

Supporting information

Effect of elongational flow on immiscible polymer blend/nanoparticle composites: a molecular dynamics study

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1. Effect of system size

In the main text, all simulations were conducted with a simulation box length of 16.76. Simulations with larger box lengths revealed that the number of lamellae and the morphology transitions points change somewhat but also that the NP placement observed using the smaller box size continues to hold.

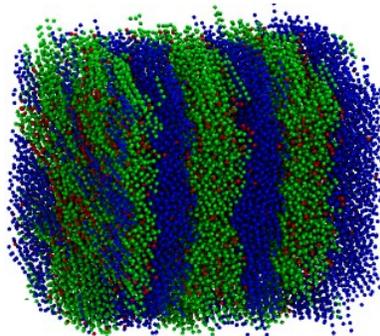


Figure S1: Visualization for elongation rate = 0.1, box length = 36, S-NP in blend.

| Box length | El. Rate | Number of lamellae pairs | Phase width |
|------------|----------|--------------------------|-------------|
| 17 | .03 | 1 | 8.4 |
| 17 | .1 | 2 | 4.19 |
| 26 | .03 | 2 | 6.5 |
| 26 | .1 | 2 | 6.5 |
| 36 | .03 | 2 | 9 |
| 36 | .1 | 3 | 6 |

Table S1: Number of lamellae phase pairs observed for different conditions and the width of lamellae observed. The highlighted row corresponds to the simulation shown in Figure 1.

Table S1 shows that the phase width in the neutral flow direction and the number of lamellae vary with the box length. This is apparent in Figure 1, which shows 3 phase pairs, in contrast to the images shown in the main text. With the box length of 16.76, it was not possible to observe 3 phase pairs due to the limited repeating box size. Despite the fully periodic nature of the simulation, the box length thus acts as an artificial constraint due to the requirement that the box length be an integer multiple of the phase. Therefore, with larger box lengths, this issue is reduced and the system approaches its unconstrained

state. To fully eliminate this effect very large box sizes would be needed. Due to the comparative nature of the study, it is not expected that eliminating the box size effect would change the conclusions regarding the NP distribution and NP effect on morphology transitions.

2. Effect of chain length

Polymers with chain lengths of 20 (as opposed to 10 used in the main text) were simulated without changing the simulation box size but ordered self-assembly was not achieved. This is due to the much larger box size and time scale that would be needed for self-assembly to occur. These larger systems were not investigated due to increasing computational requirements. At the smaller box sizes there was not enough space to accommodate the larger chains and phase widths.

Polymer chain lengths of 5 were also simulated for the blend system. By reducing from a length of 10 to 5, the perpendicular separation to perpendicular lamellae morphology transition was pushed to a higher elongation rate. This is due to the improved diffusion of the shorter chains, which requires a higher elongation rate to prevent the coalescence of lamellae into the perpendicular separation morphology.

3. Effect of temperature annealing on the polymer blend

After elongational flow ended, simulations were run without flow at high temperatures to investigate the effect of post-processing high temperature annealing. It was found that with sufficient temperature ($T = 3$ MD units) the perpendicular lamellae phase could revert back to a perpendicular separation phase. This supports that the perpendicular separation phase is a lower energy state due to its smaller interface area and that the perpendicular lamellae can collapse into perpendicular separation given fast enough diffusion.

4. Validation details

As validation, the trace of the pressure tensor and the total potential energies found from our molecular dynamics code were compared to those published by Matin, Davis, and Todd, *J. Chem. Phys.* 113 9122 for a one-site LJ fluid. The trace of the pressure tensor was calculated according to the method used in the reference.

| Elongation rate | Tr(P) (this work) | Tr(P) (Matin) | Total potential energy (this work) | Total potential energy (Matin) |
|------------------------|--------------------------|----------------------|---|---------------------------------------|
| 0.01 | 7.89 | 7.85 | 622 | 627 |
| 0.02 | 7.88 | 7.86 | 632 | 627 |
| 0.05 | 7.75 | 7.87 | 629 | 627 |
| 0.1 | 7.86 | 7.89 | 630 | 628 |

Table S2: Validation details for the elongational molecular dynamics code.

5. Effect of nanoparticle diameter

For the BCP system, S-NP with diameters of 0.7 and 2.0 were simulated and compared to the diameter 1.0 NP used elsewhere in the paper. The NP volume concentration was kept constant at 10% for the

different diameters. The distributions of the S-NP in BCP were found to be similar for the tested diameters, shown in Figure S2. This is in agreement with the simulations results of Schulz, Hall, and Genzer, *Macromolecules* 38 3007, who studied a similar system under equilibrium (no flow) conditions.

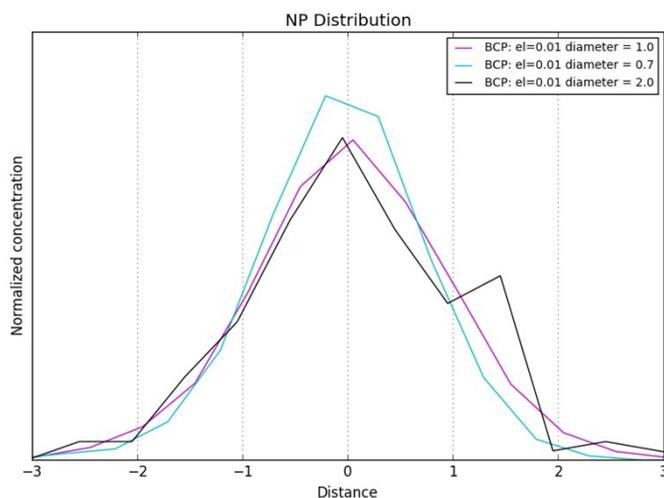


Figure S2: S-NP concentration in BCP for varying S-NP diameter. The elongation rate was kept constant at 0.01 and the S-NP volume concentration was fixed at 10%.

For the blend system, shown in Figure S3, the change in diameter of S-NP had a pronounced effect on their placement and the system morphology. The 2.0 diameter S-NP placed at the interface instead of throughout the selective phase, likely due to entropic benefits of placing in the uncrowded interface area. The 0.7 diameter had a slightly more narrowed concentration, which was also observed for the blend case. We plan on further researching the effect of NP diameter in the future to explain these results.

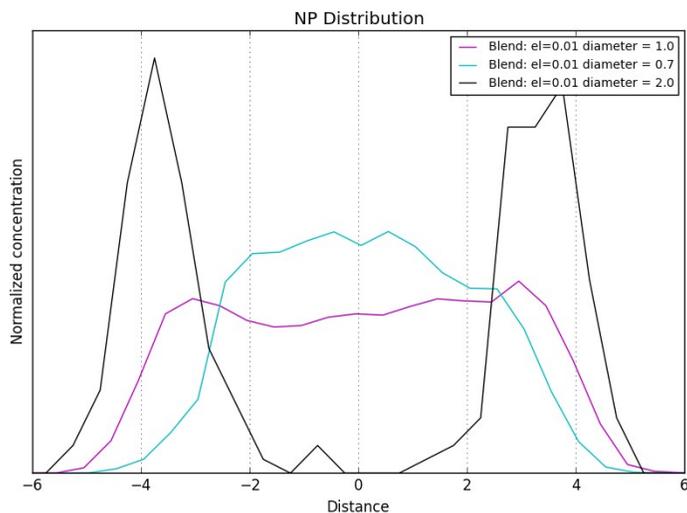


Figure S3: S-NP concentration in blend for varying S-NP diameter. The elongation rate was kept constant at 0.01 and the S-NP volume concentration was fixed at 10%.