## **Supporting Information**

## Mapping the intriguing transient morphologies and the demixing behavior in PS/PVME blends in presence of rod-like nanoparticles

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The interfacial energy of PS is 36 mN/m and that of PVME is 29 mN/m. But PVME is more polar than PS because of the high dispersive solubility parameter of PVME ( $\delta_d = 7.1$  MPa compared to that of PS ( $\delta_d = 1.1$  MPa1/2). So the MWNTs have a preferential affinity to the PVME phase. But it has to be noted that the solubility parameter of PVME ( $\delta = 22.6 \text{ MPa}^{1/2}$ ) is comparable to that of PS ( $\delta = 19.2 \text{ MPa}^{1/2}$ ). It is due to this reason that apart from a major fraction of MWNTs localized in the PVME phase, some of the MWNTs are localized at the interface.

Figure 1 a-b shows the 2D phase and 3D height images of phase separated blends of 50/50 PS/PVME with MWNTs. Due to low interfacial tension and preferential affinity, PVME wets both the air- polymer interface and silicon polymer interface significantly and leads to surface enrichment. This preferential adsorption causes a slight difference in the compositional fluctuation in the surface compared to that of the bulk. The XPS scans from the top 10 nm from the surface reveal PVME enrichment in the phase separated film. <sup>123</sup>. (See Figure S1c)



0.0

5.0 µm





Figure S1: (a) 2D height image and(b) 3D height images of phase separated blends 50/50 PS/PVME with 0.5 wt % MWNTs. Darker phase is PVME and brighter phase is PS and the bright dots/spikes in the darker phase indicate the localization of MWNTs in PVME (c) XPS of PS/PVME 50/50 showing the surface enrichment

For obtaining a better clarity on the thermal aggregation of these particles during demixing, electro rheology measurements were done. The conductivity of some of the selected samples were monitored for one hour at a temperature, which is at an intermediate quench depth (115 °C). (See figure S2) There was only a negligible increase in the conductivity at time from 400s to 3600s (2\*10<sup>-6</sup> Scm<sup>-1</sup> to 6\*10<sup>-6</sup> Scm<sup>-1</sup> in the case of 70/30 with 0.5 wt% MWNTs. This proves the lesser thermal aggregation of MWNTs in the case of these blends during phase separation.



Figure S2: Variation of conductivity with respect to time (by electrorheology measurements) for 70/30 PS/PVME blend with 0.5 wt% MWNTs

In order to obtain a clear picture on the effect of molecular weight on the mechanism of phase separation, the morphology evolution was studied for 10/90 composition with PS with higher molecular weight (Mw = 1.92, 000 g/mol). It was found that unlike the 10/90 composition with higher molecular weight of PS was characterized by a VPS mechanism. See figure S3.



Figure S3: POM images of 10/90 PS/PVME blends (high molecular weight PS) at (a) 120 °C (b) 135 °C (scale bar corresponds to 100 μm

The 50/50 PS/PVME has been characterized by spinodal decomposition. As seen in Figure S4 ac, the initial interconnected network structure formed in the initial (125 °C) and the intermediate stages (137 °C) disintegrated at high temperatures. In the case of 50/50 PS/PVME blends with 0.25 wt% MWNTs, significant refinement in morphology and retention of the higher viscoelastic phase (PVME) can be observed even at late stages of phase separation (Figures S4 d-f). However, selective localization of MWNTs in the PVME phase can alter both the viscoelastic properties of PVME and the overall kinetics of domain growth. Interestingly, for blends with MWNTs finer ligaments of interconnected network was obtained even in the late stages of phase separation.



Figure S4: POM images of 50/50 PS/PVME blends at (a) 125 °C (b) 137 °C (c) 160 °C; 50/50 PS/PVME blends with 0.25 wt% MWNT at (d) 125 °C (e) 137 °C (f) 160 °C (scale bar corresponds to 100

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