New Insights into Hierarchical Structures in Polymer Nanocomposites : A Dissipative Particle Dynamics (DPD) Simulation Study

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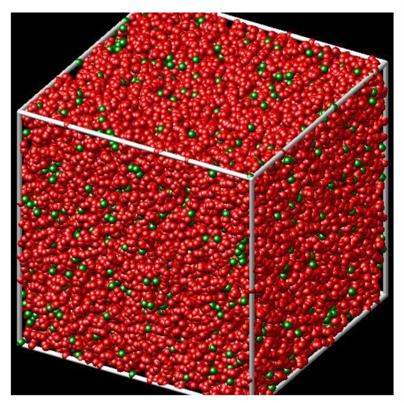
I. INTRODUCTION

Polymer nanocomposites ?

- A polymer matrix which contains nanoparticles of various sizes, and types.

Key

- Distribute fillers uniformly in the polymer matrix - dispersion vs aggregation
- Hierarchical structure, filler morphology



Experimental Techniques (USAXS)

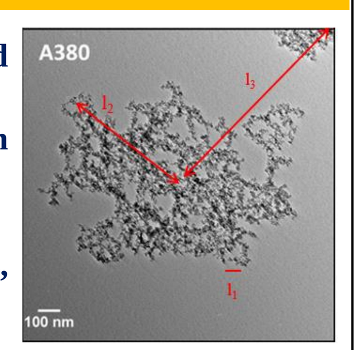
- Fractal dimensions (d_f)
- Mesh size
- Percolation
- Second virial Coefficient (A_2)

Modeling Approach

- Dissipative Particle Dynamics (DPD) simulation

II. GOALS / OBJECTIVE

- Develop a pseudo-thermodynamic model for coarse grained interactions.
- Study equilibrium carbon black & silica filler structures in rubber over multiple length scales.
- Extend model and results for wide and robust applicability.
- Explore chemical identity, volume fractions, aspect ratios, and polydispersity.



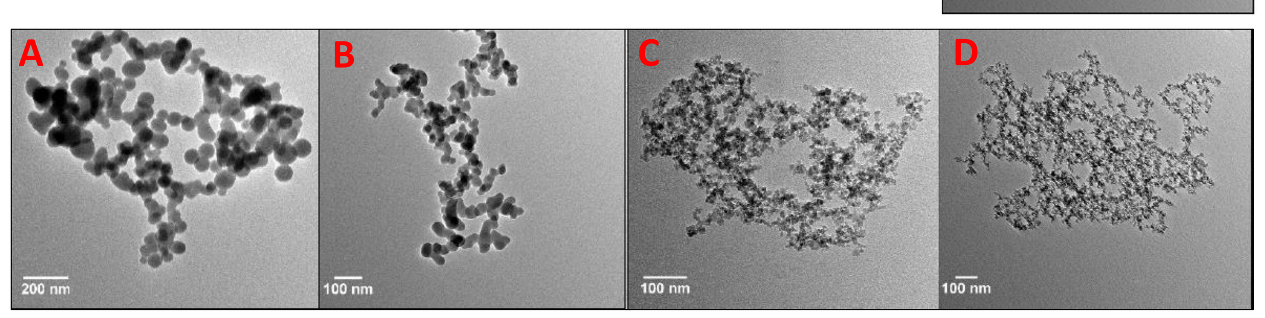


Figure 1: Transmission electron micrographs of (a) Ox50, (b) A90, (c) A300 & (d) A380 samples showing branched fractal aggregate structure. Across this sample series of increasing specific surface area, primary particle size (dp) decreased monotonically while significantly increased degree of aggregation (z) was observed.

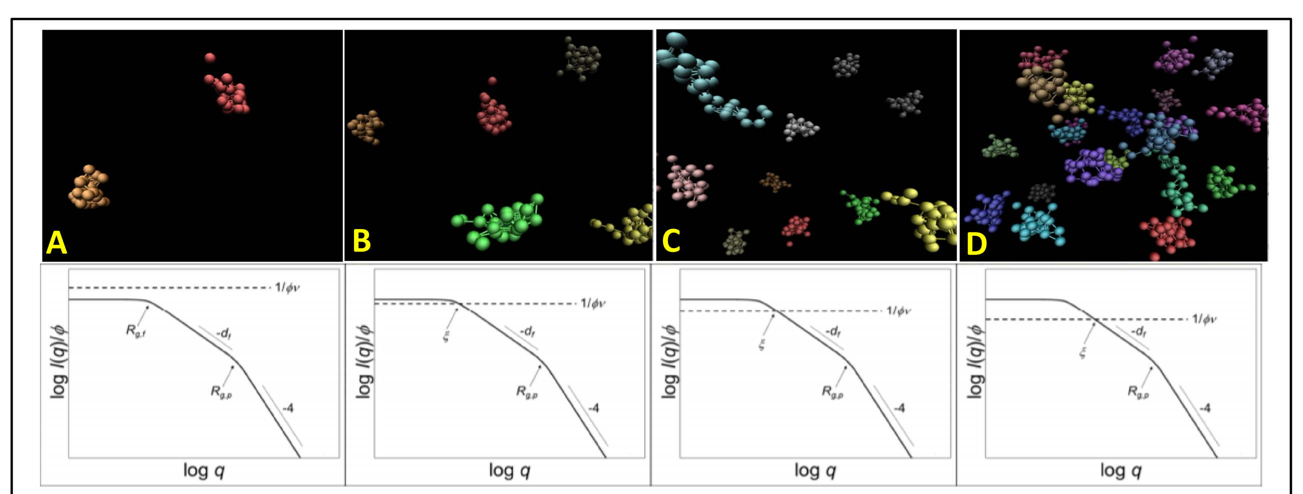
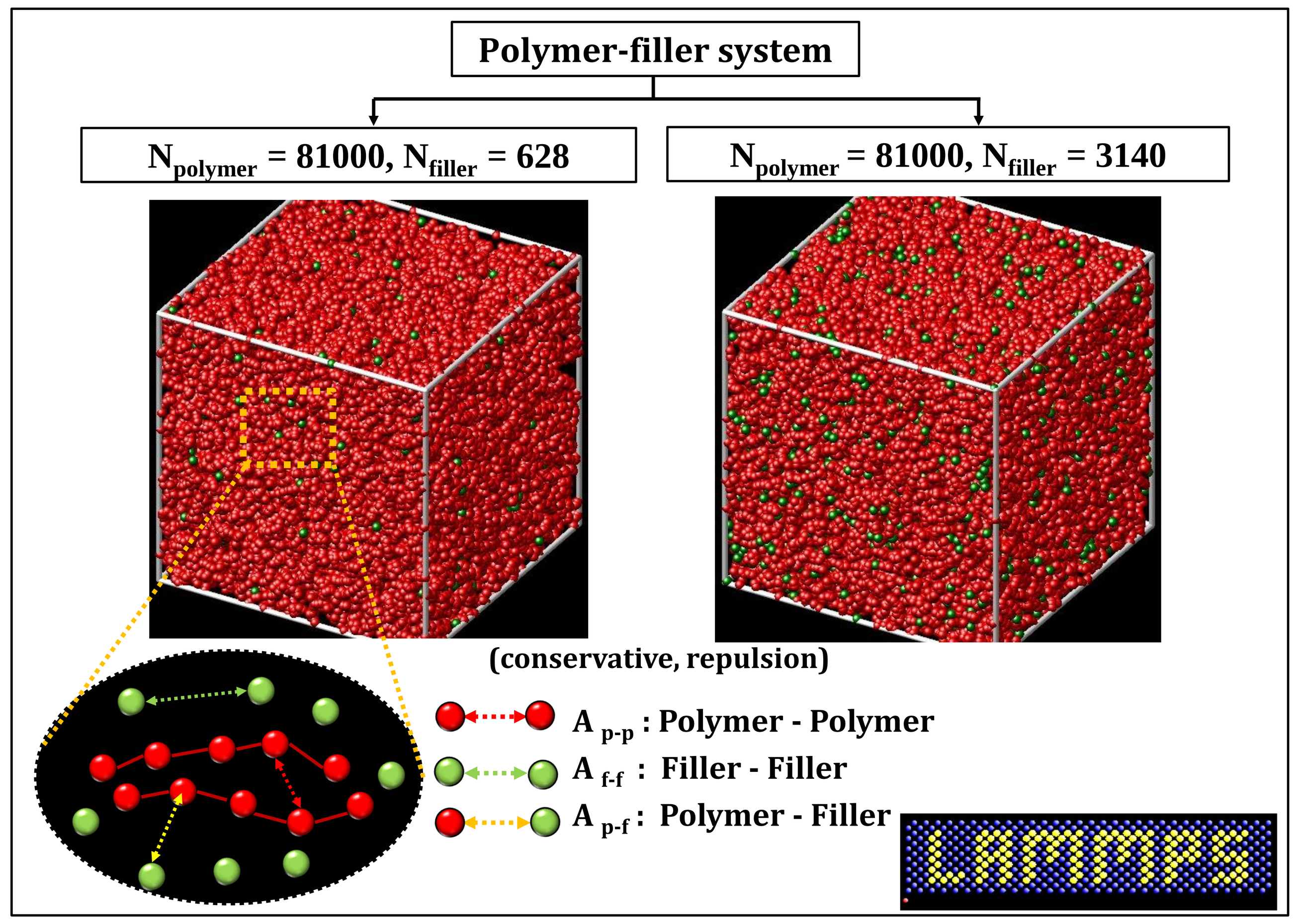


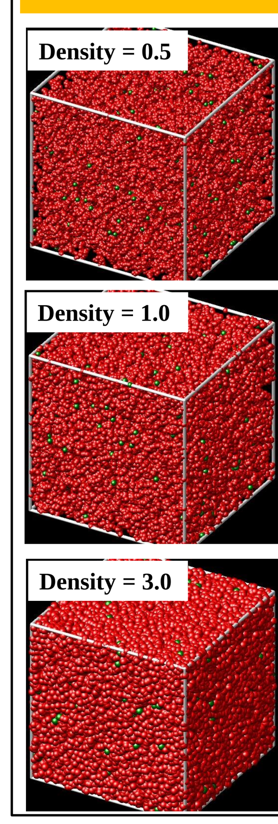
Figure 2: This idealized SAXS scattering diagram shows the relationship of the intensity of scattered X-rays per weight fraction filler, log I/Φ, with respect to the scattering vector, log q. As the filler becomes more agglomerated from A to D, the scattering intensity plateaus at larger scattering vectors. Multiple variables describing the superstructure of the filler can be calculated from theory, such as the fractal dimension of different length scale regimes of the filler structure, to the inverse of ν which can be shown to be indirectly proportional to the effective repulsion of colloidal particles relative to the background melt. This represents valuable information for both estimating relative repulsion forces for DPD species and for determining whether simulation results match the measured superstructure for a given volume fraction and composition.

III. SIMULATION BOX



IV. RESULTS & DISCUSSION

Filler cluster population (Degree of Aggregation)



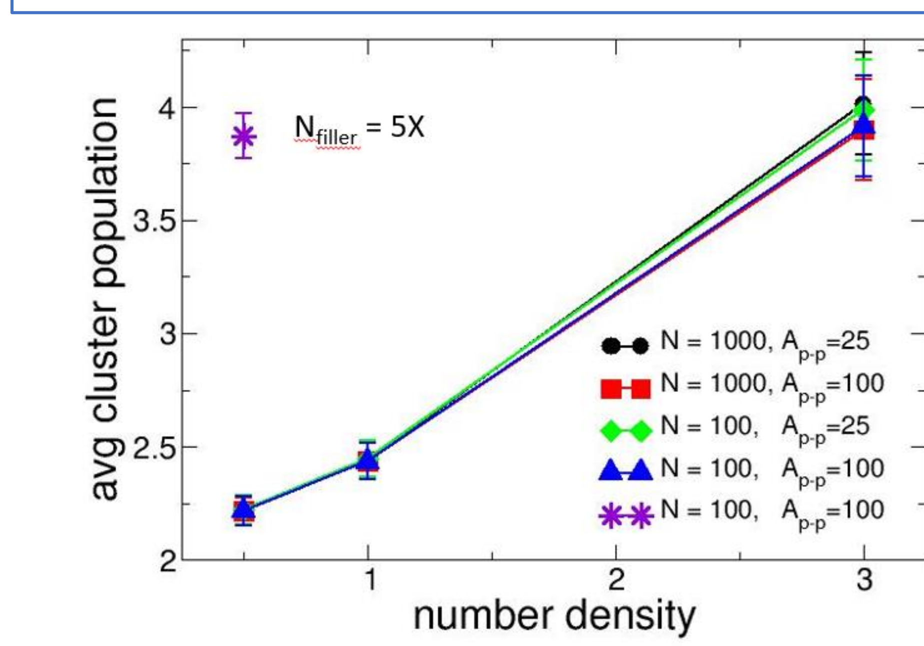
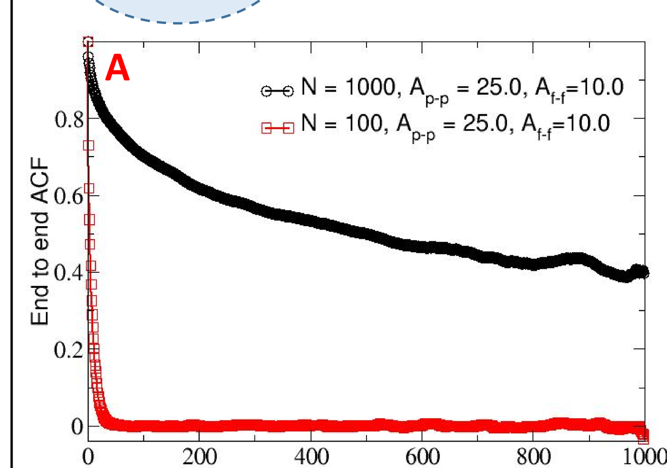
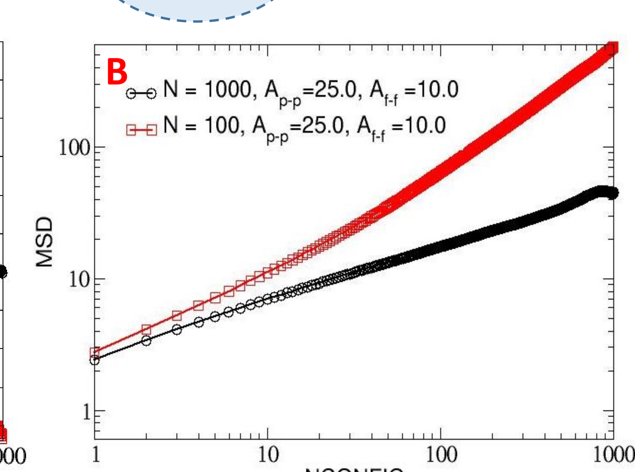


Figure 3: Plot showing Filler cluster population vs. the number density

Dynamic properties of system with different polymer chain length



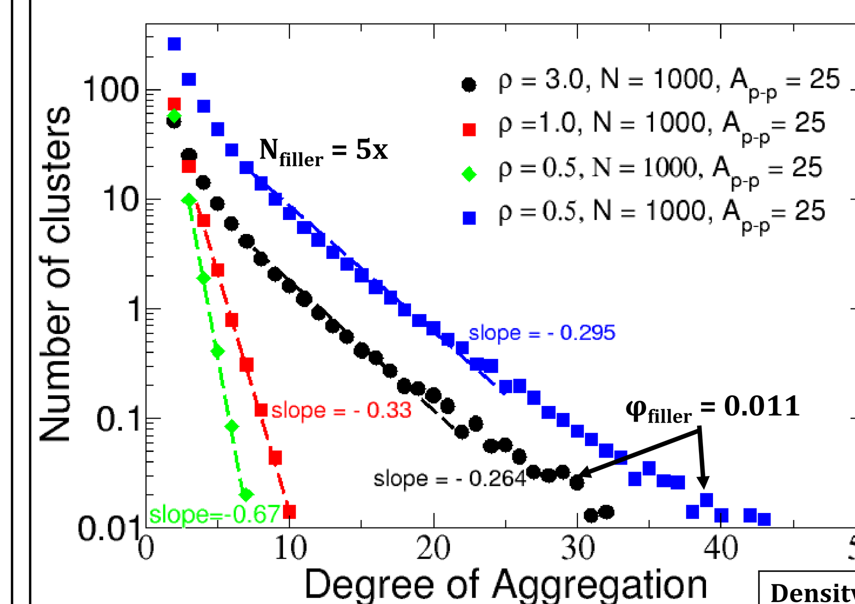


End to end autocorrelation of polymer beads | Mean square displacement of polymers beads

Figure 4: Plot showing the chain dynamics of N=1000 vs. N=100 beads polymer chains using a) End to end autocorrelation function b) Mean square Displacement.

IV. RESULTS & DISCUSSION

Population distributions



z_2 : Average size of cluster

N_1 : Total number of particles

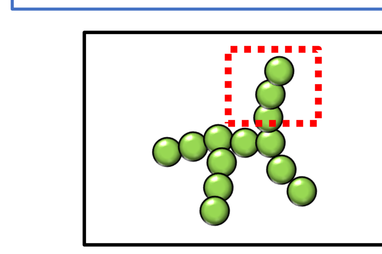
N_2 : Distribution of aggregates

n_1 : Degree of Aggregation

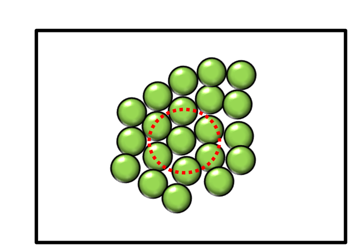
$$(N_2(n_1)) = (N_1^T/z_2^2)exp\,(-n_1/z_2)$$

Density(ρ)	φ_{filler}	Slope	z_2
3.0	0.011	-0.264	3.78
1.0	0.004	-0.33	3.03
0.5	0.002	-0.67	1.50
0.5	0.011	-0.295	3.38

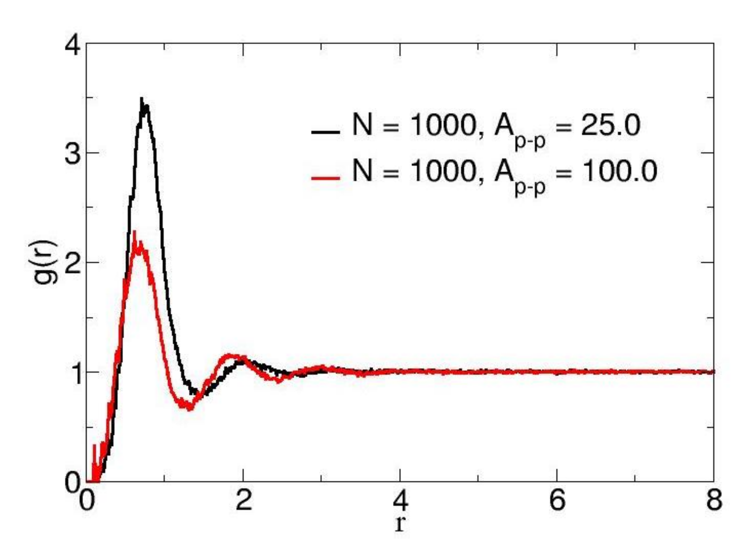
Radial Distribution function (RDF)



- Coordination number : 2
- Size of cluster (z) : 13



- Coordination number : 6
- Size of cluster (z) : 20



Filler-filler RDF

Radius of Gyration of the Largest cluster

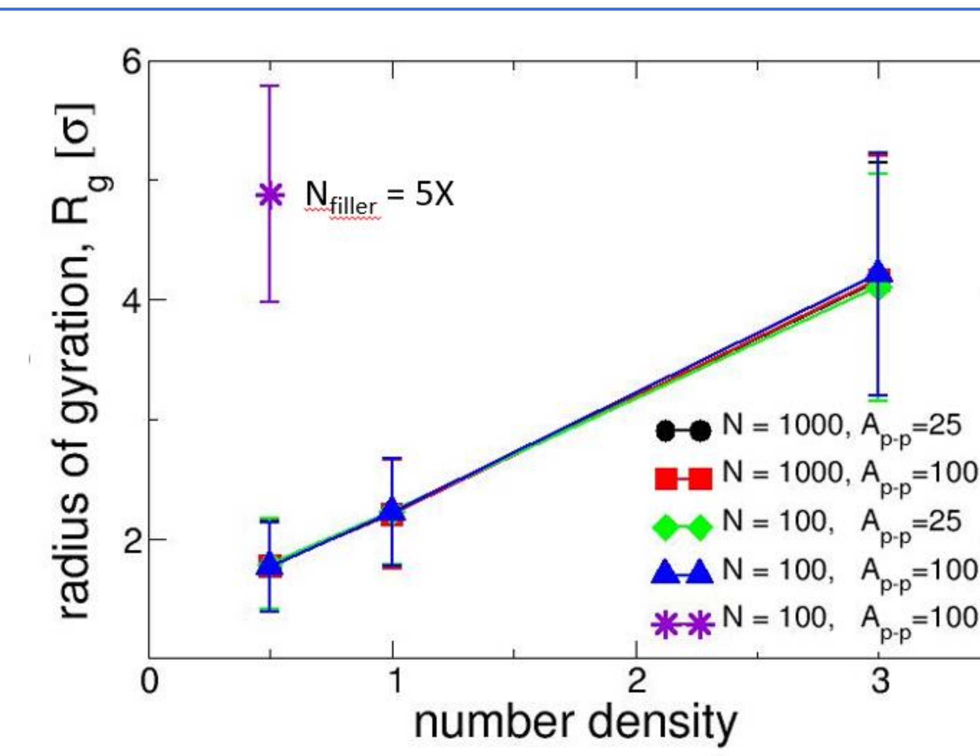


Figure 5: Plot showing the Radius of Gyration of clusters over different number densities.

V. CONCLUSION

DPD simulations to look at polymer-filler blends, focusing on filler structure

Role of density

- Unsurprisingly, higher density promotes cluster formation: mapping back to real systems is still a challenge

Filler volume fraction

- Cluster (used as an analog for aggregate) formation strongly depends on φ_f
- Weakly interacting fillers follow established thermodynamic models

The road ahead

- Use fractal aggregates with bonded primary particles
- Elucidate local (nanoscale) and global (mesoscale) percolation, length-scales

(Related Talk by Gogia and Kuppa et al. (Session L33.00012, 10:12 AM, March 04, Room : 505)

VI. REFERENCES

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