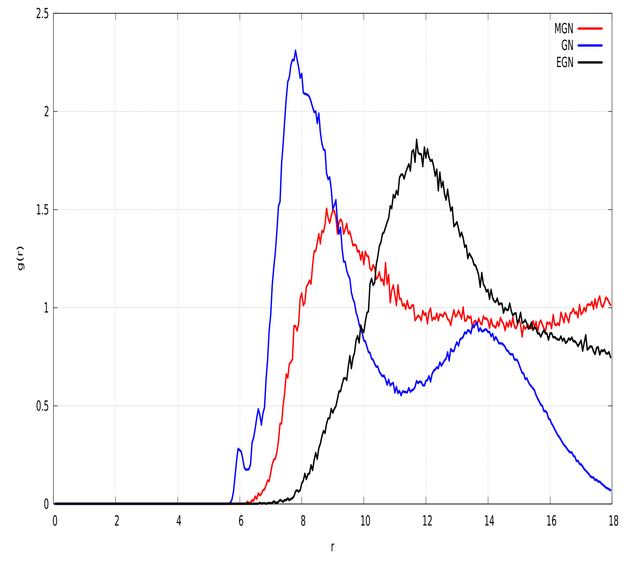

Fig 4: RDF of nanoparticles after solvent evaporation.
Reduction in first peak in systems 2 and 2 suggest there is better dispersion in the absence of solvents.

Conclusion

The results from this set of simulations show that perhaps better dispersion is enhanced by the presence of matrix polymers in the system. This is not a definite conclusion at this time as more work will be done to confirm these results.

References:

1. Palli, Babji, and Venkat Padmanabhan. "Chain flexibility for tuning effective interactions in blends of polymers and polymer-grafted nanoparticles." Soft matter 10.35 (2014): 6777-6782.
2. Ibrahim, Mohd, et al. "Correlation between grafted nanoparticle–matrix polymer interface wettability and slip in polymer nanocomposites." Soft Matter 14.29 (2018): 6076-6082.

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