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Interfacial Compatibilization in Ternary Polymer Nanocomposites: Comparing Theory and Experiments

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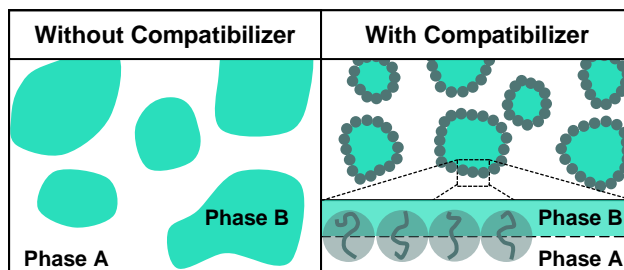
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ABSTRACT

In this work, we examine model binary and ternary nanocomposites of poly(methyl methacrylate) grafted silica nanoparticles (PMMA-NP), in poly(styrene-*ran*-acrylonitrile) (SAN), and poly(methyl methacrylate) matrices as a platform to directly probe the governing parameters guiding phase behavior and nanoparticle assembly in composite materials. Through the addition of PMMA homopolymer to the binary polymer nanocomposite (PNC), it is demonstrated that directed interfacial segregation of PMMA chains stabilizes the composite, leading to increased miscibility in off-critical compositions. A simple interfacial model provides a general guideline for predicting the extent of compatibilization. Further insights on compatibilization behavior are provided by polymer particle pair correlation functions and structure factors obtained using PRISM theory calculations as well as polymer concentration profiles from MD simulations. This study serves as a guideline to facilitate PNC miscibility at elevated temperatures, which is a critical parameter in designing technological applications, such as organic devices.

INTRODUCTION

The ability to control the dispersion state of nano-sized organic or hybrid fillers in polymer nanocomposites (PNCs) has been a continuous challenge in the development of functional hybrid materials for a wide array of applications. Examples include the addition of rigid polymer nanoparticles (NP) to a liquid or polymer electrolyte for enhanced mechanical modulus without sacrificing ionic conductivity,¹⁻³ the incorporation of gold nanorods to a polymer matrix for tuning optical absorption and polarization,⁴⁻⁶ or using polymer-grafted silica nanoparticles to create membranes with controllable separation capabilities.⁷ Since the bulk material properties of the composite are directly correlated with the spatial distribution of the nanoparticles within the polymer matrix,⁸⁻¹² the ability to achieve uniform nanoparticle dispersion through different processing techniques, including self-assembly and external fields, has attracted considerable attention. While there have been significant advances made utilizing these methods, often these are non-equilibrium processes, resulting in composites having metastable morphologies. These kinetically trapped PNCs are therefore unsuitable for applications that operate at high temperatures, which accelerate NP motion and instability, leading to phase separation and degradation. Therefore, finding ways to increase the miscibility windows of these composites at elevated temperatures is enticing for industrial applications that rely on controlled spatial distributions of NPs within the polymer phase.

Previously, it has been shown by Schmitt *et al.* that a binary PNC system of silica particles grafted with polystyrene (PS) and PMMA ligands with an upper critical solution temperature (UCST) can impart phase behavior comparable to analogous linear polymer blends.¹³ However, while the trends in phase behavior between the two systems were similar, the PNC demonstrated increased miscibility and reduced kinetics of domain growth. The apparent increase in miscibility was rationalized as a consequence of a reduced thermodynamic driving force for phase separation by decreasing the number of unfavorable segmental interactions between each ligand. Additionally, the presence of NP cores resulted in a smaller number density of segmental contacts.¹³ Similarly, work by Karim and coworkers compared the phase separation behavior of a system of gold nanoparticles grafted with PS (AuPS) inside a PMMA matrix to that of a binary homopolymer blend composed of PS and PMMA.¹⁴ Comparison of the surface

topologies of the two systems revealed a lower interfacial tension between AuPS and PMMA than that in the homopolymer blend. This difference was attributed to the sterically hindered interactions of PMMA matrix chains with the chains grafted to the surface of the nanoparticle. Taken together, these studies offer insights into potential routes of facilitating PNC miscibility, specifically, by focusing on the interface between the grafted nanoparticle and matrix.

To probe if the PNC miscibility can be expanded *via* increased interfacial compatibilization, a polymer system has to be judiciously chosen such that the phase behavior of the homopolymer blend is documented and has an accessible critical point for the tracking of changes in miscibility. The binary homopolymer blend of poly(styrene-*ran*-acrylonitrile) (SAN, 33 wt% AN) and PMMA has been shown to have an accessible lower critical solution temperature (LCST) of 160°C that can be tuned through changing the composition of SAN.^{15–19} The addition of nanoparticles to the PMMA/SAN blend has been demonstrated as a way to further manipulate both the phase behavior and phase separation temperature of the system.^{20–25} While the aforementioned studies focused on UCST PNCs with unfavorable segmental interactions below a critical temperature, the favorable interactions below a critical temperature of the PMMA/SAN blend with LCST phase behavior allows for direct validation of the proposed interfacial tension and limited segmental interaction theories. Previously, favorable interactions between SAN graft polymers and PMMA matrix polymers in PNCs containing SAN grafted silica nanoparticles have been shown to promote uniform dispersion where chosen design parameters like large particle size, small molecular weight of graft chains and high molecular weight of matrix chains favored phase separation.²⁶ However, PNCs with graft-matrix interactions that follow LCST phase behavior, exhibiting favorable interactions at low temperatures that become progressively weaker and eventually repulsive as temperature increases, show a sharp dispersion to aggregation transition on increasing temperature as seen for polystyrene (PS) grafted silica particles in poly (vinyl methyl ether) (PVME) matrix in past experiments and simulations.²⁷ Accordingly, at high temperatures through the addition of a third component, namely, PMMA homopolymer to a binary PMMA-NP/SAN composite, the number of favorable segmental contacts between each chemical species can be restored to reduce the thermodynamic driving force for phase separation.

In the present work, we examine binary and ternary nanocomposites of poly(methyl methacrylate) grafted silica nanoparticles (PMMA-NP) mixed with SAN (binary), and PMMA-NPs, SAN, and PMMA homopolymer (ternary), as model systems to directly probe the governing parameters guiding phase behavior and nanoparticle assembly. As-cast PNC films are characterized as a function of nanoparticle loading, revealing well dispersed NP systems. Phase behavior of the binary and ternary PNC was investigated between 155 and 195°C and characterized using a combination of cloud point observations, transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS). For both binary and ternary PNCs, cross-sectional TEM micrographs reveal a transition from discrete to string-like to bicontinuous NP domains with increasing NP loadings when annealed in the two phase regime. The scattering profiles obtained through SAXS reveal the emergence of two distinct length scales underpinning the binary and ternary PNC phase behavior — specifically, a smaller length-scale feature representing the average center-to-center interparticle distance as well as a larger length-scale feature representing the scattering between nanoparticle clusters. Modeling of these two scattering features allows for the accurate capture of the phase transition within the binary and ternary PNCs. By compiling the cloud point, TEM, and SAXS results, we demonstrate that the addition of 5 wt% PMMA homopolymer to the binary PNC stabilizes the composite material through directed segregation of PMMA to the PMMA-NP/SAN interface, leading to increased miscibility in off-critical compositions. To explain this compositional dependence, a simple interfacial scaling model is derived, providing a general guideline for predicting the extent of compatibilization. Polymer Reference Interaction Site Model (PRISM) theory calculations and molecular dynamics (MD) simulations based on a coarse-grained (CG) model are performed to elucidate the effect of the amount of added PMMA matrix (quantified in terms of volume fraction) on PNC structure. Experimental plots of the composite structure factors, which show a dispersion to aggregation transition in PNCs on increasing temperature, are compared to particle-particle structure factors obtained using PRISM theory to verify the ability of the CG model to capture experimental phase behavior. Thereafter, MD simulations based on the CG model are used to calculate concentration profiles for graft and matrix polymers in the vicinity of the particle at various PMMA matrix volume fractions. Results from MD simulations show that when PMMA graft and SAN matrix interactions are unfavorable (at high temperatures), PMMA matrix concentration increases near the particle surface, suggestive of compatibilization. Further,

particle-particle pair correlation functions and particle structure factor plots from PRISM theory show that increased volume fraction of PMMA matrix chains leads to a reduced tendency for aggregation in PNCs at high temperatures.

EXPERIMENTAL SECTION

Materials. Poly(styrene-*ran*-acrylonitrile) (SAN, $M_w = 118$ kg/mol, $M_w/M_n = 2.24$, $T_g = 114^\circ\text{C}$, containing 33 wt% acrylonitrile) was provided by Monsanto and purified twice by adding a solution of SAN and chloroform ($\geq 99.9\%$, for HPLC) into methanol ($\geq 99.9\%$, for HPLC) at a 1:10 volume ratio. After allowing SAN to precipitate for 1 h, the solvent was removed, and the precipitant was dried for 48 h. Once dry, the SAN was redissolved in chloroform and precipitated with methanol once more. Poly(methyl methacrylate) (PMMA, $M_w = 21$ kg/mol, $M_w/M_n = 1.14$, $T_g = 110^\circ\text{C}$) was purchased from Polymer Source Inc. and used as received. Silica nanoparticles (15 nm diameter) grafted with PMMA brushes, denoted as PMMA-NPs, were prepared using surface-initiated atom transfer radical polymerization.²⁸ The brush weight-average molecular weight and grafting density were 19 kg/mol and 0.7 chains/nm², respectively, as determined by thermogravimetric analysis (TGA, TA Instruments Q600 SDT) at a heating rate of 10°C/min under argon flow between the temperatures of 25°C and 550°C. The glass transition temperature (T_g) of each polymer was measured using a differential scanning calorimeter (DSC, TA Instruments Q2000) between the temperatures of 25°C and 150°C. In all cases, two heating/cooling cycles were performed at a heating/cooling rate of 5°C/min. The T_g values were obtained from the second heating in order to eliminate any thermal history. Details of the TGA and DSC characterization of PMMA, SAN and PMMA-NPs are shown in the Supporting Information. EpoxiCure 2 epoxy hardener and epoxy resin were purchased from Buehler. N-type, <100> oriented silicon wafers (dopant Ph, 10-20 $\Omega\cdot\text{cm}$ resistivity, 475-575 μm thickness, single side polished) were purchased from Silicon Quest International. P-type, <100> oriented silicon wafers (dopant B, 0.001-0.005 $\Omega\cdot\text{cm}$ resistivity, 500 μm thickness, single side polished) with a 300 nm wet thermal oxide layer were purchased from University Wafer.

METHODS

Cloud Point Observations. Phase diagrams for the binary and ternary PNCs were first mapped qualitatively *via* cloud point observations. This was defined as the temperature at which the film

changed from transparent to opaque when viewed against a black background. Polymer solutions with varying compositions were dissolved in methyl isobutyl ketone (MIBK, $\geq 98.5\%$, Certified ACS, Fisher Chemical) and stirred for 24 h using a magnetic stir bar. The solutions (17 wt% in MIBK) were spin-coated (1000 rpm, 60 seconds) onto 1 cm² glass substrates (washed with methanol and toluene and dried under nitrogen flow) and dried at 105°C for 1 h to remove residual solvent. All films were smooth and homogeneous as-cast. Film thickness, measured with reflectometry (Filmetrics F3-UV), ranged from 2000-2500 nm depending on the composite composition. Samples were subsequently annealed to the desired temperature on a hot stage (Mettler FP-82, Mettler Toledo, INC.) under continuous argon flow and immediately quenched to room temperature after 24 and 72 h.

Small-Angle X-Ray Scattering (SAXS). To prepare samples for small-angle X-ray scattering, PNC solutions (17 wt% in MIBK) were spin-coated (1000 rpm, 60 seconds) onto 1 cm² silicon wafers with a 300 nm thermal oxide layer and then dried at 105°C for 1 h to remove residual solvent. Following drying, the samples were annealed on a hot stage for varying amounts of time under continuous argon flow and then immediately quenched to room temperature. To lift the films, the edges of the substrate were scored and then floated on a 1:5 vol% solution of NaOH (50% w/w NaOH) and DI H₂O. After lifting from its substrate, the films were transferred to pure DI H₂O and then onto 2 x 2 cm² Kapton[®] films. In order to achieve a sufficient signal-to-noise ratio, 4 films were stacked on top of one another, resulting in a film stack thickness of approximately 10 μm . The films were allowed to dry for 6 h at room temperature between each sequential stack. SAXS measurements were performed on a Xenocs Xeuss 2.0 at the University of Pennsylvania, with a sample-to-detector distance of 6.36 m with a Cu-K α source, providing an available q-range of 0.003-0.09 \AA^{-1} . Raw two-dimensional scattering spectra were collected on a Pilatus 1M detector for 20 minutes per sample, and were then azimuthally integrated into one dimensional patterns for analysis using Foxtrot software.

Transmission Electron Microscopy (TEM). To prepare the samples for electron microscopy characterization, the floated films (see SAXS Methods) were lifted from the liquid-air interface of the NaOH solution, transferred onto Teflon[®], and sputter-coated with a gold and palladium layer (a guide for the eye during microscopy). After sputter-coating, the specimens were lifted from the Teflon[®] and embedded in two-part epoxy. Once the epoxy cured, ~ 70 nm cross-sections

of the PNCs were prepared by ultramicrotomy (Leica Ultracut S Ultramicrotome) with a room temperature diamond knife. TEM characterization of the ultramicrotomed cross-sections, transferred onto carbon coated TEM grids, was performed with a JEOL JEM-1400 TEM at 120 kV. Radial autocorrelation functions of TEM images were produced to discern the average center-to-center interparticle distances (ID) of the grafted nanoparticles in as-cast films using Gwyddion software.

COMPUTATIONAL APPROACH

Coarse-grained (CG) model. Graft and matrix polymers (denoted with subscripts G and M, respectively) were modeled as bead-spring²⁹ chains with harmonic bonds in CG simulations. The PMMA graft (G) and PMMA matrix chains (matrix_2, M2) were comprised of N_G and N_{M2} number of CG beads, where each bead of diameter $1d$ was equal to the Kuhn segment length of PMMA (1.53 nm). The first bead of each graft chain is tethered to the nanoparticle of size D_p via a surface grafting site. The number of grafting sites on the nanoparticle was chosen based on the particle size and the desired surface grafting density. The SAN matrix chains (matrix_1, M1) were comprised of N_M number of CG beads, where each bead of diameter $1d$ was equal to the Kuhn segment of SAN, similar to that of PMMA. In all chains the harmonic bonds were modeled using the form

$$U_{\text{bond}}(r) = k_{\text{bond}}(r - r_0)^2 \quad (1)$$

with the force constant $k_{\text{bond}} = 50kT/d^2$ and the equilibrium bond distance $r_0 = 1d$. No angle restrictions were imposed on the graft and matrix CG beads to model flexible graft and matrix chains.

Pairwise non-bonded interactions between all graft and matrix bead pairs (GG, GM1, and M1M1 for binary PNCs and GG, GM1, GM2, M1M1, M1M2, and M2M2 for ternary PNCs) were modeled using the cut and shifted Lennard Jones³⁰ (LJ) interaction potential given by

$$U_{ij}(r) = \begin{cases} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] + \varepsilon_{ij} ; r \leq 2.0\sigma_{ij} \\ 0 ; r > 2.0\sigma_{ij} \end{cases} \quad (2)$$

with $\sigma_{ij} = 1d$ for all pairs. In the case of binary PNCs, $\epsilon_{ii} = 0.1$ kT for all like beads pairs (GG, M1M1) and ϵ_{GM1} is varied from 0.2-0.07 kT, thereby tuning the graft-matrix interaction from being energetically favorable ($\epsilon_{GM1} = 0.2$ kT), to athermal ($\epsilon_{GM1} = 0.1$ kT), and finally unfavorable at $\epsilon_{GM1} = 0.09$ kT and 0.07 kT. Thus, the LCST transition for graft (PMMA) and matrix_1 (SAN) polymer chemistries with increasing temperature is captured by decreasing ϵ_{GM1} in the model. Accordingly, PNCs with $\epsilon_{GM1} = 0.2$ kT correspond to PNCs at low temperatures in experiments (below LCST), while PNCs with $\epsilon_{GM1} = 0.1$ kT and $\epsilon_{GM1} = 0.07$ kT correspond to PNCs at intermediate and high temperatures in experiments, respectively. In the case of ternary PNCs, the GG and M1M1 bead pair-wise interactions were similar to the binary PNCs. With G and M2 beads representing the same chemistry, the ϵ_{ij} for all G bead pairwise interactions were identical to M2 bead pairwise interactions (*i.e.*, $\epsilon_{GG} = \epsilon_{M2M2} = 0.1$ kT, $\epsilon_{GG} = \epsilon_{GM2} = 0.1$ kT, $\epsilon_{GM1} = \epsilon_{M2M}$). Lastly, all pairwise interactions involving the nanoparticle (with pairs $ij = PP, PG, PM1,$ and $PM2$) were modeled as purely repulsive using the Weeks Chandler Andersen (WCA)³¹ potential with $\epsilon_{ij} = 0.5$ kT and σ_{ij} equal to the mean diameter of ij beads pairs.

Parameters Varied. The relative lengths of graft and matrix polymer chains were based on relative molecular weights for PMMA and SAN polymers used in experiments (Table S1). We selected $N_G = 15$ and $N_{M1} = 75$ for both binary and ternary cases. In the case of ternary PNCs, the matrix polymer was composed of two types of polymer matrix chains: $N_{M1} = 75$ and $N_{M2} = 15$. The size of the nanoparticle, $D_p = 5d$, and surface grafting density of graft polymer chains, $\Sigma = 0.76$ chains/ d^2 , were maintained constant for all PNCs. We note that in the computations, the above choices of particle diameter and graft and matrix chain lengths were smaller than those in experiments, but maintained a similar ratio of matrix to graft chain length, particle curvature, and grafted monomer crowding as in the case of experiments (see Table S1). For all cases, the fraction of any volume occupied by particle, graft and matrix (M1 and/or M2) beads is kept at $\eta = 0.36$; this packing fraction approaches the behavior of an incompressible melt-like polymer matrix. PNC composition was defined in terms of two parameters; the grafted NP filler fraction, $\phi_{PGP} = \frac{V_{\text{graft}} + V_{\text{particle}}}{V_{\text{graft}} + V_{\text{particle}} + V_{\text{matrix}_1} + V_{\text{matrix}_2}}$ and the matrix_2 volume fraction $\phi_{M2} = \frac{V_{\text{matrix}_2}}{V_{\text{graft}} + V_{\text{particle}} + V_{\text{matrix}_1} + V_{\text{matrix}_2}}$. For binary and ternary PNCs, the SAN polymer matrix volume fraction is $1 - \phi_{PGP} - \phi_{M2} = \phi_{M1}$.

Molecular Dynamics (MD) simulations. Molecular dynamics (MD) simulations with the CG model for PNCs described above were performed using the LAMMPS³² package. For all simulations, the starting configuration consisted of a nanoparticle of size $D_p = 5d$ grafted with 60 chains, leading to a grafting density of $0.76 \text{ chains}/d^2$. The grafted chains were relaxed from the starting configuration during a short simulation run with all (GG and PG) interactions set as purely repulsive using the WCA potential. The relaxed grafted nanoparticle configuration was placed in a large box ($\eta \sim 0.006$), with $\phi_{\text{PGP}} = 0.01$, along with matrix chains with the desired composition defined by the ϕ_{M2} value. The large simulation box volume allowed mixing of graft and matrix chains in the NVT ensemble for 5×10^6 time steps, at a reduced temperature of $T^* = 1$ maintained using the Nose-Hoover^{33,34} thermostat with a damping time of 1τ . In this mixing stage, the equations of motion were integrated using the velocity Verlet algorithm with time step $\Delta t = 0.001 \cdot \tau$. The cubic simulation box is then shrunk isotropically in all three dimensions over 2×10^6 time steps to achieve a final simulation box volume packing fraction of $\eta = 0.36$. At the final box size, PNC configurations are further equilibrated for 1×10^7 time steps with $\Delta t = 0.005 \cdot \tau$, and equilibrated configurations were then used to generate production run configurations every 10^5 time steps for an additional 2×10^7 time steps to perform structural analyses.

MD simulations of a single grafted nanoparticle inside of a polymer matrix with a low $\phi_{\text{PGP}} = 0.01$ were performed with ϕ_{M2} ranging from 0 (binary case with matrix chain length $N_{\text{M1}} = 75$) to $\phi_{\text{M2}} = 0.043$ and 0.1 (ternary cases with a low volume fraction of matrix_2 chains similar to matrix_2 composition used in experiments, see Table S2). An additional case of $\phi_{\text{M2}} = 0.99$ (≈ 1) corresponding to a binary PNC case with the matrix entirely composed of matrix_2 chains of length $N_{\text{M2}} = 15$ (and $\phi_{\text{M1}} = 0$) was run as well. Additionally, for PNC cases of experimental relevance with higher grafted filler fractions of $\phi_{\text{PGP}} = 0.039$ and $\phi_{\text{PGP}} = 0.079$ and with aforementioned ϕ_{M2} values, Polymer Reference Interaction Site Model (PRISM)³⁵ theory calculations described below were performed. This combination of MD simulations and PRISM theory enables calculation of structure factors at large length scales (*i.e.*, small wave vectors, q) with a significantly lower computational expense than MD simulations by eliminating the need

to run large system sizes of multiparticle PNCs with high ϕ_{PGP} . Furthermore, unlike MD simulations, PRISM theory results are devoid of artifacts arising from chosen simulation box/system sizes and/or kinetic trapping effects.

Polymer Reference Interaction Site Model (PRISM) theory. Polymer Reference Interaction Site Model (PRISM)³⁵⁻³⁷ theory is a liquid-state theory that describes structure in polymer solutions and melts using the Ornstein-Zernike³⁸ like mathematical form:

$$\hat{H}(\mathbf{q}) = \hat{\Omega}(\mathbf{q})\hat{C}(\mathbf{q})[\hat{\Omega}(\mathbf{q}) + \hat{H}(\mathbf{q})] \quad (3)$$

Here, $\hat{H}(\mathbf{q})$ is an $N \times N$ matrix comprised of the total intermolecular pair correlations, $\hat{C}(\mathbf{q})$ is an $N \times N$ matrix comprised of direct pair correlations, $\hat{\Omega}(\mathbf{q})$ is an $N \times N$ matrix comprised of intramolecular pair correlations, N is the number of interaction site types, which in this study can be 3 or 4 types of interaction sites corresponding to particle, graft, matrix_1 and/or matrix_2 beads depending on the chosen matrix composition ($\phi_{\text{M}_2} = 0, 0.043, 0.1$ and 0.99) for PNCs. Although graft and matrix_2 beads refer to the same chemistry (PMMA), they are designated as separate types of interaction sites since the intramolecular correlations for tethered graft chains are expected to be significantly different from matrix_2 chains.

The intramolecular pair correlation matrix, $\hat{\Omega}(\mathbf{q})$, given as an input to PRISM theory, is composed of intramolecular structure factor elements, $\widehat{\omega}_{\text{XY}}(\mathbf{q})$, for site pairs XY in each molecule. At any PNC grafted filler fraction ($\phi_{\text{PGP}} = 0.039$ and $\phi_{\text{PGP}} = 0.079$) and matrix_2 filler fraction ($\phi_{\text{M}_2} = 0, 0.043, 0.1, 1$), $\widehat{\omega}_{\text{XY}}(\mathbf{q})$ was approximated³⁵ from single particle PNC MD simulations at low $\phi_{\text{PGP}} = 0.01$ and low $\phi_{\text{M}_2} = 0.043$ as follows:

$$\widehat{\omega}_{\text{XY}}(\mathbf{q}) = \left\langle \frac{1}{N_{\text{X}} + N_{\text{Y}}} \sum_{i=1}^{N_{\text{Y}}} \sum_{j=1}^{N_{\text{X}}} \frac{\sin(\mathbf{q}r_{ij})}{\mathbf{q}r_{ij}} \right\rangle \quad (4)$$

where N_{X} and N_{Y} are the total number of interaction sites of type X and type Y, respectively, within the same molecule, and r_{ij} is the inter-site distance.

In addition to $\hat{\Omega}(\mathbf{q})$, to solve the PRISM equation, a direct pair correlation matrix, $\hat{C}(\mathbf{q})$ needs to be given as an input. Each element of the $\hat{C}(\mathbf{q})$ matrix is a pairwise direct site correlation function, c_{XY} , expressed using a closure equation, in terms of the interaction potential,

U_{XY} , and the total intermolecular pair correlation, h_{XY} , of any site pair XY . For particle-particle pairs, hypernetted chain closure (HNC)^{39,40} was used as follows:

$$c_{PP}(r) = h_{PP}(r) - \ln[h_{PP}(r) + 1] - \beta U_{PP}(r), r > D_P \quad (5)$$

For the remaining site pairs, XY (GG, GM1, GM2, M1M2, M2M2, PG, PM1, and PM2), Percus Yevick (PY)^{35,37,41,42} closure was used as

$$\begin{aligned} c_{XY}(r) &= (1 - e^{\beta U_{XY}(r)})(h_{XY}(r) + 1), \quad r > d_{XY} \\ (h_{XY}(r) + 1) &= g_{XY}(r) = 0, \quad r \leq d_{XY} \end{aligned} \quad (6)$$

with d_{XY} equal to the mean diameter of sites X and Y .

For a given input, the output in the form of pairwise total intermolecular correlations for all pairs of sites, in real and Fourier space using numerical methods, was provided by the pyPRISM⁴³ package.

Analyses. The spatial arrangement of graft, matrix_1 and matrix_2 beads as a function of distance from the particle surface was quantified from configurations sampled in MD simulation trajectories in the form of concentration profiles defined as

$$C_{i|r} = \left\langle \frac{n_i(r)}{4\pi r^2 \Delta r} \right\rangle \quad (7)$$

where i refers to the bead type (G, M1, or M2) and n_i refers to the number of beads of type i within a shell volume of thickness Δr at a distance r from the grafted nanoparticle surface. To plot the graft and matrix concentration profiles, we normalized the $C_{i|r}$ with $C_{i|r}$ at $r = 0$ (surface) for graft beads and $C_{i|r}$ at $r = \infty$ (bulk) for matrix_1 and matrix_2 beads. This normalized fraction is denoted as $C_{i|r}/C_{i|r=0}$ and $C_{i|r}/C_{i|r=\infty}$ for graft and matrix beads, respectively.

The thickness of the graft polymer layer on the nanoparticle surface was quantified by calculating the ensemble averaged grafted brush height, H_b , from the MD simulation configurations, defined as

$$H_b = \left\langle \sqrt{\frac{\sum_1^{n_G} r_i^2}{n_G}} \right\rangle \quad (8)$$

with r_i is equal to the distance of an i -th graft polymer bead from the surface of the particle and n_G is equal to the total number of graft polymer beads on the particle (*i.e.*, N_G times the number of graft chains on the particle). All quantities from MD simulations are reported as block averages obtained from 4 blocks of 50 configurations each and the error bars are standard deviations in the average values of the 4 blocks.

The structural output from PRISM theory calculations include the total intermolecular correlation matrix, $\hat{H}(q)$, with the elements of the matrix $h_{XY}(q)$ for a site pair XY converted to real space counterparts, $h_{XY}(r)$. The intermolecular pair correlation function in real space, $g_{XY}(r)$, is calculated from $h_{XY}(r)$ as follows

$$g_{XY}(r) = h_{XY}(r) + 1 \quad (9)$$

In Fourier space, the structure factor matrix, $\hat{S}(q)$, is obtained using $\hat{H}(q)$ and $\hat{\Omega}(q)$ as

$$\hat{S}(q) = \hat{H}(q) + \hat{\Omega}(q) \quad (10)$$

The elements of the structure factor matrix, include the particle-particle structure factor, $S_{PP}(q)$, and graft-graft structure factor, $S_{GG}(q)$.

RESULTS AND DISCUSSION

i.) As-cast Binary and Ternary PNCs

Figures 1a and 1b show representative TEM micrographs of as-cast binary and ternary PNC films as a function of composition, respectively. The binary PMMA-NP/SAN polymer blend nanocomposites are denoted by A/B, where A and B represent the weight fractions of PMMA-NP and SAN, respectively. The ternary PMMA-NP/SAN/PMMA PNCs are denoted by A/B/C, where A and B are the weight fractions of PMMA-NP and SAN from the binary PNCs, and C is the weight fraction of the PMMA compatibilizer with respect to the total amount of polymer (PMMA-NP and SAN). This notation is adopted to more easily compare the two systems.²¹ The images reveal that the films exhibit remarkable dispersion of particles with little

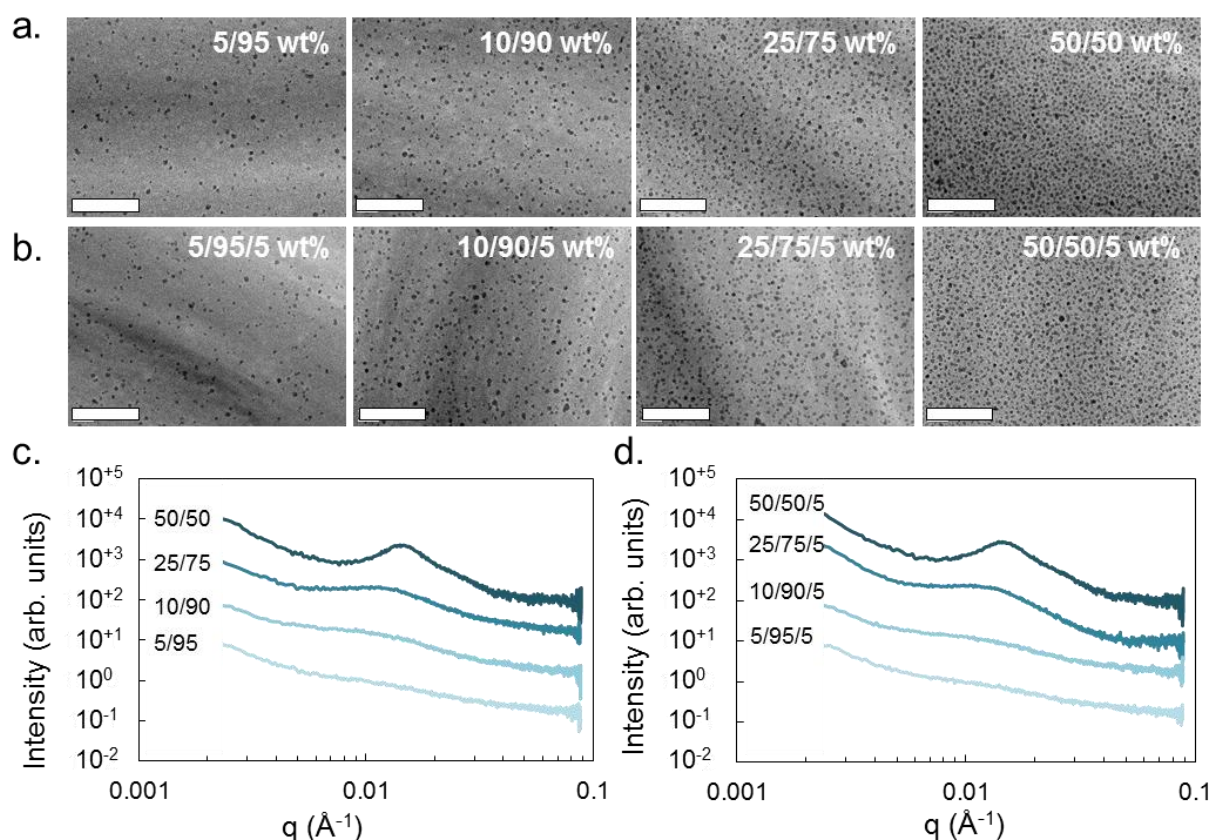


Figure 1. Representative cross-sectional TEM micrographs of ultramicrotomed as-cast (a) binary (PMMA-NP/SAN) and (b) ternary (PMMA-NP/SAN/PMMA) films as a function of nanoparticle loading showing individually dispersed PMMA-NPs. Image scale bars are 300 nm. Figures 1(c) and (d) show the corresponding small-angle X-ray scattering profiles for the binary and ternary PNC films. The profiles are vertically shifted for clarity.

to no clustering. The lowest loadings of particles (5/95 and 5/95/5) result in average center-to-center interparticle distances (ID) of ~ 70 nm, as determined through image analysis using ImageJ. The IDs decrease rapidly as the weight percent of NPs increases, resulting in a value of ~ 30 nm at the highest loadings (50/50 and 50/50/5). Transmission SAXS was utilized as a second method to confirm dispersion and to measure the center-to-center NP correlation lengths. As shown in Figures 1c and 1d, a scattering peak occurs at progressively lower q values as particle loading decreases. The relative magnitude of each peak decreases as loading decreases, consistent with the reduced scatterer populations (scattering at compositions of 5/95 and 5/95/5 was too weak to produce any discernable peak). IDs extracted from hard sphere structure factor fits to the data were ~ 70 nm ($q \sim 0.009 \text{ \AA}^{-1}$) at 10 wt% NPs and decreases to ~ 42 nm ($q \sim 0.015 \text{ \AA}^{-1}$) at 50 wt%. These values are in good agreement with those obtained through autocorrelation functions of each TEM micrograph (Figure S6). For instance, the lowest loadings of particles results in no correlation peak, while the highest loadings (50 wt%) exhibits an average center-to-center interparticle distance of ~ 45 nm. For NPs that are randomly distributed in the polymer matrix, the theoretical ID is given by^{44,45}

$$\text{ID}(\sigma) = d_m \left\{ \left(\frac{\pi}{6\varphi_{\text{NP}}} \right)^{\frac{1}{3}} [\exp(1.5(\ln \sigma)^2)] - \exp[0.5(\ln \sigma)^2] \right\} \quad (11)$$

where d_m is the mean diameter (15.5 nm), φ_{NP} is the volume fraction of NP cores, and σ is the NP polydispersity (Equation S2). The interparticle distance measured here is consistent with the theoretical predictions, indicating that the as-cast PNC films are homogeneous and mixing between the grafted NP and matrix polymers is thermodynamically favorable (Figure S7).

ii.) Phase Separation in Binary and Ternary PNCs

To probe differences in mixing/demixing behavior of the binary and ternary PNC, phase diagrams are mapped out as a function of temperature and composition. Starting with the well dispersed NP systems at room temperature, the films are annealed between 155-195°C and analyzed using a combination of cloud point observations, TEM, and SAXS. The phase diagram of the binary PNC serves as a reference system and is determined by monitoring the cloud point transitions of $\sim 2 \mu\text{m}$ bulk films (Figure S8). The films transitioned from transparent to opaque with increasing annealing temperature, with a lower critical solution temperature (LCST) of

$\approx 160^\circ\text{C}$, consistent with PMMA/SAN blends studied by Newby *et al.*⁴⁶ This behavior demonstrates that PMMA grafted nanoparticles ($\Sigma = 0.7$ grafts/nm²) in a SAN matrix exhibit enthalpic interactions comparable to the PMMA/SAN blend. While this binary PNC behavior is not new,^{13,14} the effect of adding a third component on phase separation is still unknown. Here, we add the identical polymer as the brush, namely PMMA, at fixed composition (5 wt%), and match their molecular weights ($M_{w, \text{PMMA}} \cong M_{w, \text{PMMA-NP}}$). We can then make direct comparisons between the interactions of SAN matrix and grafted PMMA versus free PMMA chains.¹⁴ Similar to the binary PNC, cloud point measurements (not shown) were performed on the ternary PNC to determine the phase diagram. Interestingly, cloud point observations suggest a slight increase in miscibility for compositions of 5/95/5 and 10/90/5 where PMMA-NPs are the minority component.

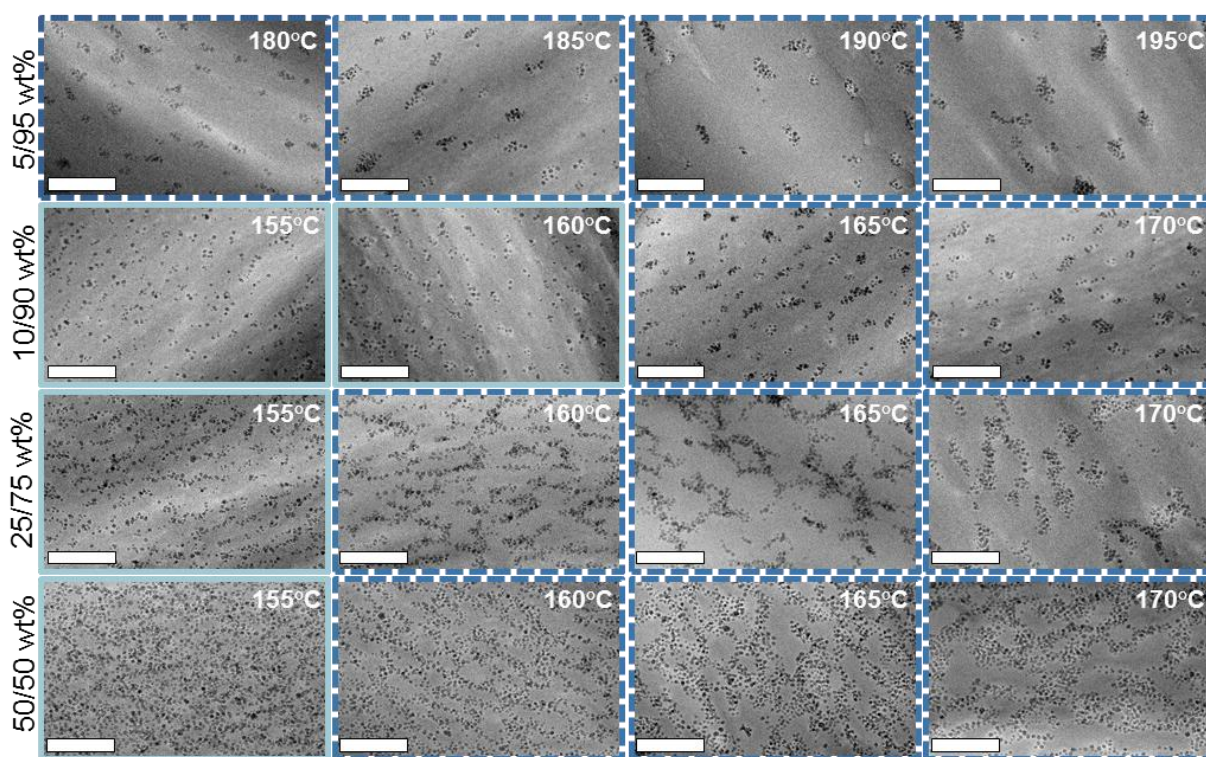


Figure 2. Representative cross-sectional TEM micrographs of ultramicrotomed binary PMMA-NP/SAN = 5/95 (row 1), 10/90 (row 2), 25/75 (row 3), and 50/50 (row 4) films annealed at the indicated temperatures for 24 h. Border colors denote one (teal, solid) and two (blue, dashed) phase regions. Scale bars are 300 nm.

A more quantitative characterization of PNC phase evolution can be obtained from TEM and SAXS. Figure 2 depicts representative TEM images of binary PNCs at varying compositions: PMMA-NP/SAN = 5/95, 10/90, 25/75, and 50/50 after 24 h of annealing at the respective temperatures. At temperatures below the optically determined phase boundary of $\approx 160^\circ\text{C}$, the TEM micrographs reveal that the overall distribution of NPs is homogeneous as shown by the morphologies outlined by the solid teal boxes. Notably, there are several dispersed NP clusters within the one phase region. This suggests that the potential of mean force between two particles is not purely repulsive and slight aggregation occurs at $T > T_g$, similar to what has been seen previously.^{47,48} However, as the samples are quenched into the two phase region, macro-phase separation readily occurs as shown by morphologies outlined by the dashed blue boxes. The degree of phase separation appears to increase with temperature, which is expected based on the increased mobility of the constituents and deeper quench depth. Interestingly, discrete NP domains are formed for 5/95 and 10/90 off-critical compositions, whereas the 25/75 system qualitatively exhibits string-like and more connected domains. The 50/50 system exhibits a bicontinuous morphology, similar to the previously reported PMMA/SAN blend.^{46,49} Within domains of NP aggregates, the average center-to-center interparticle distance is ~ 28 nm as quantified through image analysis. 50/50 samples were also annealed for 72 h in order to confirm that the 24 h annealing times are sufficiently long to reach quasi-equilibrium morphologies, (Figure S9). When annealed in the one phase region, no discernable difference in PNC morphologies is observed. Likewise, when annealed in the two phase region, the aggregate domain size only slightly increases after 72 h. This comparison indicates that an annealing time of 24 h is sufficient to discern morphology differences between binary and ternary PNC's.

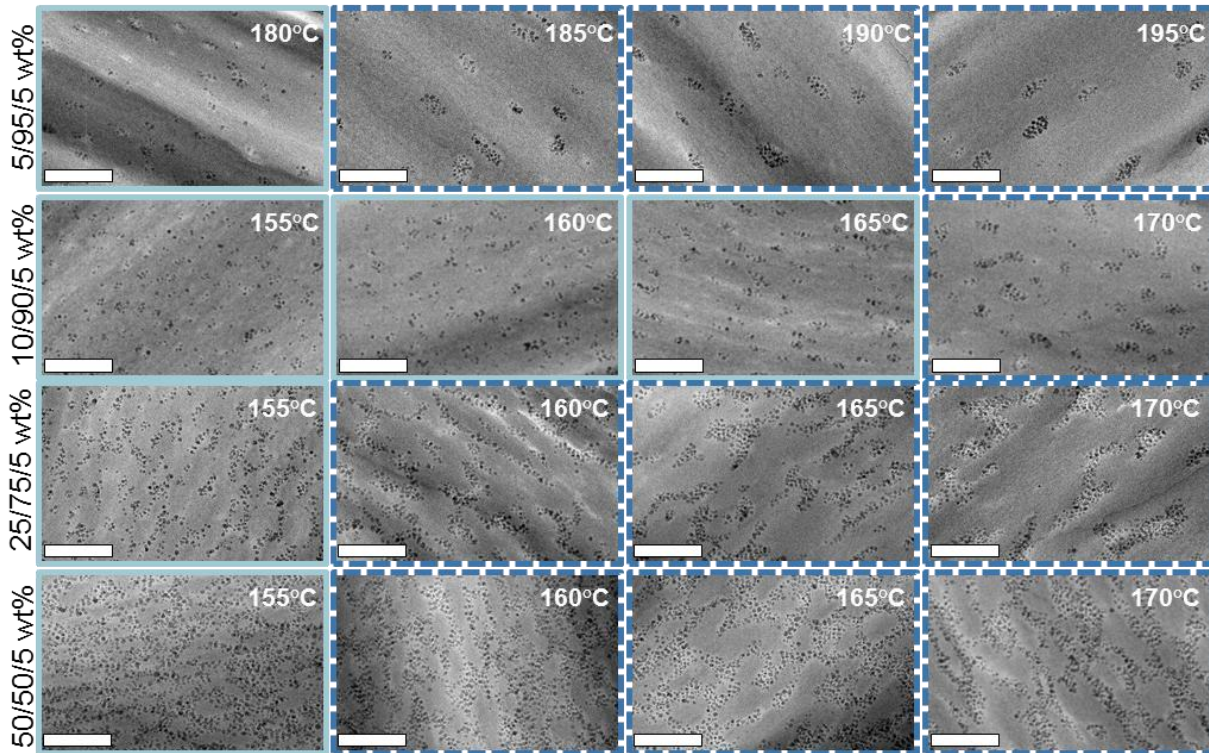


Figure 3. Representative cross-sectional TEM micrographs of ultramicrotomed ternary PMMA-NP/SAN/PMMA = 5/95/5 (row 1), 10/90/5 (row 2), 25/75/5 (row 3), and 50/50/5 (row 4) films annealed at the indicated temperatures for 24 h. Border colors denote one (teal, solid) and two (blue, dashed) phase regions. Scale bars are 300 nm.

Figure 3 shows cross-sectional TEM micrographs for ternary compositions analogous to the binary systems shown in Figure 2 after 24 h of annealing at the indicated temperatures. For 5/95/5 films, particles remain dispersed at temperatures up to 180°C. At temperatures of 185°C and higher, the uniform distribution of NPs becomes disrupted and the NPs form discrete aggregates that increase in size as temperature increases. Similarly, 10/90/5 films exhibit macro-phase separation into discrete domains at temperatures of 170°C. While comparable, the reduced domain size for the 10/90/5 composite compared to the 5/95/5 is attributed to the smaller thermodynamic driving force and slower diffusivity at lower temperatures. The phase separation evolution of PNCs near the phase separation temperature ($\approx 160^\circ\text{C}$) and at intermediate compositions (*i.e.*, 25/75/5 and 50/50/5) show a transition from dispersed to aggregated, forming string-like and bicontinuous morphologies, respectively. While these trends are similar to the binary composite, several interesting features emerge. Specially, off-critical compositions of 5/95/5 (180°C) and 10/90/5 (165°C) reveal, on average, uniformly distributed particles and

clusters of much smaller size compared to their binary counterpart. At 180°C, 5/95/5 films exhibit significantly less aggregation compared to the binary analogue (Figure S10). This aggregation suppression is also observed in the 10/90/5 case, but less pronounced. Compositions approaching the critical composition show no appreciable difference in miscibility upon addition of linear PMMA, similar to what was observed in the cloud point transitions.

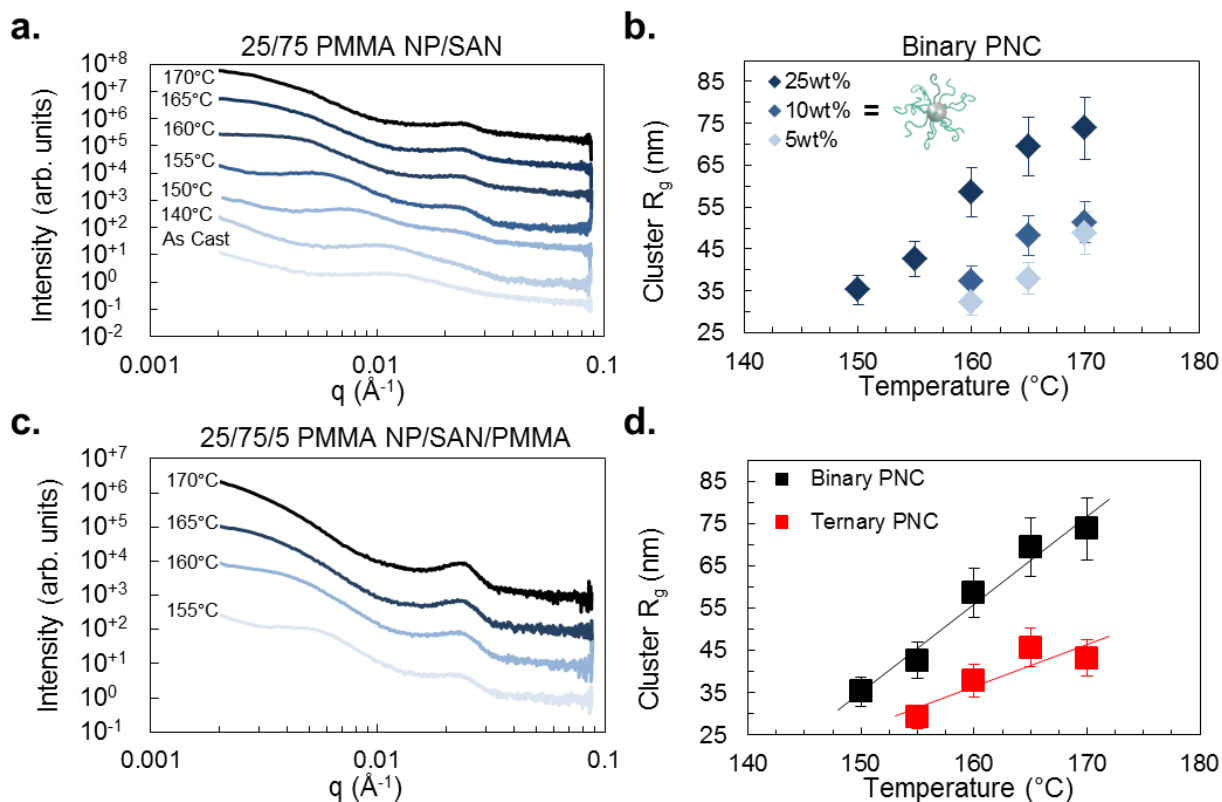


Figure 4. (a) Small-angle X-ray scattering profiles of 25/75 wt% binary PMMA-NP/SAN films annealed at the indicated temperatures for 24 h. Figure 4b shows the corresponding average nanoparticle cluster radius of gyration as a function of temperature obtained through SAXS modeling. Figure 4c shows scattering profiles for the 25/75/5 wt% ternary PNC under identical annealing conditions to those in (a). A direct comparison of the average aggregate size as a function of temperature for (a) and (c) is shown in Figure 4d. The profiles are vertically shifted to avoid overlap and more clearly track evolutions in scattering peaks.

We performed SAXS measurements on the annealed PNCs in parallel with TEM to further quantify the length scales of phase separation as a function of temperature and NP loading. Figure 4a shows the one-dimensional scattering intensity as a function of wavevector for a representative 25/75 wt% binary PNC (data for other compositions are in Supporting Information). The background-subtracted 1-dimensional scattering intensities were modeled using two scattering contributions to represent isolated/paired NPs and aggregated NP clusters (see Supporting Information). We first consider the scattering profile for the as-cast samples, which shows a single, weak scattering feature near $q \sim 0.0123 \text{ \AA}^{-1}$. This represents the average center-to-center interparticle distance (51 nm) which is greater than the diameter of a single grafted NP. This observation is consistent with well-dispersed NP cores, in agreement with TEM images in Figure 1. However, after annealing, we observe the emergence of two separate scattering features; one at higher q , and one at lower q . The peak position of the higher q feature remains relatively unchanged at higher temperatures, while the lower q feature increases in intensity while also moving to even smaller values. Modeling of the data indicates that the higher q feature represents the average center-to-center interparticle distance, which initially (slightly) decreases with increasing temperature, and eventually becomes well defined as the PMMA-NPs aggregate at elevated temperatures. The lower q feature represents the scattering between the small nanoparticle clusters as seen in Figures 2 and 3, which continue to grow at elevated temperatures as smaller clusters coalesce. Both of these observations indicate a phase transition between $\approx 150\text{-}160^\circ\text{C}$, commensurate with observations from TEM. The scattering feature representing the aggregated NPs can be used to determine the average size of a single ‘cluster’ of NPs. For the binary system at 5, 10 and 25 wt%, Figure 4b shows how the average cluster radius of gyration (R_g) increases as temperature increases, consistent with an increase in the thermodynamic driving force for phase separation. For example, at 25 wt%, R_g increases by more than a factor of two as temperature increases from 150°C to 170°C . There is also a significant increase in the cluster size as the NP loading increases from 10 wt% to 25 wt%, consistent with a smaller as-cast interparticle distance at higher loading (cf. Figure S7). Namely, because NPs are initially closer to one another at higher loadings, larger aggregates are easier to form for the same annealing times.

It is important to note that even at temperatures below the LCST (160°C), a shoulder can be observed in the scattering intensity at q values close to the aggregate ID. Based on the TEM

micrographs in Figure 2, we interpret this as the formation of small NP clusters when $LCST > T > T_g$ even though macro-phase separation is not thermodynamically favorable. Annealing the samples above their glass transition allows the NPs to diffuse more readily, leading to the formation of small clusters due to the short-range attractive forces between the particles noted earlier. Noticeably, the measured ID (28 nm) for the center-to-center interparticle distance is slightly less than the diameter of the PMMA-NP, suggesting that PMMA brushes are weakly interpenetrating with one another at elevated temperatures despite being in the concentrated brush regime (CPB).

Figure 4c shows scattering data for the PMMA-NP/SAN/PMMA ternary composite at identical NP loadings as the binary system shown in Figure 4a. Modeling of the data reveals two notable differences between the binary and ternary systems. First, the high- q scattering feature is at slightly smaller q -values in the ternary PNC than in the binary one at 170°C (0.024 \AA^{-1} vs. 0.026 \AA^{-1} , respectively). This is attributed to less PMMA brush interdigitation and a lower degree of brush collapse, indicative of a slightly more miscible PNC. Second, the average NP aggregate size is smaller in the ternary composite than in the binary case. This reduction in cluster size is substantially more than what one could surmise from a simple dilution argument through the addition of the ternary component. Figure 4d compares the aggregate size as a function of temperature for the binary (black squares) and ternary (red squares) systems. The addition of only 5 wt% PMMA homopolymer decreases the average aggregate size by as much as a factor of two at 170°C , indicating a suppression in aggregation and an increase in PNC miscibility. These experimental observations will be supported by PRISM calculations and MD simulations later in the paper.

Figure 5 shows a phase diagram for both binary and ternary composites constructed by compiling cloud point, TEM,

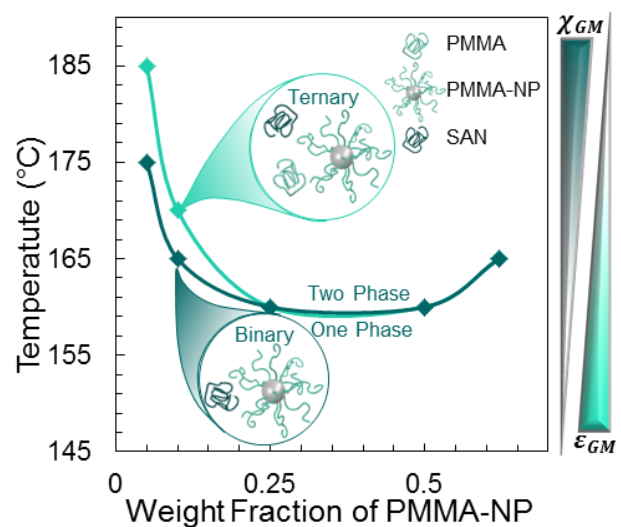


Figure 5. Phase diagrams of binary PMMA-NP/SAN and ternary PMMA-NP/SAN/PMMA nanocomposites. The ternary composites exhibit increased miscibility in off-critical compositions. The solid lines have been drawn to guide the eye.

and SAXS results. Near the critical temperature, the binary phase diagram is relatively flat between 20 wt% and 50 wt% PMMA-NP and increases sharply below 10 wt% and above 63 wt%. Accounting for the polydispersity of SAN, this behavior is consistent with other blends containing a polydisperse component.⁵⁰ From the observed phase separation behavior, the addition of linear PMMA increases the miscibility of the binary PMMA-NP/SAN system at the most off-critical compositions (*i.e.*, 5/95/5) by as much as 10°C. To begin to understand this, we recall the work presented by Schmitt *et al.*, who studied a binary system of silica particles grafted with polystyrene (PS) and PMMA ligands with an upper critical solution temperature (UCST). They demonstrated that the specific ligand interactions in mixtures of these polymer-grafted nanoparticles imparts similar phase behavior as in analogous linear polymer blends, similar to our findings for PMMA/SAN systems.¹³ While general trends in phase behavior between the two systems were alike, distinct differences were recognized. Specifically, the binary PNC demonstrated increased miscibility and slower kinetics of domain growth as compared to the neat polymer blend. The apparent increase in miscibility was rationalized as a consequence of a reduced thermodynamic driving force for phase separation attributed to fewer unfavorable segmental interactions between PMMA-PS ligands. Additionally, the presence of NP cores resulted in a smaller number density of segmental contacts.¹³ Here, it is important to reiterate that these segmental interactions are unfavorable due to the systems UCST behavior. Therefore, the work by Schmitt and coworkers is consistent with the presented LCST work thus far, with our results demonstrating that the addition of linear PMMA reduces aggregation of PMMA-NPs and increases miscibility. We attribute this phenomena to an interfacial compatibilization between the SAN matrix and grafted PMMA brush due to localization of the free PMMA chains. The addition of linear PMMA increases the number of favorable segmental contacts between each chemical species and therefore reduces the thermodynamic driving force for phase separation (parsing of the specific enthalpic and entropic contributions to this will be discussed later). Importantly, this miscibility increase was only observed for 5/95/5 and 10/90/5 off-critical compositions.

The improved miscibility from homopolymer compatibilization can be understood from a simple geometric model that considers the interaction between the free and grafted PMMA chains. Under the assumption that the free PMMA chains are Gaussian coils with a pervaded volume described as spheres, the number of chains needed to cover the surface area of a PMMA-NP can be directly calculated.⁵¹ As shown in Figure 6, two regimes are considered: (1) PMMA chains wetting the PMMA brush (wet brush state) and (2) PMMA excluded from the PMMA brush layer (dry brush state). For the wet brush case, approximately ~650 homopolymer chains are needed to completely cover a PMMA-NP/matrix interface, whereas ~740 chains are needed for the dry brush state. The total number of available PMMA homopolymer chains for compatibilization at a constant 5 wt% loading can be calculated. Under wet brush conditions, the ratio of required to available PMMA chains for the 5/95/5 composite is approximately 1:1. As the composition of the films increases to higher loadings of PMMA-NPs, the ratio decreases to 2:1, 4.5:1, and 9:1 for 10/90/5, 25/75/5, and 50/50/5 films, respectively. While similar, the ratios

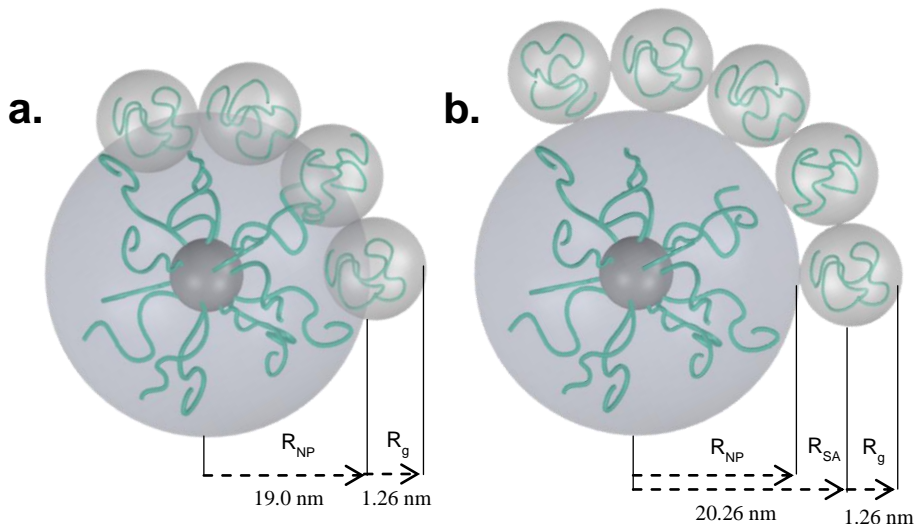


Figure 6. This cartoon illustrates two possible scenarios of linear PMMA covering the surface the PMMA-NPs. Case one (a) assumes that linear PMMA chains wet the PMMA-NP brush layer. Case two (b) adopts both PMMA-NPs and linear PMMA as hard spheres, resulting in complete exclusion of PMMA chains within the brush corona.

derived for the dry brush regime are smaller given that more PMMA homopolymer is needed to shield the NP surface. Due to the small amount of PMMA-NPs in 5/95/5 films, the proposed scaling model suggests that a 5 wt% addition of PMMA is sufficient to compatibilize the PMMA-NP/SAN system. However, as the concentration of NPs increases, 5 wt% of PMMA becomes insufficient to completely shield the PMMA brush from the SAN matrix, demonstrated by the aforementioned ratios. This behavior is captured by our experimental findings shown in Figure 5 where the highest miscibility increase occurred in 5/95/5 films, and progressively decreased with particle loading.

iii.) Comparing Theory and Experiments

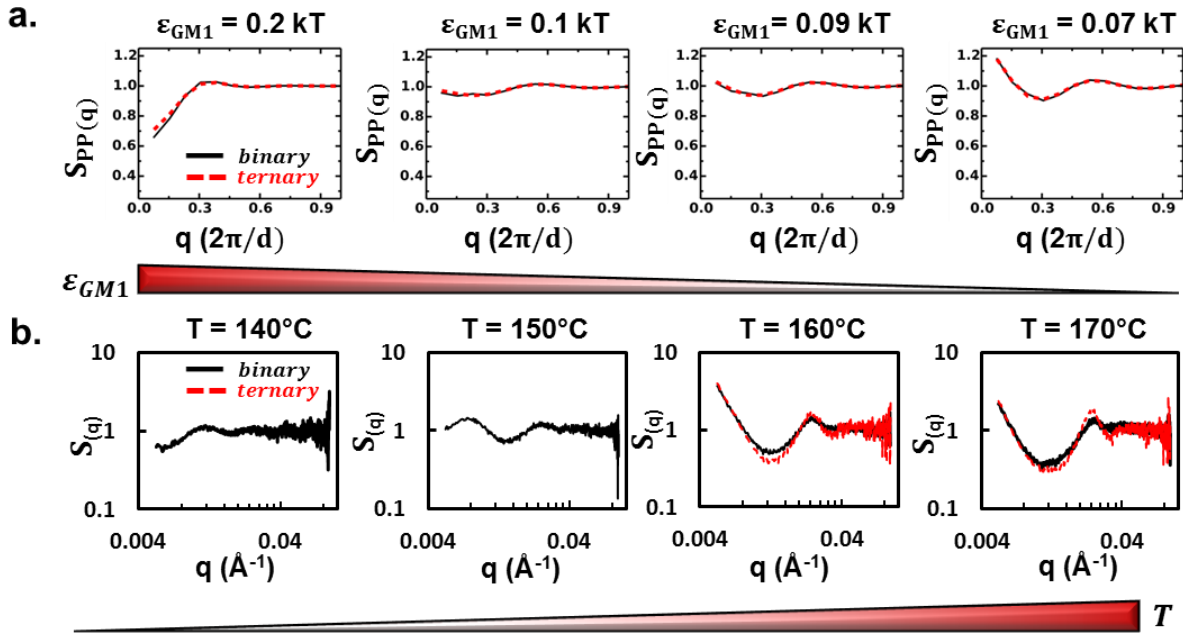


Figure 7. Particle-particle structure factors, $S_{pp}(q)$, obtained using PRISM theory for PNCs with $\phi_{PGP} = 0.039$ (a) with $\epsilon_{GM1} = 0.2$ kT, $\epsilon_{GM1} = 0.1$ kT, $\epsilon_{GM1} = 0.09$ kT and $\epsilon_{GM1} = 0.07$ kT. Figure 7b shows the corresponding particle-particle structure factors, $S(q)$, obtained using SAXS for 25/75 wt% PNCs. The binary PNC case with $\phi_{M2} = 0$ is shown as a black line and the ternary case with $\phi_{M2} = 0.043$ (5 wt%) is shown as a red dashed line. Results in part (a) are obtained using PRISM theory for PNCs with $\epsilon_{GG} = \epsilon_{M1M1} = 0.1$ kT, $D_p = 5d$, $N_G = 15$, $N_{M1} = 75$, $N_{M2} = 15$, $\Sigma = 0.76$ chains/ d^2 .

The compatibilization effect of the added PMMA chains can be systematically investigated using polymer reference interaction site model (PRISM) theory, which serves as a theoretical comparison to the experimental results. In PRISM theory, the choice of the graft-matrix₁ (ϵ_{GM1}), graft-graft (ϵ_{GG}), and matrix₁-matrix₁ (ϵ_{M1M1}) attraction strengths dictates whether the modeled PNC exhibits net favorable interactions (*i.e.*, below the LCST), effectively athermal interactions, or net unfavorable interactions (*i.e.*, above the LCST). Figure 7a shows a series of particle-particle structure factors calculated using PRISM theory for PNCs with decreasing values of ϵ_{GM1} at a constant ϵ_{GG} and ϵ_{M1M1} of 0.1 kT; corresponding structure factors from experiments at increasing temperatures are also shown in Figure 7b. For PNCs with $\epsilon_{GM1} = 0.2$ kT, corresponding to the PNCs at low temperatures, the $S_{pp}(q \rightarrow 0)$ shows no upturn, confirming that the nanoparticles remain relatively well-dispersed for binary (black solid lines) and ternary (red dashed lines) PNCs. This is in agreement with the experimentally obtained

structure factors for systems below the LCST (Figure 7b). For the binary PNCs with $\epsilon_{GM1} = 0.1$ kT, there is a distinct increase in both the value of $S_{pp}(q \rightarrow 0)$ as well as the slope of $S_{pp}(q)$ at low q values as compared to the PNCs with $\epsilon_{GM1} = 0.2$ kT. Furthermore, PNCs with $\epsilon_{GM1} = 0.09$ kT and 0.07 kT show an upturn when $S_{pp}(q \rightarrow 0)$, which is consistent with the shapes of the structure factors obtained from experiments performed at higher temperatures where phase separation occurs. Structure factor measurements obtained from PRISM and SAXS for the ternary PNC systems are also in good agreement. These results confirm that the PRISM theory results for PNCs with judiciously chosen model parameters and decreasing values of ϵ_{GM1} at constant ϵ_{GG} and ϵ_{M1M1} qualitatively capture similar morphologies observed in experiments.

PRISM theory can thus be used to probe and explain the hypothesized compatibilization observed experimentally in the ternary PNCs. Whereas the amount of PMMA in ternary PNCs is kept at 5 wt% for the experimental systems, MD simulations and PRISM theory allow us to systematically investigate the effect of increasing the PMMA volume fraction on the structure of the grafted chains and the bulk PNC morphology. In binary PNCs when $\epsilon_{GM1} = 0.2$ kT, the net interactions between the graft and matrix_1 chains are favorable. However, the matrix_1 chain length is much greater than the graft chain length (*i.e.*, $N_{M1} = 75 > N_G = 15$), which leads to entropic driving forces disfavoring graft-matrix_1 interpenetration due to a large loss in conformational entropy of long matrix chains upon wetting the grafted layer. In ternary PNCs with $\epsilon_{GM1} = 0.2$ kT and graft and matrix_2 chains being chemically identical and equal in lengths (*i.e.*, $N_{M2} = N_G = 15$), the shorter matrix_2 (PMMA) chains have a higher entropic driving force to wet the grafted layer than the enthalpically favored longer matrix_1 (SAN) chains. As ϵ_{GM1} decreases (*i.e.*, temperature increases), to disentangle the contributions of these two competing factors remains complex. Using MD simulations, the grafted layer structure and the extent of interpenetration of the matrix_1 and matrix_2 chains into the grafted layer can be quantified using concentration depth profiles as a function ϵ_{GM1} to investigate these two competing forces.

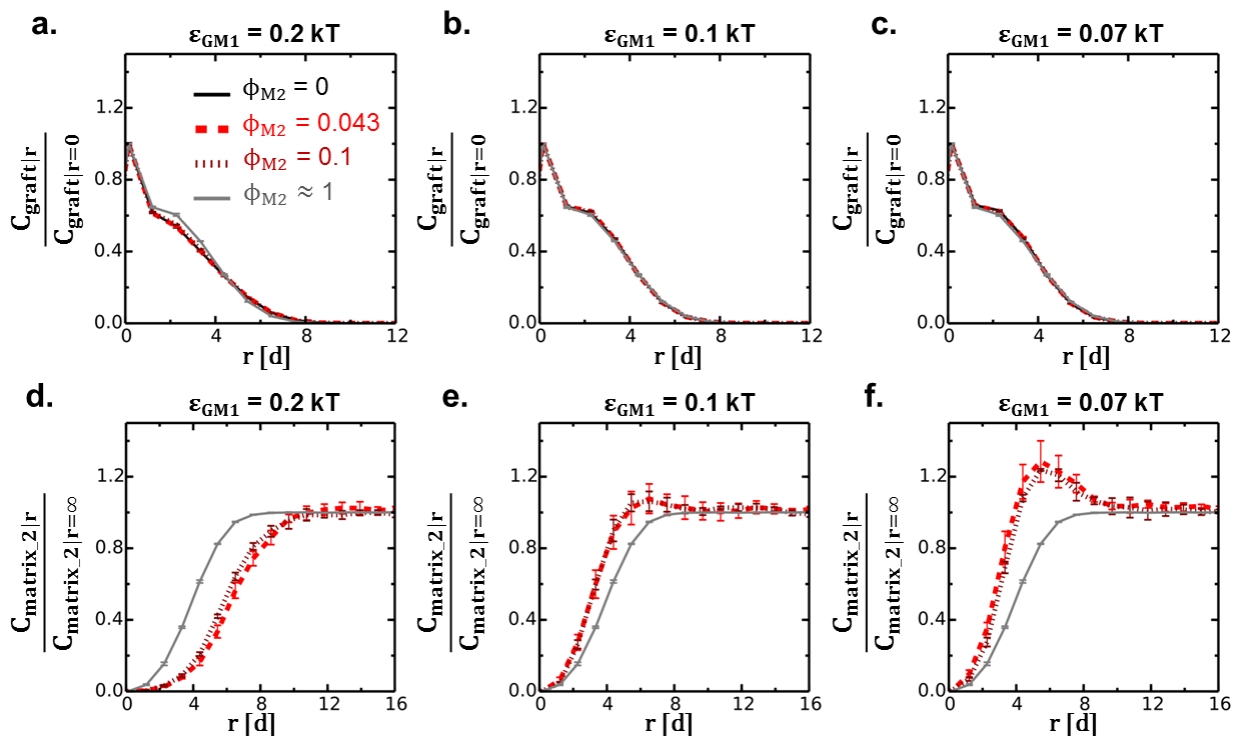


Figure 8. Concentration profiles for graft, G (a, b, and c) and matrix_2, M2 (d, e, and f) beads as a function of distance from the particle surface, r [in units of d] using MD simulations for PNCs with $\epsilon_{GM1} = 0.2$ kT (a, d), $\epsilon_{GM1} = 0.1$ kT (b, e) and $\epsilon_{GM1} = 0.07$ kT (c, f). Colored lines represent varying volume fractions of matrix_2 chains with $\phi_{M2} = 0$ (black line), $\phi_{M2} = 0.043$ (red dashed line), $\phi_{M2} = 0.1$ (dark red dotted line) and $\phi_{M2} \approx 1$ (gray line). The legend in part (a) applies to all parts in this figure. These results are for $\epsilon_{GG} = \epsilon_{M1M1} = 0.1$ kT, $D_p = 5d$, $N_G = 15$, $N_{M1} = 75$, $N_{M2} = 15$, $\Sigma = 0.76$ chains/ d^2 and $\phi_{PGP} = 0.01$. The error bars have been obtained from block averages of 4 blocks of 50 configurations each, sampled in a simulation run.

Figure 8 shows a series of normalized concentration profiles of the graft, matrix_1, and matrix_2 polymers as a function of radial distance from the NP core for decreasing values of ϵ_{GM1} . At the highest ϵ_{GM1} value (low temperature), Figure 8a shows that the brush structure for both binary and ternary PNCs with free PMMA chain loadings of $\phi_{M2} \leq 0.1$ are similar. This suggests that adding low amounts of matrix_2 does not alter the spatial arrangement of graft polymers around the particle when ϵ_{GM1} is high. However, when $\phi_{M2} = 1$, the concentration of graft polymer is slightly higher than in PNCs with $\phi_{M2} = 0 - 0.1$ between the ranges of $r \sim 1d - 4d$. This difference is attributed to the enthalpic driving forces between the SAN matrix and PMMA graft at low ϕ_{M2} , which extends the grafted polymer more than the favorable entropic driving forces in PNCs with shorter PMMA matrix chains where $\phi_{M2} \approx 1$. Figures 8b and c,

show a slight collapse of the graft layer ($\sim 1d$) with decreasing ε_{GM1} , consistent with what has been observed in the SAXS experiments. Similar to the grafted chains, we do not see a significant difference in matrix_1 bead concentration profiles with decreasing interaction strength (Figure S12). The concentration profiles of matrix_2 beads (Figure 8d) show that increasing ϕ_{M2} from values of 0.043 to the limiting case of $\phi_{M2} \approx 1$ (gray line) leads to increased penetration of the matrix_2 chains into the grafted layer. This is because at $\varepsilon_{GM1} = 0.2$ kT and at low ϕ_{M2} values, the favorable interactions between SAN polymer (matrix_1) and PMMA grafts (graft) compete with the entropically driven penetration of short PMMA matrix chains (matrix_2) to wet the grafted layer. As ε_{GM1} decreases to $\varepsilon_{GM1} = 0.1$ kT, both the graft-matrix_1 and graft-matrix_2 interactions become comparable, and the entropic driving forces cause matrix_2 chains to penetrate the grafted layer more than the long matrix_1 chains.⁵² Comparison of the matrix_2 concentration profiles in ternary PNCs (Figures 8d and 8e) confirms this higher interpenetration at smaller interaction strengths. Strikingly, in Figure 8e, the matrix_2 chain concentration in the brush is slightly greater than that of the bulk. In addition, the concentration of the matrix_2 chain is greater than the binary PNC case when $\phi_{M2} \approx 1$. This suggests that not only are the free PMMA chains penetrating the brush corona, but also localizing at the PMMA-NP/SAN interface within the ternary PNCs. This effect is further amplified at $\varepsilon_{GM1} = 0.07$ kT, shown in Figure 8f. This is supported by the competition between the entropic and enthalpic driving forces within the ternary PNC. For instance, in ternary PNCs at $\varepsilon_{GM1} = 0.07$ kT, the shorter and athermal matrix_2 chains have a higher concentration near the particle surface since matrix_1 chains are not only longer than graft chains (making it entropically unfavorable to interpenetrate the graft layer), but also interact unfavorably with graft chains.

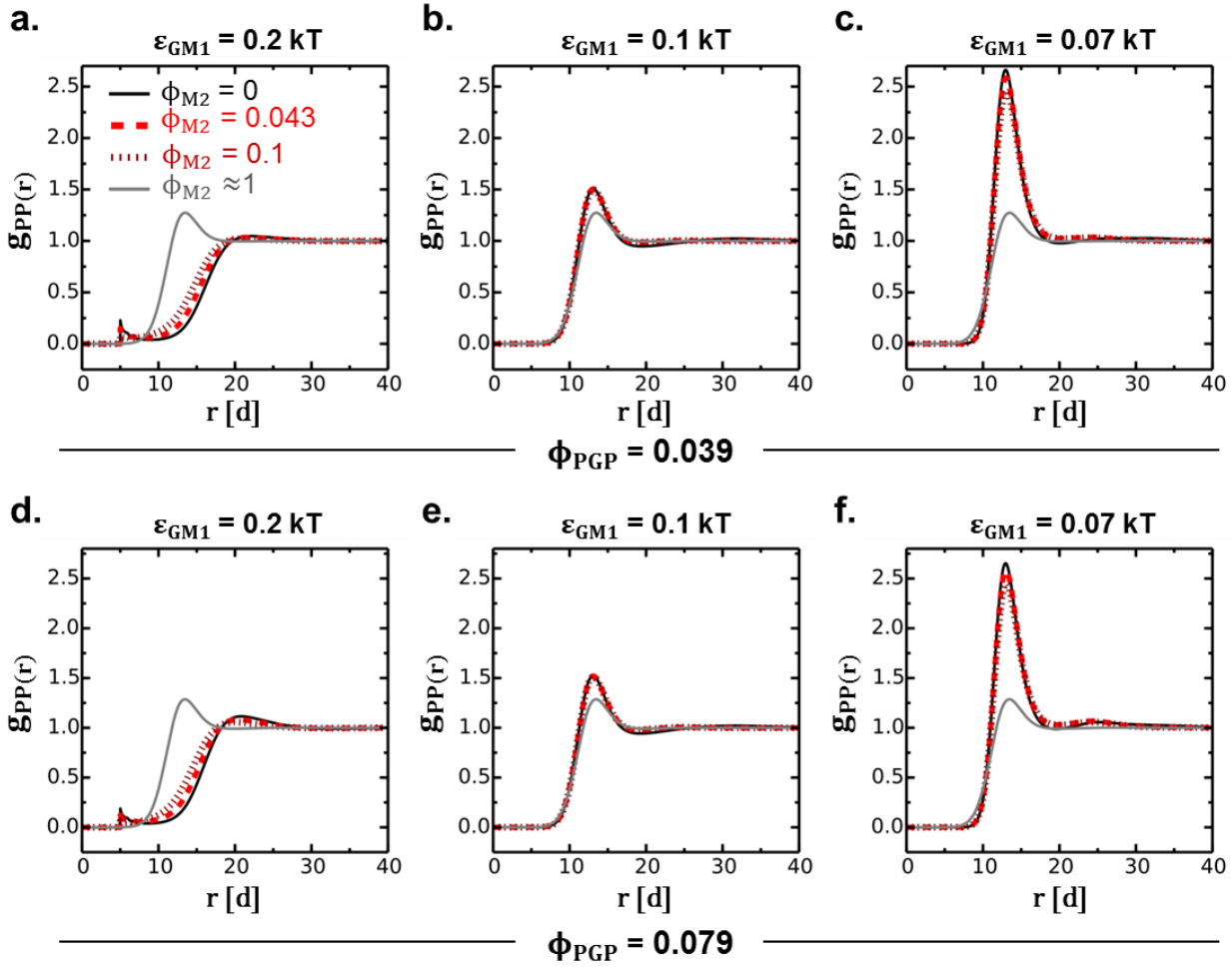


Figure 9. Particle-particle pair correlation function, $g_{PP}(r)$, obtained using PRISM theory for PNCs with $\phi_{PGP} = 0.039$ (a-c) and, $\phi_{PGP} = 0.079$ (d-f) with $\epsilon_{GM1} = 0.2$ kT (a, d), $\epsilon_{GM1} = 0.1$ kT (b, e) and $\epsilon_{GM1} = 0.07$ kT (c, f). Varying matrix_2 volume fractions are shown using colored lines with $\phi_{M2} = 0$ (black line), $\phi_{M2} = 0.043$ (red dashed line), $\phi_{M2} = 0.1$ (dark red dotted line) and $\phi_{M2} \approx 1$ (gray line). The legend in part (a) applies to all parts in this figure. These results are for $\epsilon_{GG} = \epsilon_{M1M1} = 0.1$ kT, $D_p = 5d$, $N_G = 15$, $N_{M1} = 75$, $N_{M2} = 15$, and $\Sigma = 0.76$ chains/ d^2 .

Going beyond the graft/matrix interface at low ϕ_{PGP} , PRISM theory calculations show the impact of varying the grafted nanoparticle and PMMA compatibilizer loadings on the PNC morphology. Figure 9 shows a series of particle-particle pair correlation functions, $g_{PP}(r)$, as a function of matrix_2 loading and ϕ_{PGP} . At $\epsilon_{GM1} = 0.2$ kT (Figure 9a), the $g_{PP}(r)$ shift to lower particle separation distances and exhibits a peak when $\phi_{M2} \approx 1$. This is because as ϕ_{M2} increases, the volume fraction of matrix_1 chains that interact favorably with graft chains

decreases, resulting in a slight decrease in the brush layer thickness (see brush heights plotted in Figure S13) and smaller interparticle distances. At $\epsilon_{GM1} = 0.1$ kT (Figure 9b), when both matrix_1 and matrix_2 chains equally interact with the grafted chains, the $g_{PP}(r)$ peak heights are larger than for $\epsilon_{GM1} = 0.2$ kT, indicating reduced particle dispersion. The $g_{PP}(r)$ profiles are also similar in all of the ternary PNCs at this interaction energy, where the majority of the matrix is made of the longer matrix_1 chains. Binary PNCs with $\phi_{M2} \approx 1$ show a slightly reduced $g_{PP}(r)$ peak height, suggesting better dispersion of nanoparticles driven by the entropic forces between graft and matrix_2 beads. When $\epsilon_{GM1} = 0.07$ kT, the $g_{PP}(r)$ peak heights for ternary PNCs are substantially higher than the 0.2 kT and 0.1 kT systems. This is attributed to the net graft-matrix_1 interactions being unfavorable at $\epsilon_{GM1} = 0.07$ kT. Remarkably, at $\epsilon_{GM1} = 0.07$ kT, the $g_{PP}(r)$ peak height of the binary PNC with $\phi_{M2} \approx 1$ is significantly smaller than the ternary PNCs, and remains comparable throughout all three interaction energies. Upon increasing the grafted filler fraction to $\phi_{PGP} = 0.079$, we find similar trends to those highlighted so far when $\phi_{PGP} = 0.039$ (Figure 9b). Particularly, with increasing loadings of matrix_2 chains, the grafted nanoparticles are more dispersed than in the binary systems.

Taken together, the results in Figure 9 suggest that at low temperatures (below the experimental LCST), the miscibility in ternary PNCs comprised of chemically dissimilar graft (PMMA) and majority matrix (SAN) polymers with a small amount of chemically identical matrix (PMMA) is *greater* than in binary PNCs with chemically identical and chain-length matched graft and matrix polymers. This confirms the role of the PMMA chains in the ternary PNCs in stabilizing the interface between graft and matrix chains. We note that at elevated temperatures above the LCST for PMMA/SAN (or due to the generality of the model, at temperatures below the UCST for a UCST graft-matrix system), the PNC miscibility in ternary PNCs comprised of chemically dissimilar graft and majority matrix polymers with a small amount of chemically identical matrix is *lower* than in a binary PNC with chemically identical and chain-length matched graft and matrix polymers.

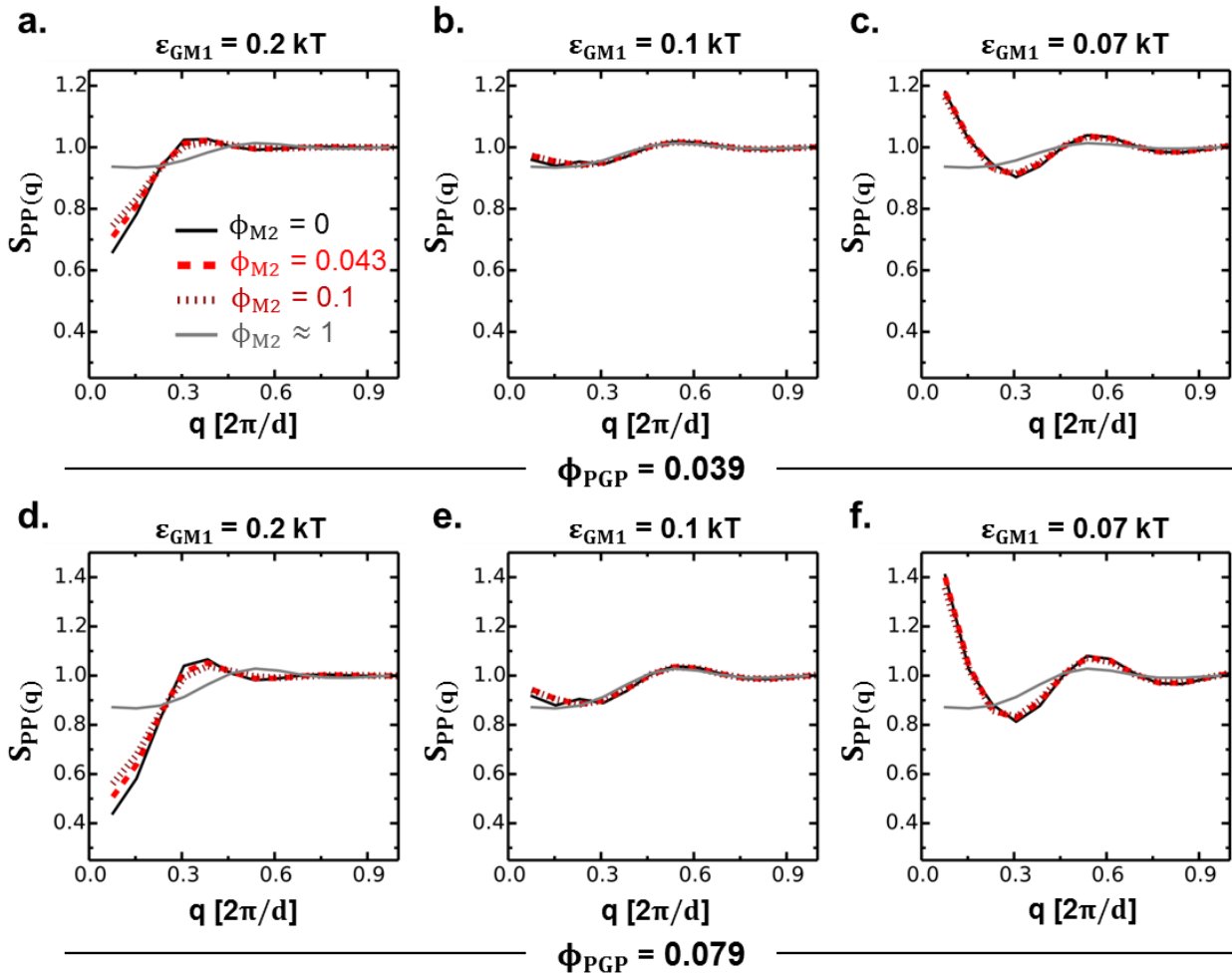


Figure 10. Particle-particle structure factor, $S_{PP}(q)$ for PNCs with $\phi_{PGP} = 0.039$ (a-c) and, $\phi_{PGP} = 0.079$ (d-f) with $\epsilon_{GM1} = 0.2$ kT (a and d), $\epsilon_{GM1} = 0.1$ kT (b and e) and $\epsilon_{GM1} = 0.07$ kT (c and f). Varying matrix_2 volume fractions are shown using colored lines with $\phi_{M2} = 0$ (black line), $\phi_{M2} = 0.043$ (red dashed line), $\phi_{M2} = 0.1$ (dark red dotted line) and $\phi_{M2} \approx 1$ (gray line). The legend in part (a) applies to all parts in this figure. These results are for $\epsilon_{GG} = \epsilon_{M1M1} = 0.1$ kT, $D_P = 5d$, $N_G = 15$, $N_{M1} = 75$, $N_{M2} = 15$, and $\Sigma = 0.76$ chains/ d^2 .

Finally, we quantified the macroscale PNC morphologies (Figure 10) *via* pairwise structure factors to complement the local structures elucidated by the $g_{PP}(r)$ in Figure 9. For PNCs with $\phi_{PGP} = 0.039$ and $\epsilon_{GM1} = 0.2$ kT (Figure 10a), $S_{PP}(q \rightarrow 0)$ increases with increasing matrix_2 loading. The binary PNC containing only PMMA chains ($\phi_{M2} \approx 1$) exhibits a slight upturn in the low q data and has the largest $S_{PP}(q \rightarrow 0)$ magnitude. This suggests that at high values of ϵ_{GM1} , the enthalpic interactions between graft and matrix_1 chains in both binary and ternary cases serve to better disperse the NPs than the purely entropic forces between graft and

matrix_2 chains. This confirms our conclusions based on $g_{PP}(r)$ in Figure 9. At $\varepsilon_{GM1} = 0.1$ kT, $S_{PP}(q)$ curves shown in Figure 10b are similar for PNCs with $\phi_{M2} = 0 - 0.1$ with a slight upturn at low q . However, when $\phi_{M2} \approx 1$, $S_{PP}(q \rightarrow 0)$ is the lowest. This again appears to represent a balance between the enthalpic and entropic interactions. For the lowest investigated interaction strength of $\varepsilon_{GM1} = 0.07$ kT, PNCs with $\phi_{M2} = 0 - 0.1$ show a significant upturn as $q \rightarrow 0$, which reflects NP aggregation due to unfavorable enthalpic interactions with the matrix_1 chains. Further increasing ϕ_{M2} to ≈ 1 causes a reduction in peak height at $q \rightarrow 0$, indicating increased miscibility of nanoparticles relative to ternary PNCs with low ϕ_{M2} values. These trends in $S_{PP}(q)$ are also seen in graft-graft structure factors $S_{GG}(q)$ (See Figure S14). At a higher grafted nanoparticle loading of $\phi_{PGP} = 0.079$ (Figures 9d-f), we see trends similar to those highlighted above for PNCs with $\phi_{PGP} = 0.039$. Importantly, at the lowest value of ε_{GM1} (Figure 9f), it is observed that the $S_{PP}(q \rightarrow 0)$ values at $\phi_{M2} = 0 - 0.1$ are higher for PNCs with $\phi_{PGP} = 0.079$ than the corresponding PNCs with $\phi_{PGP} = 0.039$. This demonstrates that the interfacial compatibilization effects of the matrix_2 are reduced as the grafted nanoparticle loading increases. This is in agreement with what has been observed experimentally in terms of a compositional dependent compatibilization effect at a fixed loading of PMMA homopolymer.

Overall, results from PRISM theory and MD simulations support the notion that matrix_2 chains compatibilize the interface between the graft and long matrix_1 chains. Additionally, their extent of compatibilization and the resultant particle miscibility in the PNC is dependent on the interactions between graft and matrix_1 chains, which can be tuned by varying the temperature in experiments, as well as the composition (ϕ_{PGP}, ϕ_{M2}) of the PNC.

CONCLUSION

In this study, binary and ternary phase diagrams were experimentally mapped using a combination of cloud point observations, TEM, and SAXS for PMMA-NP/SAN and PMMA-NP/SAN/PMMA composites, respectively. When compared, they illustrate that the addition of a ternary component, namely, PMMA homopolymer to the binary PMMA-NP/SAN composite, results in an increased miscibility window at low loadings of grafted nanoparticles. The improved miscibility from the added homopolymer can be understood as a result of an interfacial compatibilization between the SAN matrix and grafted PMMA brush due to the PMMA

homopolymer localization. A simple geometric model is presented that predicts the extent of homopolymer compatibilization based on the relative loadings of each constituent. In addition, using PRISM theory calculations and MD simulations, the compatibilization effect of the added PMMA chains is systematically probed and compared to the experimental results. Importantly, these computation methods confirm the role of the PMMA chains in stabilizing the interface between graft and matrix chains in ternary PNCs. PRISM theory and MD simulations predict that the extent of compatibilization can be further tuned by varying the temperature and composition of the ternary PNCs to extend the miscibility window. We hope that these results motivate further experimental and theoretical studies aimed at optimizing the vast parameter space in ternary nanocomposites in order to achieve the greatest miscibility enhancements. This study serves as a guideline to facilitate PNC miscibility at elevated temperatures, which is a critical parameter in designing technological applications, such as organic devices, that operate at high temperatures.

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